

**Der Einfluss von physikalischen und chemischen Polymer-Füllstoff-Bindungen
auf die Nassrutschfestigkeit von PKW Reifen**

**Influence of Physical and Chemical Polymer-filler Bonds
on Wet Skid Resistance and Related Properties of Passenger Car Tire Treads**

E. Cichomski (Sp), W. K. Dierkes, J. W. M. Noordermeer, University of Twente, Enschede (NL);
T. V. Tolpekina, S. Schultz, Apollo Vredestein BV, Enschede (NL)

Abstract

Knowledge about the influence of rubber – filler interactions on the wet skid behavior of tire treads is insufficient, in order to quickly develop new compounds with improved wet skid performance. The rubber compound used for a tire tread is in fact a composite material of which the dynamic properties can be adjusted over a relatively broad range by modification of the polymer – filler interaction. In case of silica reinforced rubber, due to silanol-groups present on its surface, it possesses unique opportunities to control the chemistry of the polymer-filler interface. Control over the polymer-filler interface is realized by chemical modification of the silica surface. In order to achieve this modification, different silane coupling agents must be applied. By changing the type of coupling agent, different molecular structures can be obtained which lead to changes in macroscopic material properties including wet skid resistance. A better understanding of one of the influencing factors, the polymer-filler interaction and its influence on wet skid resistance helps to answer the central question: Which type of polymer-filler bonds govern wet skid phenomena?

In this paper, the effect of physical and chemical polymer-filler bonds on the macroscopic dynamic properties of a silica reinforced tire tread compound, including wet skid resistance are discussed. In order to obtain different bond types, various silanes are used. The influence of the different silane types on the other properties of the material will also be discussed.

Introduction

The goal of the present study is to characterize the underlying mechanisms involved in rubber-filler interactions for the wet skid resistance of tires, a dynamic viscoelastic phenomenon. To characterize the dynamic properties of rubber, storage and loss moduli are commonly measured. The ratio of loss to storage modulus is indicated as the tangent delta. A first assumption is based on increasing interaction between filler and polymer, to lead to improvement of the wet skid resistance by raising the tangent delta values in the low temperature region (0 – 20 °C) and decreasing the same in the higher temperature region¹. Another assumption is that the filler-polymer interaction should be limited ultimately to physical interactions. Physical interaction means that under the influence of energy resulting from skidding, polymer molecules can easily be detached from the filler surface, what should increase energy dissipation. The influence of the silica-polymer interaction on wet skid performance was investigated by testing the dynamic properties, the tangent delta in the temperature range from 0 – 20 °C at 10Hz. The values of the loss angle in this temperature range are so far the most suitable indicators for the wet skid performance of a tire tread². However, in order to check a more practical value of the wet skid resistance, additional measurements on a Laboratory Abrasion Tester 100 (LAT 100) are performed in the final stage of this investigation.

Experimental

Materials

To assess the influence of silica-polymer interactions on the wet skid and other physical properties of the tire tread compounds, two cases are investigated. In the first case, silica – polymer interactions are aimed for to be mostly chemical of nature, inducing a strong and rigid interface. In the second case the interactions aimed for shall be limited to mostly physical – weak interactions. In order to meet those demands two silane modifiers are applied. Bis(3-triethoxysilylpropyl)tetrasulfane (TESPT) was chosen as a silane which can react directly with unsaturated polymers for a strong silica-polymer interaction, and 1,6-bis-(triethoxysilyl)hexane (TESH) which possess a similar molecular structure as TESPT, however it does not have sulfur atoms which makes it inert towards reaction with the polymer. Both silanes are shown in Figures 1 and 2.

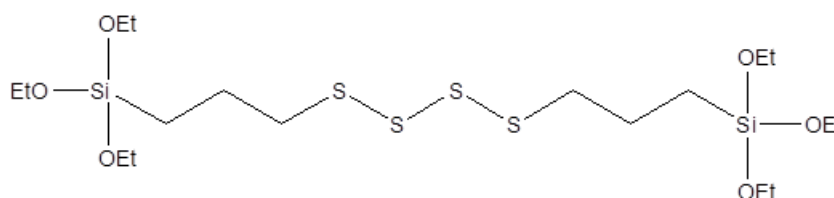


Figure 1: Bis(3-triethoxysilylpropyl) tetrasulfane
MW = 532 g/mol (TESPT)

