SILICA-FILLED TIRE TREAD COMPOUNDS

AN INVESTIGATION INTO THE VISCOELASTIC
PROPERTIES OF THE RUBBER COMPOUNDS AND THEIR
RELATION TO TIRE PERFORMANCE

Somayeh Maghami

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With Summary in English and Dutch

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DISSERTATION

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the degree of doctor at the University of Twente,

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on account of the decision of the graduation committee,

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by

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«It is your road, and yours alone.

Others may walk it with you, but no one can walk it for you.»

Rumi

to Morteza and my parents

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Chapter 1

Introduction

1.1 Overview

Fossil fuel consumption is a worldwide environmental concern and the automotive world as a main contributor is receiving more and more pressure to decrease its share. Although tires are only responsible for less than 30% of the energy consumption in a passenger car¹, yet decreasing this portion is highly desired. Part of the energy provided to the tires is consumed to overcome the so called *Rolling Resistance*, a property which arises from the fact that tire compound materials are viscoelastic. Under dynamic deformation, a portion of the input energy to the tire is converted into heat and has to be supplied as external work; meaning fuel consumption². On the other hand, tires as the only part of the vehicle coming in contact with the road play an absolutely important role in the safety of the drive. The interactions between the road surface and the tire material form the required forces for traction (*Skid Resistance*), acceleration and breaking. Therefore improving both Rolling Resistance and Wet Skid Resistance particularly under wet conditions is conflicting, as improving one causes a decrease in the other and a compromise between the two should be aimed for.

New legislation in Europe, since July 1st, 2012, obliges all the tire manufacturers to provide an efficiency label indicating fuel efficiency (related to Rolling Resistance (RR) performance), safety (related to Wet Skid (WS) performance) and the noise level³, Figure 1.1.

Figure 1.1- passenger car tire efficiency label obligatory in Europe

The dynamic and mechanical properties of particularly the tire tread compounds can be used to predict the real tire performance on the road. In particular, the dependence of the dynamic mechanical loss factor ($\tan\delta$) on temperature can be employed⁴⁻⁵. The temperature range between 40°C and 70°C and a frequency of 10Hz represents the operating conditions of a typical tire and under these conditions the loss factor can be used as an indication for the RR. Difficulty arise to estimate the WS performance, as a good correlation is only found when the WS performance is related to the viscoelastic behavior of the elastomers in the tire tread compound in the transition region between glassy behavior and the rubber plateau, which is typically in the frequency range of 1 kHz till 1 MHz⁶. Due to the limited capability of measuring instruments, this high frequency range is often not accessible.

1.2 Aim of this thesis

The aim of the investigations described in this thesis is twofold: to obtain a better understanding of the relationship between the viscoelastic properties of the rubber compound and the actual tire performance with emphasis on WS performance; and to explore the possibility of employing functionalized elastomers in an optimized tire tread formulation. Dynamic and mechanical properties are measured in two different manners: constant strain-based and constant stress-based, and viscoelastic mastercurves are produced to evaluate the behavior of the compounds at a higher frequency range to simulate WS performance.

In the 90'ies of last century silica in combination with coupling agents has been introduced as the main reinforcing filler for passenger tire tread rubber, because of its beneficial effect on RR, compared to traditional carbon black⁷. Since then, the use of silica for passenger car tires has become standard state-of-the-art in Europe in particular.

Silica as a polar material is naturally not compatible with the non-polar hydrocarbon elastomers. The idea is that polar functional groups placed along the elastomer chains could aid in improving the affinity between silica and the elastomer. Total elimination of need for a coupling agent would still remain rather demanding. Yet the ability of the new generation of SBR-rubbers in interacting with the polar silica could be a big step towards this goal in the tire industry, particularly to further improve RR and WS.

1.3 Structure of this thesis

Two main performance characteristics of the tire, i.e. rolling resistance and skid resistance, are reviewed in *Chapter 2*. The current state of the knowledge on the relationship between the viscoelastic properties of the rubber compound used in a tire tread and these two tire characteristics and the methods to measure these are reviewed. In addition, an overview on the new generation of the Styrene Butadiene Rubbers (SBRs) and their preparation method is included in this chapter.

In *Chapter 3* the construction of viscoelastic mastercurves over a broad temperature/frequency range for the tire tread compounds filled with different amounts of silica is discussed. Applying the time-temperature superposition (TTS) principle delivers the viscoelastic properties of the compounds in a wide frequency range which may be used to predict the real tire performance. The effect of filler networking on the dynamic behavior of the rubber compounds is also explained.

Chapter 4 presents the viscoelastic mastercurves for the same series of compounds as discussed in Chapter 3, measured in a different Dynamic Mechanical Analyzer (DMA) instrument which enables to perform the tests under constant stress and high strain conditions.

The results of the investigation on the effect of three different functionalized SBRs on the dynamic and mechanical properties of a silica-reinforced tire tread compound are shown in *Chapter 5*. Additionally, the interference of Zinc oxide (ZnO), as a well-known activator in sulfur cure systems, with the silanization process and the polar moieties on the polymer chains is explored.

To avoid the interference of ZnO mentioned in *Chapter 5*, this ingredient is added in a later stage of mixing. The consequent compounds properties are quite promising favoring the Rolling Resistance of the tires made thereof, but bring along lower hardness values, which can affect other properties of the compounds, such as tire traction. In order to avoid misinterpretations, compounds were prepared with adjusted hardness levels and their dynamic and mechanical properties are presented in *Chapter 6*.

Chapter 7 is focused on the evaluation of the effect of oligomeric resins, derived from natural and synthetic monomers, on the viscoelastic behavior of the silica-reinforced tire tread compounds and their potential to improve passenger car tire performance.

Chapter 8 contains the overall conclusions of the thesis.

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Chapter 2

Tires and parameters determining their performance

A literature review

2.1 Introduction

The major application of filled elastomers is in the manufacture of automotive tires. The rubber tire interacts with the hard road surface by deforming under load, thereby generating the forces responsible for traction, cornering, acceleration, and braking. It also provides increased cushioning for ride comfort. A disadvantage, however, is that energy is expended as the pneumatic tire repeatedly deforms and recovers during its rotation under the weight of the vehicle.

The three major periods of development in the tire industry are:

- (a) The early era coinciding with the mass introduction of the automobile from the early 1900s into the 1930s;
- (b) The middle of the 20th century, when synthetic rubber became a commodity, and major design innovations such as tubeless and radial-ply tires were introduced;
- (c) The period since the mass introduction of radial tires in North America in the early 1970s.

Radial tires accounted for about 60% of passenger tire shipments in 1980, 97% by the end of the 1980s, and 99% in 2005 ¹.

A tire is an assembly of numerous components which are assembled on a drum and then cured in a press under heat and pressure. Typical components used in tire assembly are shown in Figure 2.1.

The tire tread is the part of the tire which comes in contact with the road surface. The tread's design, including its grooved pattern, helps in the removal of road surface water and other contaminants from the tire-road interface while maintaining an adequate level of frictional adhesion between the tire and the road to generate torque, cornering, and braking forces under a wide range of operating conditions.

Figure 2.1- Tire cross section

The magic triangle of tire technology (Figure 2.2) shows the relationship between the three major properties of a rolling tire: rolling resistance, (wet) skid resistance and abrasion resistance. According to this principle, any improvements in one of these properties would lead to a change - mostly undesirable - in the other two properties. Rolling resistance and wet skid resistance are the main fields of interest in this work. So in this chapter, these two tire properties and the different parameters affecting them will be discussed. In addition, the relationship between these properties and dynamic–mechanical properties of the tread material will be reviewed.

Figure 2.2- Magic triangle of tire technology

2.2 Rolling resistance

2.2.1 Introduction

A tire running under load is a classic example of repeated stress-loading; every point in the tire passes through a stress-strain cycle once every rotation. Some of the elastically stored energy is thereby converted into heat and has to be supplied as external work (more fuel consumption), which appears as the rolling resistance of the tire ². In other words, rolling resistance of a free rolling tire can be considered as a force that opposes vehicle motion. According to the definition of rolling resistance, its unit is Joule per meter (J/m) or simply Newton (N).

In simplified terms, the engine fuel energy consumed by a vehicle is dissipated by 6 energy sinks (in approximate order of decreasing importance) ³:

1. Drivetrain losses while delivering power (including heat loss to the air, exhaust stream, and coolant due to the thermal inefficiency of the engine),
2. Tire rolling resistance,
3. Aerodynamic drag,
4. Braking energy (i.e. translational and rotational inertia dissipated as heat by the brakes),
5. Drivetrain friction while stopped, and
6. Accessories.

Due to the fact that by lowering rolling resistance, the fuel consumption will also reduce, the tire and rubber industries are very interested in developing ways to reduce the rolling resistance of tires. Figure 2.3 summarizes the reduction in rolling resistance (relative to the 1990 level) of Michelin tires. Each data point represents the lowest rolling resistance construction in high-volume mass production³.

According to Michelin Tire Company, 20% of the fuel used in an average car, and four percent of worldwide carbon dioxide emissions from fossil fuels, is caused by rolling resistance. A 10% reduction in rolling resistance can improve consumer fuel efficiency by 1 to 2 percent for passenger and light truck vehicles ⁴.

Figure 2.3- Relative rolling resistance of Michelin tires since 1978

Rolling resistance can be calculated by Equation 2.1 ⁵, which is the total mechanical energy loss divided by the corresponding distance after the tire had performed one loop on the road surface:

$$RR = U'' / (2\pi\rho_r) \quad (2.1)$$

where RR is the rolling resistance, ρ_r is the valid rolling radius of the tire, and U'' is the total mechanical energy loss of rolling one loop.

If a block of rubber is subjected to a sinusoidal shear deformation of amplitude γ_0 and frequency ω , the resulting amplitude would be

$$\gamma(t) = \gamma_0 \sin \omega t \quad (2.2)$$

The stress then will lag behind the strain by the phase angle δ :

$$\sigma(t) = \sigma_0 \sin(\omega t + \delta) \quad (2.3)$$

The stress therefore consists of the sum of in-phase and out-of-phase components, and the constants of proportionality are the elastic shear modulus, E' , and the loss shear modulus, E'' , respectively:

$$\sigma(t) = \gamma_0 (E' \sin \omega t + E'' \cos \omega t) \quad (2.4.a)$$

And the loss factor is:

$$\tan \delta = \frac{E''}{E'} \quad (2.4.b)$$

The energy lost as heat over a single cycle, Q , is ³:

$$Q = \int_0^{2\pi/\omega} \sigma \dot{\gamma} dt = \pi \gamma_0^2 E'' = \pi \gamma_0 \sigma_0 \sin \delta \quad (2.5)$$

The amount of energy lost per cycle can be graphically represented by plotting stress against strain. Figure 2.4 shows this plot where stress according to Equation (2.3) is plotted against the strain from equation (2.2). The elliptical shape of the hysteresis loop is due to the sinusoidal variation of stress and strain. As δ approaches zero, the area decreases and the ellipse approaches a straight line. The material is pure elastic when δ equals zero.

This energy loss will be turned into heat which results in an increase in the temperature of the tire. The temperature in the tire rises until heat generation equals heat losses through radiation and transmission to the surrounding.

Figure 2.4- Hysteresis loop showing its relations to storage and loss moduli and phase angle, δ

2.2.2 Models describing rolling resistance

There are many models describing rolling loss of a tire, from empirical to thermal and viscoelastic models. Some viscoelastic models are based on the following correlations: If one considers that all important tire rubber parts such as tread, sidewalls, and plies (without cords) are subjected to both constant strain and constant stress modes, the total rolling loss, F_R , would be the sum of constant strain and constant stress energy losses. Accordingly,

$$F_R = \sum_1^n [A_i E_i'' + B_i D_i''] + F_{RC} \quad (2.6)$$

Where n is the number of tire elements considered and D'' is loss compliance with $D'' = E''/(E^*)^2$. The constant strain mode, $A_i E_i''$, was assigned to "bending"; the constant stress mode, $B_i D_i''$, to "compression". The term F_{RC} encompasses the cord energy losses ⁶.

The most severe shortcoming of this method and other similar models is the neglect of any interaction between tire parts.

A model considering main interaction effects but neglecting quadratic effects would use a correlation of the kind:

$$F_R = A_0 + A_1 E_T'' + A_2 E_C'' + A_{12} E_T'' E_C'' \quad (2.7)$$

Where E_T'' and E_C'' are the loss moduli of tread and carcass, respectively.

There is another hypothesis that tire rolling loss follows the relation:

$$F_R = (C_1 + C_2 F_z / p^2) F_z \quad (2.8)$$

where F_z is the vertical load on the tire and p is the inflation pressure. The constant C_1 would reflect the loss properties of the tread ($F_R = C_1 \cdot F_z$ at $p = \infty$) and the constant C_2 the loss properties of the carcass ⁷.

2.2.3 Tire operating conditions and rolling loss

A number of tire operating conditions affect rolling resistance. The most important ones are load, inflation pressure, speed and road surface.

Inflation pressure affects tire deformation. Tires with reduced inflation exhibit more sidewall bending and tread shearing. The relationship between rolling resistance and pressure is not linear, several functional dependencies have been proposed to predict the influence of pressure on rolling resistance, including $(1/P)$, $(1/P)^{0.5}$, and linear and quadratic interactions between load (Z), speed (V), and pressure (P).

Load and rolling loss often are linearly dependent: the more a tire at a given pressure is loaded, the more it deforms; hence hysteresis increases with tire load. Indeed, the relationship between rolling resistance and sidewall deflection due to load is approximately linear, so increasing the load on a tire results in a near-proportional increase in total rolling resistance.