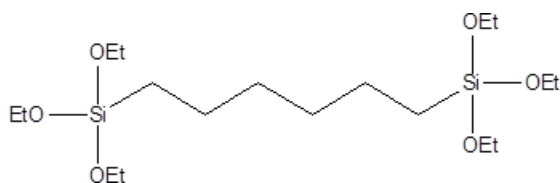


Figure 2: 1,6-bis-(triethoxysilyl)hexane
MW = 410 g/mol (TESH)

The experiments were performed using a recipe based on a well-known Green Tire formulation³ as given in Table 1. A blend of styrene-butadiene rubber 37,5 phr oil-extended, with high-cis butadiene rubber was used as compound base. Silica Zeosil 1165 MP was chosen as filler. Four compounds containing TESPT in varying amounts and a same number of compounds containing corresponding equimolar amounts of TESH were prepared. The TESPT content was adjusted for the first compound according to the surface area of the silica type by using the empirical equation proposed by L. Guy (Equation 1). The amount of free sulfur added with the curatives was adjusted to keep the total molar amount including the sulfur contained in the coupling agent at a constant level in all batches.

$$TESPT (phr) = 5.3 \times 10^{-4} \times (CTAB)_{silica} \times (phr)_{silica} \quad \text{Equation 1}$$

Mixing and curing

To prepare the compounds, an internal laboratory mixer - Brabender 350 S with mixing volume of 390 cm³ was used. The mixing procedure is specified in Table 2. The total volume of the batches was adjusted to a fill factor of 70 %. Preparation of sheets for testing was done on a two roll mill (Schwabentan).

Table 1. Recipes

Compound name	TESPT 7	TESPT 9.5	TESPT 12.0	TESPT 14.4	TESH 5.3	TESH 7.3	TESH 9.3	TESH 11.3	
SSBR	103	103	103	103	103	103	103	103	
BR	25	25	25	25	25	25	25	25	
Silica	80	80	80	80	80	80	80	80	
Coupling agent	phr	7	9,5	12	14,4	5,3	7,3	9,3	11,3
	mol	0,013	0,018	0,023	0,028	0,013	0,018	0,023	0,028
Processing oil	5	5	5	5	5	5	5	5	
ZnO	2,5	2,5	2,5	2,5	2,5	2,5	2,5	2,5	
Stearic acid	2,5	2,5	2,5	2,5	2,5	2,5	2,5	2,5	
Sulphur	1,4	0,8	0,24	0	3,1	3,1	3,1	3,1	
TBBS	1,7	1,7	1,7	1,7	1,7	1,7	1,7	1,7	
DPG	2	2	2	2	2	2	2	2	

Table 2. Mixing procedure

Stage I	
Rotor speed: 110 RPM Initial temp.:50 °C	
Timing (Min. sec.)	Ingredient
0.0	Add polymers
1.0	Add ½ silica, ½ silane, ZnO + Stearic acid
2.3	Add ½ silica, ½ silane, Oil, TMQ, 6PPD
3.0	Sweep
4.0	Dump @ ~ 155 °C
Stage II	
Rotor speed: 130 RPM Initial temp.:50 °C	
Timing (Min. sec.)	Ingredient
0.0	Add I stage batch
3.0	Dump @ ~ 155 °C
III stage	
Mixing of the curatives was performed on a two roll mill	

Vulcanization of the sheeted samples for tensile tests was performed on a Wickert laboratory press at 160 °C and 100 bars for the optimal curing time (t_{90}) obtained from RPA 2000 (Alpha Technologies) rheometer measurements according to ISO 6502. The samples for hardness tests were prepared in cylindrical molds and cured for a period of twice the t_{90} time. The samples for the DIN abrasion tests were cured for t_{90} times 1,2. The adjustment of the curing times as measured in the rheometer was necessary due to the large thickness of the samples and the generally well known low thermal conductivity of the rubber compounds.

Characterizations

The Mooney viscosity ML(1+4) of the compounds was measured at 100 °C on a Mooney viscometer MV 2000E (Alpha Technologies) according to ISO 289-1.

Mechanical properties of the samples were tested using a Zwick Z020 tensile tester according to ISO-37 at crosshead speed of 500 mm/min.

Abrasion resistance was measured with a DIN abrader according to method A of DIN 53516. The weight loss was measured and recalculated to a volume loss for each sample.