Speed has a limited effect on rolling resistance except for the highest speeds reached during highway driving. This limited effect is due to the frequency and temperature dependence of the loss properties of a rubber compound: The loss tangent, $\tan\delta$, of a rubber compound increases with frequency under isothermal conditions. At normal conditions, an increase in frequency will cause an increase in $\tan\delta$, but with time passing the increased energy input raises the temperature, thus the loss tangent, being as well a function of temperature, decreases as the temperature goes up as illustrated in Figure 2.5⁷. Tires operated at the top speeds associated with normal highway driving may exhibit increases in rolling resistance as the frequency of tire deformation increases. Also, at high speeds, standing waves can develop in the tire that dramatically increase heat generation in the tire as the speed further increases. However, as speed increases, the tire's internal temperature rises, offsetting some of the increased rolling resistance.

Figure 2.5- Rolling loss as a function of speed (flatbed tests) a) constant temperature; b) equilibrium temperature⁷

The combined effect of inflation pressure (P), speed (V) and load (Z) can be fitted within an empirical model:

$$F_R = P^\alpha Z^\beta (a + bV + cV^2) \quad (2.9)$$

This equation has been demonstrated to match the measured rolling resistance across a wide range of V , Z and P for passenger and light truck tires⁸.

From experience, the exponent alpha usually varies between -0.3 and -0.5 for modern radial construction pneumatic tires. The beta exponent usually varies between 0.8 and 1.1 for radial construction tires, but for most tires it is less than 1³.

Road surface contributes to rolling loss by inducing tire deformation. This effect can increase energy losses by 5 to 20%⁹⁻¹⁰. Road roughness has two components: macrotexture and microtexture. The first relates mainly to the surface condition on the scale of centimeter and reflects the presence of cracks, ruts, bumps, and other surface irregularities. The second component, microtexture, relates to smaller-scale asperities in the road surface that are millimeters or even fractions of a millimeter in size and reflect the coarseness of the surface texture. Tires operated on either rough macrotexture or rough microtexture will deform more and suffer greater energy loss. They will also experience faster tread wear.

The amount of energy lost will depend on the rigidity of the roadbed and overlay as well. Dirt and gravel roads deform the most and give rise to twice as much rolling resistance as harder paved surfaces ¹⁰.

2.2.4 Effect of compound formulation on rolling resistance

The tread contains much of the hysteretic material in the tire. So it is reasonable to investigate the tread compound properties in relation to rolling loss.

There are three ingredients in the tread compound which are mainly involved in the viscoelastic behavior of it: rubber, extender oil and filler, and to a lesser degree curing systems and additives like resins.

The type of rubber influences rolling resistance; tire materials with a low loss modulus E'' and a high storage modulus E' are the best candidates for low loss tires. Generally speaking, synthetic rubbers tend to exhibit greater rolling resistance than natural rubber. Of course the loss properties of the base polymer will be modified by the compounding materials, particularly by the amount of reinforcing filler, carbon black (CB) or silica and oil.

Schuring ⁷ has reported a linear relationship between rolling resistance (F_R) and the amount of sulfur (sulf), carbon black (black) and oil:

$$F_R = b_0 + b_1(sulf) + b_2(oil) + b_3(black) \quad (2.10)$$

Where b_0 , b_1 , b_2 and b_3 are constants. These results have been obtained with a designed experiment in which the amount of carbon black, oil and sulfur was varied in a 7:3 blend of high cis-polyisoprene and polybutadiene. However, there are reports stating that interactions exist between oil and carbon black. If the oil level is held constant, an increase in carbon black content will increase rolling loss at any given oil level. However, if both, oil and carbon black level, are varied, rolling loss may decrease at higher carbon black levels ¹¹. In a work done by Lou ¹², the same results were obtained.

Figure 2.6 shows the loss modulus curves of three tread compounds as function of extended frequency, $\log a_T f$, obtained from torsion pendulum measurements and transformed into an extended frequency range at their respective standard reference temperatures using the William-Landel-Ferry (WLF) equation (see 2.3.6). Butadiene rubber (BR) is expected to have a

lower rolling resistance than SBR and it doesn't depend significantly on speed and temperature¹³.

Figure 2.6- The loss modulus of three tread compounds differing in polymer type as a function of $\log a_r f$

Fillers interact with the polymer and thus increase the losses in the material. They form structures within the polymer network which are broken down during deformation leading to stress-softening and additional losses and heat build-up in the material. These effects not only depend on frequency and temperature but also on the amplitude of the deformation. It is very well documented that rolling resistance is reduced by an improved filler dispersion¹⁴⁻¹⁷. The possible ways to improve dispersion, besides increasing the energy input during mixing, include the reduction of filler-filler interactions and the increase of polymer-filler interactions. The stronger the filler-filler interaction, the more developed is the filler network, hence the higher the rolling resistance of tires¹⁴.

From a compounding point of view, lowering the hysteresis of the compound can improve tire rolling resistance. This is achieved for example by increasing the mixing time, Figure 2.7.

Hirakawa and Ahagon¹⁸ observed a significant reduction of the loss tangent when a blend of NR, chlorinated butyl rubber and BR was mixed in two stages instead of one stage. In the first stage, all CB was mixed with only a part of the tread rubber to obtain a well-mixed stock with high CB loading. In the second stage, the highly loaded stock was mixed with the

remaining rubber. Tires build with two-stage tread compounds showed 5% lower rolling loss and no change in both, wet traction and wear¹⁹.

Figure 2.8 shows the loss modulus as function of the shear amplitude for an SBR based compound filled with different types of carbon black¹³. It is seen that the very fine and highly active blacks cause a higher loss modulus of the rubber.

Figure 2.7- The G'' plotted versus G' and G''_{max} plotted as a function of mixing time

Figure 2.8- Loss modulus as a function of shear amplitude at a constant temperature of 70°C and a frequency of 10 Hz for an SBR based compound filled with 80 phr of different types of carbon blacks

During the early 1990s, Michelin introduced a silica filler in conjunction with a silane coupling agent as a means of reducing rolling resistance while retaining wet traction. Figure 2.9 shows the storage modulus, E' , and loss factor, $\tan\delta$, as a function of the logarithm of the

double strain amplitude for Carbon Black (N110), silica and TESPT (bis[3-(triethoxysilyl)propyl] tetrasulfide)-modified silica filled NR compounds. The high dynamic modulus of the silica filled compound falls below that of N110 for the TESPT-modified silica. $\tan\delta$ of the TESPT-modified silica formulation is at first slightly higher than for the non-modified silica, but over the entire range investigated lies far below the values for N110 compound ²⁰.

Figure 2.10 shows the temperature dependencies of $\tan\delta$ measured at 2.5% strain amplitude and 10 Hz. Relative to carbon black, silica and CRX4210, a carbon-silica dual phase filler - CSDPF, give very low $\tan\delta$ at higher temperatures and very high hysteresis at lower temperatures. Based on the commonly accepted correlation between rolling resistance and $\tan\delta$ at high temperature (60 – 70 °C), it can be expected that the rolling resistance of silica-filled or CSDPF-filled tires is much lower than for the carbon black-filled ones ¹². Similarly based on the commonly quoted $\tan\delta$ at 0 – 20 °C as indicative for traction (see later in 2.3) silica-filled or CSDPF-filled tires should perform much better than carbon black-filled ones.

Figure 2.9- The storage modulus, E' and the loss factor, $\tan\delta$ as a function of logarithm of the double strain amplitude on Carbon Black, silica and TESPT-modified Silica filled NR compounds

Figure 2.10- Temperature dependences of $\tan \delta$ at a strain amplitude 2.5% and 10 Hz for OE-SSBR/BR compounds with a variety of fillers

2.2.5 Measurement

The Society of Automotive Engineers (SAE) has established two standard procedures for measuring tire rolling resistance: J1269 and J2452. Because the procedures are both laboratory tests, they allow for repeatability and instrumentation accuracy as well as control of operating conditions and other exogenous influences. What distinguishes the two test procedures the most, is that the first measures rolling resistance at a single speed (80 kph), while the latter measures it over a range of speeds. Of course, neither procedure can take into account all the conditions an individual tire will experience under varied driving and operating conditions over tens of thousands of kilometers.

Laboratory tests are accomplished by bringing the tire into contact with a road wheel (drum), as depicted in Figure 2.1, and measuring either the spindle force or the torque required to maintain a constant drum speed and subtracting parasitic losses.

Figure 2.11- Schematic of wheel on test drum to measure rolling resistance

2.3. Traction (Skid Resistance)

2.3.1 Introduction

Traction (or skid resistance) refers to the maximum frictional force that can be produced between surfaces without slipping. In the design of vehicles, high traction between the wheel and the road surface is desirable, as it allows for more energetic acceleration (including cornering and braking) without wheel slippage.

The coefficient of traction is defined as the usable force for traction divided by the weight on the running gear (wheels, tracks etc.), so it decreases with increasing load. As the coefficient of traction refers to two surfaces which are not slipping relative to one another it is the same as the coefficient of friction.

Friction force is directly proportional to the normal reaction force (N) between two surfaces, and can be written as:

$$F = \mu N \quad (2.11)$$

where μ is the friction coefficient.

The friction coefficient depends on pressure, temperature and sliding speed as well as rubber type.

Frictional force is proportional to real area of contact, A_r ,

$$F = \phi A_r \quad (2.12)$$

Soft, highly viscous rubber can deform and increase its real area of contact. The proportionality constant depends on sliding speed and temperature as well as on the type of rubber. It is assumed that it doesn't depend on pressure. The pressure dependence of rubber friction is then entirely determined by the changes of the real contact area with load (A_r)¹³.

A_r can be written as:

$$A_r = A_0 \left[\frac{P}{E} \right]^{2/3} \quad (2.13)$$

where E is the modulus and P is pressure (load divided by area) ²¹.

Hence the pressure dependence of the friction coefficient is as follows:

$$\mu = \mu_0 \left[\frac{P}{P_0} \right]^{-1/3} \quad (2.14)$$

where P is pressure and P_0 and μ_0 are reference values ¹³.

Schallamach ²¹ measured the friction coefficient on smooth glass for non-reinforced NR compounds of different moduli. The theoretical law (equation 2.12) was obeyed with good accuracy for rubbers of low modulus, however for very hard compounds, deviations were quite large. In another investigation ²², he measured the load dependence of the friction coefficient for different tread compounds on polished glass and found a power law relationship (Figure 2.12).

On rough surfaces the decrease of the friction coefficient with increasing pressure is much smaller. Theoretically it has a power law relationship with an index of $-1/9$ ¹³.

Figure 2.12- The load dependence of the friction coefficient on polished glass for 4 different polymers; 3, 4 IR = 3, 4 synthetic polyisoprene; speed: 0.015 m/s

2.3.2 Friction on dry, smooth surfaces

Unlike the friction between hard solids, the friction coefficient of rubber sliding on a hard surface depends strongly on temperature and sliding speed. Data obtained at different speeds and temperatures can be transformed into a 'master curve' by multiplying the speed with a suitable shift factor (a_T , as defined by the WLF equation) and plotting it on a log scale as illustrated in Figure 2.13²³:

Figure 2.13- Friction coefficient data obtained at different temperatures and sliding speeds for a NBR gum compound on dry wavy glass, transformed into a master curve of the friction coefficient as function of $\log a_T v$ by using the WLF equation²³

The friction master curves for different polymers have similar shapes, but differ in the position they take up on the $\log a_T v$ axis: the lower the glass transition temperature the higher the $\log a_T v$ value of maximum friction if the reference temperature is the same for all rubbers, say 20°C. If the curves are referred to the standard reference temperature, T_{ref} , the maxima of different rubbers almost coincide⁴. Differences which do occur can be attributed to differences in the frequency at which the loss modulus E'' has its maximum (Figure 2.14).

Figure 2.14- Comparison between friction master curves (top) of different rubbers on dry glass and the corresponding loss modulus frequency curves (bottom) obtained with a torsion pendulum at different temperatures and transformed to $\log a_r v$ values; all referred to 20°C

This close relationship with the loss modulus, which represents, to a first approximation, the relaxation spectrum of the polymer, indicates that on smooth, dry surfaces an adhesional friction process operates which is linked to the relaxation spectrum of the rubber. This adhesional friction arises from the repeated formation and breaking of molecular bonds between the surfaces during sliding^{13, 24, 25}.

Wang et al.²⁶ have formulated the coefficient of adhesional friction, μ_a , as a function of $\tan \delta$:

$$\mu_a = K \left(\frac{\sigma_{ms}}{H} \right) \tan \delta \quad (2.15)$$

Where K is a proportionality constant and σ_{ms} is the maximum stress able to be generated on the elemental area. H is the hardness that, with the normal load W , determines the total

true contact area between polymer and rigid surface. $\tan\delta$ is the loss factor which is related to the energy dissipated to the energy stored in this stick-slip process. μ_a depends on the $\tan\delta$ of the rubber, which suggests that the principal mechanism of frictional energy dissipation from adhesion is through deformation losses, namely viscoelastic hysteresis. The role of adhesion is to increase the magnitude of the deformation loss. Only a skin layer of the rubber undergoes deformation²⁶. However, in a tire/road contact on dry surfaces the adhesional contribution is often neglected²⁷⁻²⁹.

2.3.3 Friction on dry, rough surfaces

The master curve technique can also be applied to the temperature and speed dependence of the friction coefficient on rough surfaces. However, the shape of the master curve is quite different. Figure 2.15 shows the master curves of NR on a clean silicon carbide track, curve B, and when the track is dusted with magnesium oxide, curve C. The dashed line, curve A, shows again the master curve on a smooth wavy glass surface^{13,30}. The curves on the rough track display again a maximum, but at a much higher sliding speed compared to the smooth surface.