In order to characterize the wet skid resistance, dynamic mechanical analysis was performed on a Metravib DMA in the temperature-sweep mode from -50 °C to +50 °C

with 1 % static and 0,1 % dynamic strain at a frequency of 10 Hz. In order to predict the rolling resistance, single point measurements of $\tan\delta$ at 60 °C and 6 % strain were performed on the RPA 2000.

In order to estimate the chemical and physical polymer – filler interactions, bound rubber tests were performed. These tests were done by immersing approximately 0,2 g of the uncured compound in 60 ml of toluene for 7 days to obtain equilibrium swelling. Additionally, to separate physically from chemically bound rubber, samples immersed in toluene were treated in an ammonia atmosphere. The mass of the samples before and after the test was used to calculate the bound rubber.

A Laboratory Abrasion Tester 100 (LAT 100) was used to estimate the wet skid resistance of the tire treads in conditions which better reflect the real conditions on the road. Wheel samples were made by compression molding in a special mold using the Wickert laboratory vulcanization press. Testing was performed at five different water temperatures: 2 °C, 8 °C, 15 °C, 22 °C, 30 °C and at constant slip angle of 15°. A electro-corundum disc with relative roughness: 180, was used to simulate the tire-road interactions. Tests were performed at constant speed of 1,5 km/h and load of 75 N for a distance of 33 meters.

Results and discussion

Mooney viscosities

The Mooney viscosities of the batches containing equimolar amounts of TESH and TESPT silanes are shown in Figure 3. Higher concentrations of both TESH and TESPT cause a decrease in Mooney viscosity. The effect is more evident in the case of TESH than for TESPT.

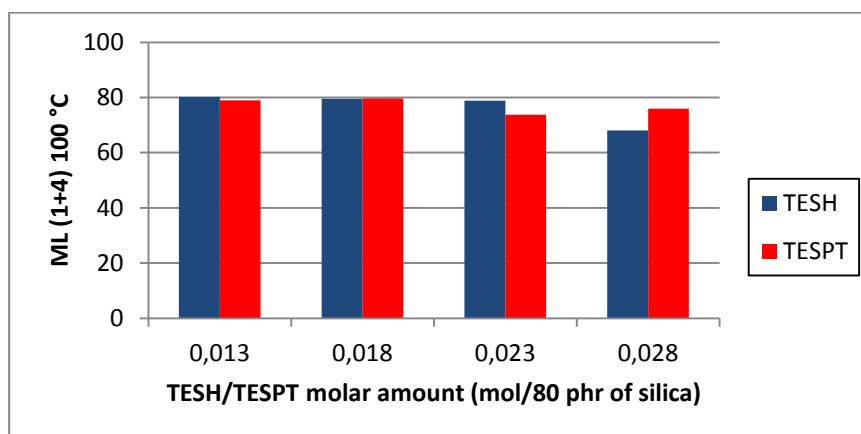


Figure 3: Mooney viscosities of the batches

Both silanes are reactive towards the silica surface and after silanization their distribution between polymer and filler phase is not homogenous. The largest amount of coupling agent molecules is concentrated on the surface of the silica. Side silanization reactions due to increased concentrations of the silanes can cause formation of a thicker

layer of partially polymerized silane on the surface of the silica ⁴. This thicker layer could act as a interface lubricant which facilitates movement of filler particles in the polymer matrix and consequently decrease viscosity.

Bound rubber

These test results shown in Figure 4 show the differences in polymer – filler interactions for the compounds containing TESH and TESPT. The compounds containing TESH silane dissolve completely, therefore the values of the chemically bound rubber are equal to zero. This confirms that silica covered by TESH will not be able to form chemical bonds with the rubber and the interactions will be limited to just physical, regardless of the silane concentration. In case of TESPT, an increased concentration entails changes in physically bound rubber. However a substantial increase in chemically bound rubber is visible at concentrations ranging from 7 phr (0,013 mol) to 9,5 phr (0,028 mol) of TESPT.