On clean carborundum, a hump appears on the master curve at speeds which are close to the speed of maximum adhesion friction. This hump disappears if the track is dusted with magnesium oxide or any other fine powder. The powder prevents the microscopic contact of the rubber necessary to produce high adhesional friction. Incidentally, if such a powder is applied to a smooth glass track, all dependence of friction on speed and temperature vanishes and a constant coefficient of friction of about 0.2 prevails over the whole range of temperature and speeds¹³.

When comparing the speeds of maximum friction on rough tracks with dynamic modulus data, it appears that the speed of maximum friction is connected with the frequency at which the maximum of the loss factor $\tan\delta$ occurs, as shown in Figure 2.16.

Figure 2.15- Master Curve of the friction coefficient of unfilled NR on a clean 180 mesh silicon carbide track (curve B) and on the same track dusted with magnesium oxide (curve C); the dashed line (A) shows the master curve on wavy glass

Figure 2.16- Comparison of the friction master curves for different gum rubbers on a silicon carbide track with the master curves of the loss factor $\tan \delta$ as a function of frequency

Figure 2.17 shows the distances between the master curve of the friction coefficient on a rough surface vs. velocity (m/s) and the curves of the loss properties vs. frequency (s^{-1}) schematically³⁰. Friction on a rough track is the outcome of two different processes, of which one is the molecular adhesion on the track which is the only source of friction on a smooth surface. The second process operating on a rough surface has been ascribed to dynamic energy losses due to deformation of the rubber surface by the asperities of the track, sometimes called hysteresis contribution.

Figure 2.17- Diagrammatic sketch to demonstrate how the shape of the master curve of a polymer on a rough track depends on the position of $\log E''$ and $\tan \delta$ on the $\log f$ axis

Wang et al.²⁶ have defined the coefficient of hysteresis friction as a function of hysteretic loss:

$$\mu_h = K' \left(\frac{P}{E'} \right)^n \tan \delta \quad (2.16)$$

where P is the mean pressure on each asperity, E' is the elastic modulus and $n \geq 1$. In this equation the constant, K' , is related to the asymmetry of pressure distribution on asperities. This factor also shows a speed dependency.

The combined deformation-adhesion friction coefficient, μ_{tot} , was defined by Veith as³¹:

$$\mu_{tot} = k_1 P \frac{\tan \delta}{E'} + k_2 \left(\frac{1}{P^m} \right) E'' \quad (2.17)$$

Taking $n=1$, where k_1 and k_2 are constants; $\tan\delta = E''/E'$; m is an exponent approximately equal to 0.2; and P is the mean contact pressure. The first term is the deformation and the second the adhesion term.

In summary, with regards to the friction between rubber and a rigid solid surface, viscoelastic properties of the rubber play a dominant role in all the mechanisms involved.

2.3.4 Friction on wet tracks

Rubber friction on wet tracks is primarily studied on rough tracks. Friction on smooth tracks is of limited interest¹³. If the sliding speed is kept low, the friction coefficient data of rubber on wet corundum stone at different speeds and temperatures can be transformed into a master curve, too. Figure 2.18 shows such a curve for a NBR compound on a 180 mesh (approximately 80 Microns roughness) corundum stone surface with distilled and +5% detergent containing water as a lubricant.

Figure 2.18- Master curves of an NBR compound on a 180 mesh corundum stone surface.

The curve on the track wetted with distilled water has all the features of the friction master curve obtained on the dry silicon carbide track (Figure 2.15); especially the adhesion hump is clearly recognizable. If a detergent is added, this hump disappears similar to adding magnesia to the dry track. According to Roberts³², if the lubricating liquid contains polar substances, a continuous film of liquid stays between rubber and surface up to high

pressures, and if it is distilled water, the liquid contracts into globules leaving the remaining area in practically dry contact. Therefore, friction on wet tracks is determined by the adhesion in the dry region rather than only by normal deformation losses. This mixture of dry and wet friction is often referred to as boundary lubrication (BL).

Lubricated friction is basically caused by two modes, boundary lubrication, BL, and elastohydrodynamic lubrication, EHL, as illustrated in Figure 2.19³¹.

Figure 2.19- (a) Boundary layer (BL) lubrication diagram, with intimate rubber countersurface contact; V : slip velocity (b) Elastohydrodynamic lubrication (EHL) diagram, showing intervening water film

The two modes are defined by the type of interfacial (hydrodynamic) pressure that exists in the contact zone. In the first mode, the thickness of the lubricant separating the two surfaces is of the order of a few molecular layers. The pressure is defined as P_C , and BL lubrication occurs under conditions of low slip velocity between the contacting surfaces.

The second mode occurs when the slip velocity between the contacting surfaces is high. For a rubber-hard countersurface combination, this high velocity results in a hydrodynamic lift due to a fluid (lubricant) pressure, P_L , that develops between the two surfaces. A second feature is an elastic indentation of the soft rubber by this pressure profile; this indentation assists in physically separating the surfaces.

The squeeze path effect is illustrated in Figure 2.20(a). As a tread element approaches a hemispherical pavement particle (sketch 1), a pressure P_L builds up as the upper surface descends (sketch 2); this pressure retards the ultimate contact and a finite squeeze time (of the order of milliseconds) is required to eliminate all the water and achieve a contact with a finite pressure P_C (sketch 3). An important feature is the transit time for a tread element

through the footprint, front to rear. At low speeds, the transit time is large relative to the squeeze time and the water is readily squeezed out giving good grip. For high speeds, the transit time may be of the same order as the squeeze time and only a short time period may remain for BL frictional force development ³¹.

Figure 2.20- (a) Diagram for “squeeze pass” effect, normal approach of a tread element toward a pavement particle, V : velocity of normal approach (b) upper diagram: profiles for P_C and P_L vs. V ; lower diagram: resultant friction coefficient μ as a function of slip velocity

Profiles for these two pressures (P_L , P_C) as a function of slip velocity are shown in Figure 2.20(b). As the velocity increases, P_C maintains a plateau value over the low velocity range and then starts a rapid decline. Concurrent with this, P_L builds up and eventually reaches a plateau value. The lower part of Figure 2.20(b) shows how the traction coefficient decreases as these two pressures change. On this basis, a simple model equation may be written for the wet traction coefficient, given by the following equation:

$$\mu(wet) = (1 - \Phi_{EHL})\mu(BL) \quad (2.18)$$

Where $\mu(wet)$ is any measured (optional) traction coefficient on a given surface; ϕ_{EHL} is a fraction of the footprint (area) in the EHL lubrication mode; and $\mu(BL)$ is the pure boundary layer traction coefficient at low speed, which is a constant.

As speed increases from the low speed BL condition, an increased fraction of the footprint moves into the EHL mode and the measured traction coefficient drops. When $\phi_{EHL} = 1$, $\mu(wet) = 0$, and full hydroplaning occurs ³¹.

To evaluate traction performance, Veith³¹ used the two term model proposed by Moore³³, and found that at constant pressure the hysteresis or deformation component of the total friction coefficient (μ_{tot}) is proportional to $\tan\delta/E'$; and the adhesion component is proportional to $(E'')^{1/2}$ for wet testing on a coarse surface:

$$\mu_{tot} = a_0 + a_1 \left(\frac{\tan \delta}{E'} \right) + a_2 (E'')^{0.5} \quad (2.19)$$

Where a_0 is a general constant, a_1 is the regression constant that contains the (P^n) term and a_2 is regression constant that contains the $(1/P^m)$ term, in comparison with Eq. 2.17.

According to Wang et al.²⁶, the weaker polymer-filler interaction and high polarity of silica would allow the rubber on the filler surface to be peeled under the shear stress during skidding of the filled rubber on a track, resulting in the exposure of the bare filler surface (this can be improved a bit by introduction of suitable coupling agents). This is especially true under wet conditions due to water adsorption. In contrast, under the same conditions, the surface of carbon black should remain covered by rubber due to its strong interaction with polymer and lower surface polarity. These phenomena were confirmed by Atomic Force Microscopy (AFM): After skid testing under wet conditions, the top skin of the worn surface contains bare silica surface in silica-filled compounds, but carbon black aggregates remain covered by rubber.

2.3.5 Glass transition temperature (T_g) and wet skid resistance (WSR)

In practice, very often, the T_g (measured by DSC) is used as an indicator for the wet skid behavior. As a rule of thumb, it is assumed that the higher the T_g , the higher the WSR, as indicated in Figure 2.21^{34,35}. This rule agrees quite well with the practical experience in the case of blocked wheel braking and for all rubbers based on butadiene, butadiene-styrene and isoprene. However, the most notable exception is butyl rubber (IIR), which has a low T_g ($\approx -65^\circ\text{C}$), but is very good in WSR. Clearly there are other factors influencing the WSR behavior of elastomers besides the T_g .

Figure 2.21– Wet skid resistance as a function of the glass transition temperature T_g ³⁴

In addition, it was proven that T_g determined dynamically at high frequencies relates well to the WSR of the rubber compound due to the fact that wet skid resistance is a high frequency phenomenon. Figure 2.22 shows a tire rolling on a road surface. The road surface is composed of many irregularities, or asperities. When a braking force is applied, the tire is pressed against the road surface due to the weight of the car, and comes into contact with most of the asperities. Since there are a large number of these asperities close together, the frequency of deformation experienced by the tire as it is sliding over the surface is very high. This frequency is difficult to calculate and depends upon the speed of the tire and the spacing of the asperities. The spacing between the asperities is estimated to be ~0.1 to 0.01 mm. Assuming a speed of slide of 8 km/h, the frequency encountered by the tire as it is sliding must be between 20 kHz and 200 kHz. Due to uncertainties associated with calculating these frequencies, a wider frequency range (1kHz – 1MHz) may be considered to be representative of wet skid ^{36,37}.

A linear viscoelastic spectrum of an amorphous polymer can be seen in Figure 2.23. G' and G'' are the storage and loss modulus, respectively. Four different regions are evident: the terminal region, the plateau region, the transition region and the glassy region. It is commonly accepted that the wet skid resistance is linked with the dynamic losses in the transition region of the bulk polymer ^{34,36,38,39}.

Figure 2.22 – Schematic diagram of a tire encountering wet skid conditions. There is a thin film of water between the tire and the road surface ³⁶

2.3.6 Time-Temperature Superposition principle

The empirical principle of time-temperature superposition was first proposed by Williams, Landel and Ferry in 1955 ⁴⁰ and is generally referred to as the WLF principle. This principle states that for materials exhibiting linear viscoelastic behavior such as amorphous polymers and unfilled elastomers, data obtained at different temperatures and frequencies can be superimposed into one smooth mastercurve by a horizontal shift factor (a_T) along the log frequency axis.

Figure 2.23- Typical linear viscoelastic spectrum of a linear amorphous polymer ³⁶

Reducing the relaxation data to the reference temperature T_{ref} leads to the following equation:

$$\log a_T = \frac{-C_1(T - T_{ref})}{C_2 + T - T_{ref}} \quad (2.20)$$

The constants C_1 and C_2 vary with the chosen reference temperature and in general also from polymer to polymer ⁴¹. If the reference temperature is taken as the glass transition temperature, the two constants for many diene rubbers have almost universal values: $C_1 = 17.4$ and $C_2 = 51.6$ °C.

The application of the WLF equation is limited to the plateau region, typically ranging from T_g to $T_g + 100$ °C.

For an unfilled system, there is a vertical shift factor coming from the density differences between different temperatures. This factor can be calculated via:

$$\log \left(\frac{T_{ref} \rho_{ref}}{T \rho} \right) \quad (2.21)$$

where ρ_{ref} and ρ are the densities of the polymer at temperatures T_{ref} and T , measured in K. this value is normally very small and neglected ⁴².

Figure 2.24 shows the process of applying this principle to an unfilled S-SBR sample, where frequency sweeps performed at different temperatures from 0.1 to 100 rad.s⁻¹, are shifted horizontally to obtain master curves for G' and G'' ranging over more than 17 frequency decades. The horizontal shift factors are independent of filler concentration, so the horizontal shift factors of a filled system can be estimated via dynamic mechanical measurements at the unfilled sample ⁴².

With the introduction of fillers as reinforcing agent, the complex interactions between the filler network and the polymer matrix cause strong nonlinear effects with respect to the amplitude of deformation. The influence of the filler system during the master procedure is considered via the introduction of a temperature-dependent vertical shift factor physically interpreted as the activation energy of the glassy polymer bridges in the vicinity of nanoscopic gaps between adjacent filler particles. Figure 2.25 illustrates the necessity to

introduce a vertical shift factor for low-frequency data, corresponding to high temperatures

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Figure 2.24- (a) storage modulus G' versus frequency at 0.5% strain of the unfilled S-SBR sample for various temperatures $T = -30$ to $T = 30^\circ\text{C}$, (b) and master curves of G' and G'' for $T_{\text{ref}} = 20^\circ\text{C}$ after horizontal shifting⁴²

Once the isothermal moduli segments are horizontally shifted with the same parameters as for the unfilled system, the poor overlapping in the low frequency region indicates that the time–temperature superposition principle is not fulfilled. According to Klüppel⁴², the failure of the time–temperature superposition principle for filled systems is a characteristic viscoelastic effect of the interpenetrating filler network, indicating that the filler network dominates the dynamic mechanical properties of the composites at small frequencies / high temperatures, because the rubber matrix is softer than the filler network.

Figure 2.25- Master curves at 0.5 %strain amplitude of the Carbon Black-filled S-SBR before vertical shifts (left) and after vertical shifts (right)

The physical origin of the observed shifting behavior is the superposition of two relaxation processes in filled elastomers, the one of the polymer matrix and that of the filler network. The applied horizontal and vertical shifting procedures allow for a separation of both relaxation processes.