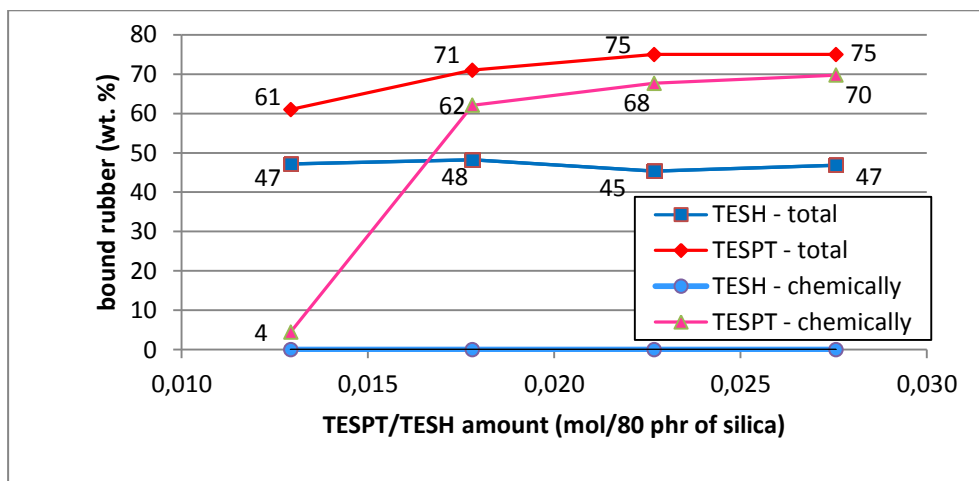


Figure 4: Bound rubber of the TESPT and TESH containing compounds

The latter suggests that 7 phr of TESPT per 80 phr of silica is still below a threshold concentration above which the chemically bound rubber reaches a plateau. In the plateau state the silica surface is saturated with bulky molecules of TESPT, and a further increase of the concentration does not lead to formation of new chemical bonds between silica and the polymer.

The results obtained from the bound rubber experiments are inherently related to the tensile strength of the vulcanizates, as shown in Figure 5. The threshold concentration of TESPT is also visible in the values of tensile strength, however to a lesser extent than in the bound rubber. Replacing strong, chemical bonds with relatively weak physical interactions lowers the values of the tensile strength.

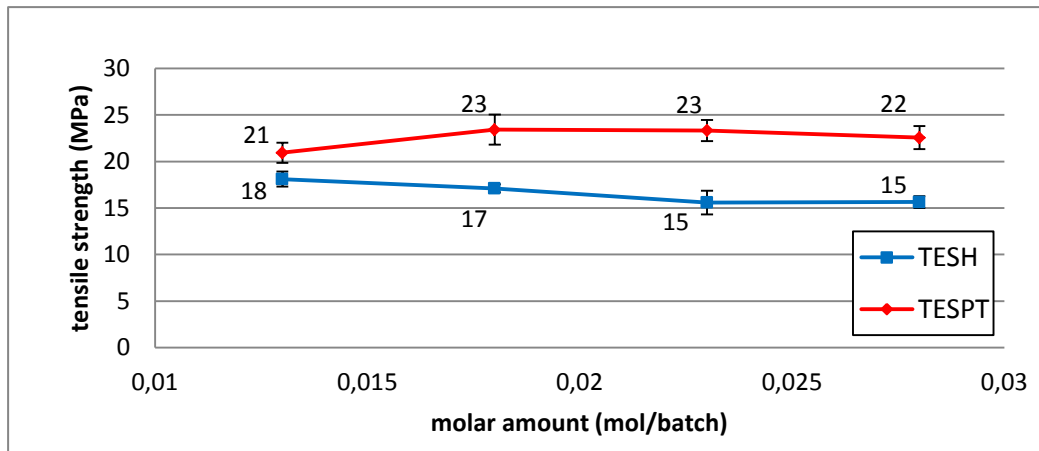


Figure 5: Tensile strength of the vulcanizates containing TESPT and TESH

The lower values obtained for the vulcanizates with TESH are most probably caused by the fact that the filler is not strongly connected with the polymer and consequently cannot actively participate in transfer of the load applied to the sample. An explanation in a mechanistic sense would be that the polymer chains under high deformations are simply sliding on the surface of silica.

Tear resistance

The tear resistance of the samples as shown in Figure 6, gives information about the crack growth throughout the material. Physical interactions also affect the tear resistance. However, contrary to what was expected from the tensile tests, the tear resistance values show a diametrically different relation. The tear resistance values for TESH samples are actually higher than those obtained for the TESPT samples.