2.3.7 Measurement techniques

Dry surfaces are believed to provide sufficient friction to avoid skidding problems; consequently, as mentioned before, wet conditions are more important to talk and most techniques for measuring skid resistance focus on wet conditions ⁴⁴.

Pendulum method: The British pendulum tester (BPT) works by releasing a pendulum fitted with a rubber shoe which contacts the surface. The extent to which the pendulum is retarded by contact with the surface is the basis for the estimate of skid resistance. The contact speed with this method is low - approximately 11 km/h - and therefore microtexture tends to dominate the readings. It is therefore representative of skid resistance in low speed situations. This device is not capable of continuous measurements at highway speeds.

Locked wheel method: Test tires, manufactured to precise specifications, are fitted to a test trailer, which may have one or two wheels. Water is sprayed in front of the tire or tires in a controlled manner. The test consists of applying the brakes to lock the wheel or wheels and measuring the torque developed on the test wheel. The measurements are taken only after a certain interval in order to allow the tire temperature to stabilize. The torque is converted into a skid number, which is identified by the speed at which the test takes place, e.g. SN40 represents the skid number obtained at a test speed of 40 km/h. This method is capable of extensive measurements at highway speed.

Side-force method: In this method, an extra wheel is fitted to the vehicle, mounted at an angle of 20° to the direction of travel. In some machines, two wheels are fitted, one in each wheel path. As the vehicle travels along, the side forces generated by the wheel is measured. The ratio of the force created - at right angles to the plane of the wheel - to the vertical load on the wheel is taken as the side force coefficient, a measure of the resistance being offered by the surface. As with the skid number, the speed at which the measurement is conducted is indicated by a subscript, e.g. SFC80. Water is sprayed in front of the test wheel in a

controlled manner. A smooth tire is used to avoid the results being affected by tire wear. Not only the measurements can be carried out at highway speed, but also there is no need for inconvenient braking operations to be carried out as is the case with locked wheel methods.

Laboratory abrasion tester (LAT)100: The rubber sample wheel runs under a set slip angle and load on the flat side of an abrasive disk at a given speed. Slip angle, load and speed can be varied over a wide range (Figure 2.26). The abrasive disks are made of high grade Alumina, with different grain size. A mixture of magnesium oxide powder and Alumina (grain size 120) is fed between track and sample to avoid smearing of the sample due to thermal-oxidative degradation of the rubber during the abrasion process. During the experiment, the side force generated on the test wheel by the slip angle is monitored.

Figure 2.26- Diagrammatic view of the laboratory abrasion tester (LAT)100⁴⁵

2.4 Correlation between rolling resistance and traction

The rolling resistance and traction and wear characteristics of tires are not independent of one another. As explained earlier, the tread has a major influence on rolling resistance because it contains much of the viscoelastic rubber in the tire that causes hysteretic energy loss. The same tread deformation contributes to the tire's traction capabilities. The higher the loss properties, the higher the traction. Figure 2.27 shows the close relation between wet traction and rolling resistance¹³.

Figure 2.27- Wet traction rating of different tread compounds on tires with the same construction and tread pattern plotted against the relative rolling resistance of the tires under constant load and speed

Considering these facts, the goal of a tire with high safety (high wet traction) and good efficiency (low rolling resistance), which has an acceptable lifetime as well, is only reached when a good balance of these three properties is achieved.

2.5 Polymers used in the tread formulations; an overview of new generation products

2.5.1 Introduction

Polymers as the main ingredient in a tire tread compound recipe are of great importance affecting the eventual properties of the compound. It has been stated that certain polymer features such as molecular weight and molecular weight distribution affect rolling resistance (and handling)⁴⁶⁻⁴⁸ of the tire. The high primary-chain molecular weight and narrow molecular weight distribution of solution-SBR contributes to reduced hysteresis and favors the balance of rolling resistance, traction and wear performance when utilized in a tread formulation⁴⁷. Also the use of such high molecular weight diene rubber in a tread formulation is claimed to result in tires with excellent wet grip and rolling resistance properties⁴⁸. Similarly, microstructure and tacticity display a big effect on rolling resistance and traction. Monomer composition and co-monomer sequence are believed to be related to wear, traction and rolling resistance, and long chain branching may also be a key factor in tire performance on the road⁴⁶. Figure 2.28 gives an overview of these structural properties

and their effect on tire performance. The vinyl/styrene ratio in the structure of SBR (as one of the important elastomers in passenger tire tread compositions) is also of great concern when considering the performance of the elastomer in the tread compound⁴⁹⁻⁵². It has been claimed that a higher styrene content will bring in better grip performance, as it increases the T_g of the compound.

Feature Performance	MW and MWD	Microstructure and Tacticity	Monomer Composition	Sequence Distribution	Branching
Wear
Traction
Rolling Resistance
Handling in Factory

Critical
 Important

Figure 2.28- Effect of polymer architecture on tire performance⁴⁶

On the opposite side are the reinforcing fillers, as the second important ingredients in the compound formulation. The interaction between the polymer and fillers plays a key role in the compound final properties and consequently on the tire performance. As was mentioned earlier, introduction of silica in the early 90's in tread compound recipes was a great success in reducing the rolling resistance of the tires. Nowadays silica is considered as the main filler in passenger car tire tread compound formulations.

Silica is an amorphous material, consisting of silicium and oxygen atoms in the form of siloxane and silanol groups. Figure 2.29 shows the three possible types of silanols on the silica surface: Isolated, Vicinal and Geminal⁵³. Due to hydrogen bonding between adjacent OH groups, primary silica particles coalesce and form aggregates of the size 100-500 nm. These aggregates flocculate via van der Waals forces to create agglomerates of micrometer dimension⁵⁴⁻⁵⁶.

Figure 2.29- Types of hydroxyl groups on the silica surface⁵³

Silica as a filler shows a very strong tendency to networking due to poor compatibility with hydrocarbon rubbers, its polar character and the ability to form hydrogen bonds⁵⁷. It has been recognized that silica possesses a low dispersive component of surface energy while that of carbon black is high. By contrast, the specific or polar component of the surface energy is much higher for silica than for carbon black^{58,59}. In a hydrocarbon polymer, this suggests that the polymer–silica interaction determined by the dispersive component of filler surface energy is lower, and the interaction between silica aggregates is higher⁶⁰. Consequently, less compatibility with the polymer and strong filler–filler interaction leads to a more developed filler-filler network⁶¹.

To enhance the filler(here silica)-polymer interactions, several approaches have been proposed: a very successful one is using an intermediate which is compatible with both parties: called the coupling agent. An alternative is the modification of either the polymer chains or the filler particles. Carbon-silica dual phase fillers are an example of such attempts to achieve better filler-polymer interactions through new fillers or filler combinations⁶²⁻⁶⁵.