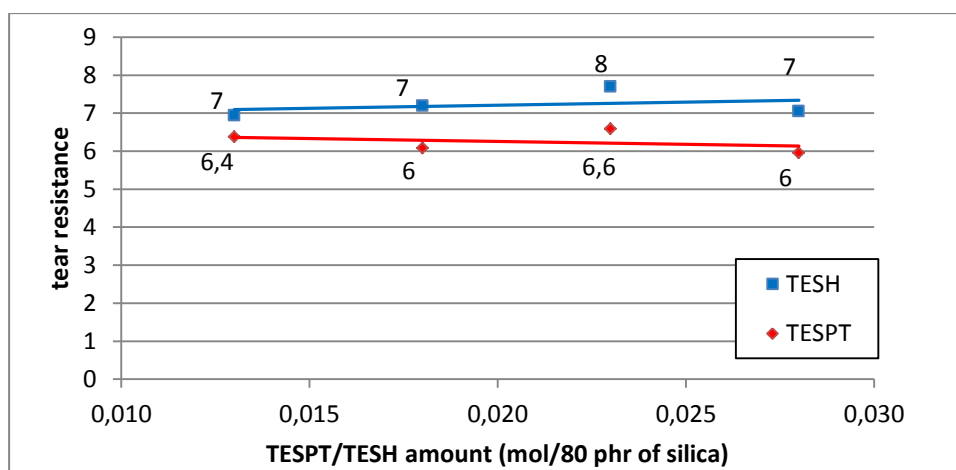


Figure 6: Tear resistance of the TESH and TESPT containing samples

Crack growth in a material with relatively more rigid polymer-filler interface: TESPT vulcanizates, should be easier than for a material with less rigid silica-polymer interface.

Weak interactions between polymer and silica mean that each silica aggregate can act as a new crack initiation center. This can be also seen as a new node in which a crack can change direction of growth, which in turn may lead to crack stopping – local extinction. In the case of TESPT the polymer-filler interface is more rigid which leads to accumulation of stress and prevents cracks from stopping.

Abrasion resistance

Abrasion resistance depends on the glass transition of a polymer. The higher the glass transition of the polymer, or the closer the $\tan\delta$ maximum to the temperature at which real abrasion is taking place, the less elastic the rubber is⁵. Rubber which is less elastic will not be able to withstand the concentrated loads coming from the asperities existing on the abrasive surface. Nevertheless, as the same polymer blend is used (SBR/BR) the abrasion resistance depends on different factors than only the glass transition temperatures. The DIN abrasion of the samples (Figure 7) depends on the concentration of silane used and therefore on the polymer-filler interactions. With increasing concentration of TESPT the abrasion volume decreases resp. abrasion resistance increases. This behavior could be explained by the fact that, along with the increasing amount of TESPT, more sulfur from the TESPT molecules is introduced into the silica surface. A higher sulfur concentration at the silica surface causes a gradient of the crosslink density from the silica surface towards the polymer phase. Consequently, the silica particles are more immobilized in the polymer matrix and their extraction by sharp asperities is impeded. In case of TESPT, the DIN abrasion correlates with the bound rubber values.

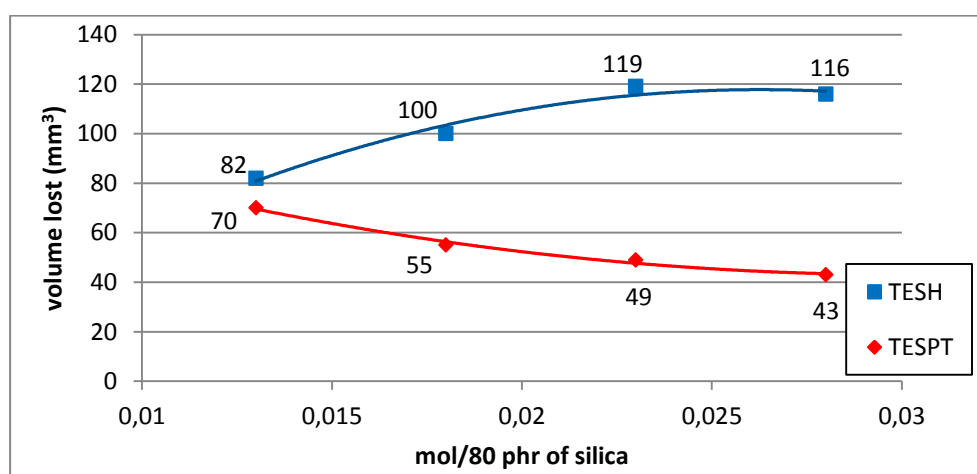


Figure 7: DIN abrasion of the samples containing TESPT and TESH silanes

On the other hand, with increasing concentration of TESH silane, the volume lost dramatically increases. This cannot be explained by the bound rubber content, because the values for bound rubber for TESH containing compounds are constant regardless of the loading. Another explanation may be based on the interface lubrication effect which was already discussed in the case of the Mooney viscosity. The hardly visible changes in Mooney viscosity caused by the increased amount of TESH seem to have a greater impact on DIN abrasion. The TESH acts like a silica-polymer interface lubricant and

facilitates polymer chain sliding on the silica surface. That in turn causes easier extraction of small particles by sharp asperities of abrasive disc and increases the wear.

Considering an average speed of a vehicle of 70 km/h and car wheel dimensions: 255/65/16, the typical frequency of deformation of the revolving tire is around 10 Hz. The hysteresis of the rubber compound causes an increase of the tire temperature to approx. 60 °C. The weight of the vehicle exerted on the tire results in around 6% tire tread deformation. Therefore, measuring the $\tan\delta$ values at 10 Hz, 6% of dynamic strain and at 60 °C (Figure 8) is a good indicator of rolling resistance. The lower the value of the $\tan\delta$, the lower the rolling resistance.

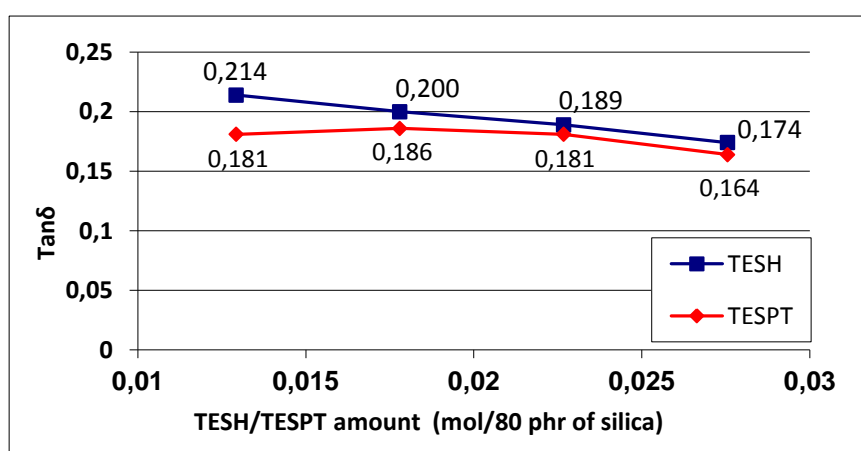


Figure 8: Values of $\tan\delta$ at 60 °C

Tan δ @ 60 °C, Rolling resistance

In general, the TESH silane containing compounds show higher values of $\tan\delta$ than those with TESPT. This indicates that chemical bonds are preferable for good rolling resistance. Less adherent particles means less reinforcement and higher energy lost at the interphase: polymer chains can slide on the silica surface. As was stated before, with increasing TESH concentration the bound rubber content did not change: bound rubber values are constant. However, increasing the TESH concentration causes decrease in $\tan\delta$ values, because of the suppressed filler-filler interaction. In the case of TESPT the $\tan\delta$ values are relatively constant until the highest silane concentration, then a drop is visible. It shows that compound hysteresis at higher temperatures and relatively high strains is almost independent of the concentration of TESPT.

Tan δ @ at low temperatures, Wet skid resistance

The practical laboratory assessment methods for wet skid resistance for carbon black filled compounds indicate that higher values of $\tan\delta$ at lower temperatures, preferably 0 °C to 20 °C, correspond to better wet skid resistance of the tire tread^{5,6}. The frequency of a rolling tire is around 10 Hz. However, when the tire stops its rotation and starts wet skidding, the frequency rises up to the megahertz region. This high frequency is the result of stick-slip phenomena during skidding⁷. Additionally, the service temperature of the tire during rolling is relatively high: around 50 °C to 60 °C. Based on the frequency-temperature superposition principle, under the influence of the high frequency the $\tan\delta$

curve shifts toward higher temperatures: the values of $\tan\delta$ at 0 – 20 °C are shifted to the range of service temperatures^{8,9}. Hence, rubbers which lose more energy in the low temperatures range should have higher wet skid resistance.

The dependence of the tangent delta on temperature for the various compounds is shown in Figure 9. In general, the TESH containing compounds have higher values of $\tan\delta$ in the temperature range of 0 to 20 °C compared with the TESPT containing compounds. In fact, replacing TESPT with TESH shifts the curves towards higher temperature and that is why the values of $\tan\delta$ at 0 – 20 °C are higher. This shift towards higher temperatures is contradictory to the results presented here before. That is, because restriction of polymer movement always means an increase of the glass transition temperature. A good example of this behavior is the increased glass transition temperature visible in compounds in which highly reinforcing silica is used in comparison with low reinforcing grades. Conversely, in the present case by unrestricted polymer movements due to replacement of strong bonds by weak once, the glass transition shifts towards higher temperatures. Higher values of $\tan\delta$ at low temperatures are related to increased hysteresis at low temperatures, as observed for TESH compounds and should correspond with higher wet skid resistance compared to the TESPT containing samples.

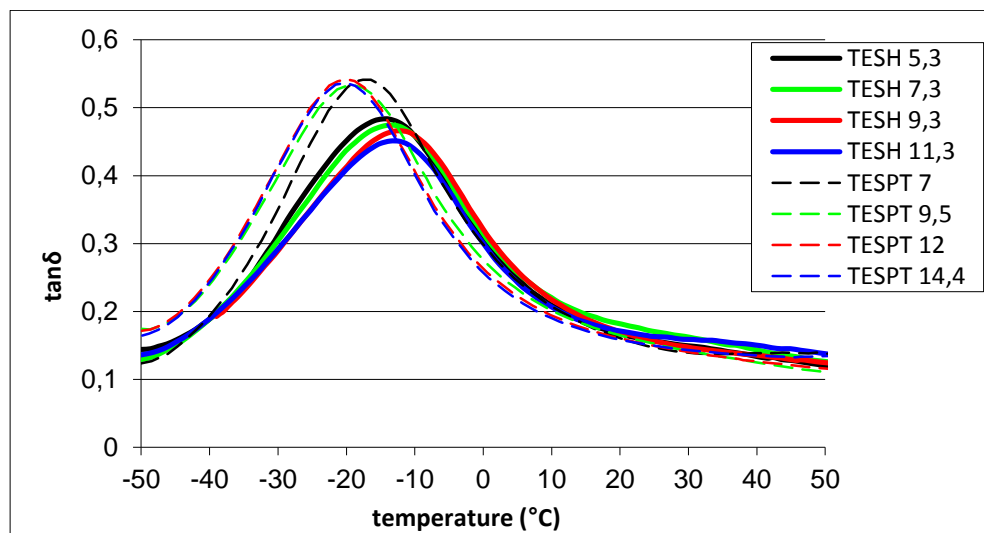


Figure 9: Tanδ – temperature dependence

LAT 100 tests

To better simulate the wet skid resistance, a laboratory abrasion tester (LAT 100) was used. This test better resembles the real conditions occurring on the wet road. Values of the side force coefficient are shown in Figure 10.

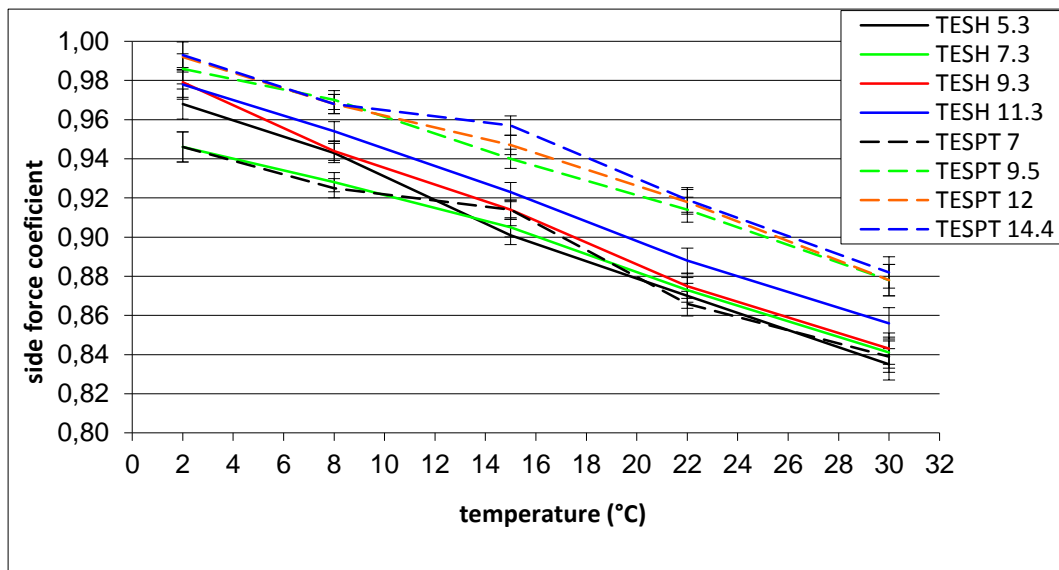


Figure 10: LAT 100 side force coefficient values in different water temperatures

Despite the fact that the samples containing TESH have higher hysteresis at low temperatures, the side force coefficient values are higher for the samples containing TESPT. In order to find an explanation for this phenomenon, mechanical properties could also be taken into consideration. The values of the tensile strength, as a result of the higher chemically bound rubber content, provide a better correlation with the side force coefficient than the dynamic properties. Micro-asperities existing on the surface of the abrasive disc or surface of the road can cause high strain deformations on a micro scale, in which fragments of rubber compound are detached from the surface of the wheel. The higher the tensile strength of rubber, the higher the force which needs to be used to tear-off micro-fragments. Hence, the larger opposing force during sliding results in higher wet skid resistance. However, other tests were performed in which a glass disc was used as testing surface instead of electro-corundum, and these indicate that the dynamic properties of the samples do have a major contribution to wet skid, contrary to what was found above.

Conclusions

Silica can be treated with TESH silane, which is inert towards bonding to the polymer chains to obtain interactions similar to these which exist between carbon black and rubber. The bound rubber content confirms this. The bound rubber content is independent on the TESH silane concentration, because above a certain threshold concentration no additional physical bonds are formed. By further increase of TESH loading a ticker multi-layered structure is formed on the silica surface which only contributes to a higher interface lubrication effect. Introduction of physical interactions instead of chemical bonds radically decrease the values of the tensile strength because of inertness of the silica surface.

The dynamic properties of the samples measured at low temperatures do not correspond very well with the wet skid resistance as measured by the LAT 100. Replacement of chemical bonds by physical interactions decreases the values of wet skid resistance measured by the LAT 100. This confirms that strong chemical interaction between filler and polymer are crucial for optimal wet skid resistance. The assumption that under the influence of energy resulting from skidding, polymer molecules physically bonded to the filler surface can easily be detached, what should increase the energy dissipation, is not correct for relatively rough test surfaces, but do provide a high contribution for smooth surfaces like glass.

Acknowledgments

The authors thank Apollo Vredestein for their support and permission to present these results. Jan van Kranenburg and Kuno Dijkhuis of Elastomer Research and Testing, Deventer, the Netherlands are acknowledged for their stimulating discussions. The financial support within the GO program (EFRO 2007-2013) from Gelderland-Overijssel province is also greatly acknowledged.

References

-
- ¹ A. A. Ward, A. A. Yehia, A. M. Bishai, *Kautschuk Gummi Kunststoffe* 61 (2008) 569.
 - ² M. J. Wang, *Kautschuk Gummi Kunststoffe* 61 (2008) 33.
 - ³ European Union Patent No. EP0501227B1, (1992)
 - ⁴ U. Goerl, A. Hunsche, A. Mueller, and H. G. Koban, ACS Rubber Division Meeting (Louisville), October 8 -10 (1996) paper 76.
 - ⁵ K.H. Nordsiek, *Kautschuk Gummi Kunststoffe* 38 (1985) 177.
 - ⁶ M. J. Wang, *Rubber Chemistry and Technology* 71 (1998) 520.
 - ⁷ A. Schallamach, "Chemistry and Physics of Rubber-like Substances" ed. L. Bateman. McLaren and Sons, London (1963) 382.
 - ⁸ A. Yoshioka, K. Komuro, A. Ueda, H. Watanabe, S. Akita, T. Masuda, A. Nakajima, *Pure and Applied Chemistry* 58 (1986) 1697.
 - ⁹ S. Cervenya, A. Ghilarduccib, H. Salvab, A.J. Marzoccaa, *Polymer* 41 (2000) 2227.