Organofunctional silanes have been used for many years to improve the adhesion between glass fibers and various polymers. In general, they can be used to increase compatibility between siliceous fillers (including silicas) with a variety of resins and polymers⁶⁶. Silanes with the appropriate functionality provide chemically bonded coupling between the silica particles and the rubber network. The role of the coupling agent is twofold: firstly, the silica particle is hydrophobized, thus improving the dispersion. Secondly, it is turning the silica particle into a polyfunctional crosslink site, thereby chemically coupling the rubber polymers to the silica surface⁶⁷⁻⁷². Bis(triethoxysilylpropyl)-tetrasulfide (TESPT) known commercially as Si69, is a bifunctional silane commonly used in the tire industry. The chemical structure is seen in Figure 2.30. It has the ability to react with the rubber chains forming sulfur bonds

and with the silica surface by Si-O-Si bonds. The average sulfur rank of the polysulfide for this silane type is 3.8⁷³.

Figure 2.30- Bis(triethoxysilylpropyl)- tetrasulfide (TESPT) chemical structure, $x \approx 3.8$.

2.5.2 Polymer modification as a successful method to increase filler-polymer interactions

A successful approach to increase the affinity between the filler particles (mostly silica) and the elastomer is to functionalize the elastomer chains (through either chain-end or backbone, Figure 2.31). Functionalized elastomers, especially styrene-butadiene-copolymer, have attracted large attention and been the subject of many researches⁷⁴⁻⁹⁹ and are reviewed in this part.

Solution-SBR is made by anionic living polymerization initiated by alkyl lithium compounds, such as sec-butyl or n-butyl lithium^{46,83,100,101}. This polymerization method creates the opportunity for functionalized polymer production.

Figure 2.31- Schematic view of a chain end-modified (a) and random backbone-modified polymer(b);

F: functional group

Functional monomers can be incorporated into anionic homo-polymerization of conjugated dienes or in the copolymerization of conjugated dienes and vinyl aromatic compounds to produce functionalized elastomers^{101,85}. Halasa¹⁰¹ presented the subject of a series of new styrenic monomers containing various amine functional groups like divinylbenzene or diisopropenylbenzene. These functional monomers were copolymerized with the conjugated diene (butadiene) and vinylaromatic (styrene) using organolithium initiators in a hydrocarbon solvent. The resulting solution SBR contained 0.25% to 20% of these functional

monomers in random non-blocky elastomers. These new elastomers resulted in a lower filler-filler interaction and better filler dispersion (carbon black and/or silica). However, it has been stated that adding new monomers may influence the normal polymerization kinetics and therefore change existing unmodified polymer grade properties. In addition, existing polymerization hardware often has difficulties in removing unconverted backbone modifiers from the chemical stream of a conventional polymerization facility, e.g. from the solvent stream. Accordingly third monomers may accumulate and hamper the switching between polymer grades ⁸⁴.

Tin-coupled SBRs are of particular interest in carbon black filled vulcanizates ¹⁰²⁻¹⁰⁶. Tsutsumi et al.¹⁰⁴ showed that hysteresis of solution-SBR-vulcanizates reduces remarkably by the introduction of tin-carbon bonds at the polymer chain ends, which correlated with a better dispersion of carbon black and reduction of the free polymer chain ends through the formation of carbon black-polymer chain bonds in the system.

Modification of SBR with polar components like 4,4-bis-(diethylamino)benzophenone (EAB) has been also reported ^{107,108}. Introduction of this modified polymer in a carbon black-filled compound gives improved rebound resilience (hence low rolling resistance) without sacrificing wet-skid resistance. This has been attributed to the better dispersion of the carbon black ¹⁰⁷. There are also some patents concerning the chain-end modification of sSBRs using benzonitrile ¹⁰⁹ to decrease Rolling Resistance and fused-ring polynuclear aromatic compound (benzanthracenes) ¹¹⁰ or Schiff bases (dimethylaminobenzylidenemethylamine) ¹¹¹ to reduce hysteresis properties in a black filled compound.

In silica-filled compounds, polar functionalities are more relevant. Hogan et al.⁷⁴ prepared alkoxysilane functionalized SBR through terminating the anionic polymerization with tetraethylorthosilicate (TEOS). They claim that using this polymer in a silica-containing tire tread recipe, yields reduced rolling resistance and improved wear compared to the similar non-functional polymer. Liu et al. ¹¹² have also synthesized an alkoxysilane-functionalized sSBR using γ -chloropropyl trimethoxysilane. The scheme of the synthesis process and following reaction with silica is seen in Figure 2.32. They have claimed that this polymer modification not only significantly reduces the free ends of macromolecular chains to

restrain their irregular thermal motions, but also promote these rubber chains to chemically anchor on the surface of silica particles, which makes it a good candidate to be used in green tire tread formulations.

Figure 2.32- Scheme of the synthesis process for chain-end functionalized sSBR (A-SSBR) and condensation reaction with silica¹¹²

Introduction of epoxy-groups on the main chain of polydiene has emerged as a fruitful route to enhance polymer-filler interactions⁹⁰⁻⁹⁶. It has been reported that the use of an epoxidised-SBR with just 7mol% of epoxidation groups in the main chains results in a reduction of around 4 times in the value of the equilibrium storage modulus at low strains, G_0 , compared to untreated SBR-silica mixed compound. This has been attributed to the weaker filler-filler network which is itself a result of hydrogen bonding or even more of chemical bonds between the epoxidised SBR and silica surface groups. The postulated reaction can be seen in Figure 2.33.

Figure 2.33- Proposed mechanism of filler-matrix interaction of an epoxidised rubber and silica⁹⁰

NBR functionalized with side-chain epoxy groups in a silica-filled compound brings reduced Mooney viscosity, reduced hardness, reduced tensile set, increased resilience and abrasion resistance, decreased elongation at break and slightly reduced tear resistance ⁷⁹. The possible reaction between silica particles and polymer chains are reported as shown in Figure 2.34.

Figure 2.34- silica-epoxy functionalized polymer reaction, $\equiv\text{SiOH}$ represents a silanol group on the surface of a silica particle and R indicates the polymeric chain ⁷⁹

Thiele et al. ⁸² prepared a series of functionalized s-SBRs using dithiol backbone modifiers; the polymer preparation and modification pathway is shown in Figure 2.35. According to their procedure, the resulting living polymer chains are, depending on the intended application, hydrolyzed (pathway i) or coupled. Coupling may be performed partially (pathway iv and v) or completely (pathway ii) using so called coupling agents. The coupling agents in this polymer modification (contrary to the silica-rubber coupling agents) are usually species like silicon- or tin-tetrachloride or tetramethoxy-tin or -silicon. As a result of coupling, the polymer solution viscosity is reduced and higher polymer concentrations in the chosen nonpolar polymerization solvent can be achieved. In addition, the free polymer chain-ends can be reacted with polar group containing molecules in the course of a polymer chain end modification process ⁸³ (see pathway iv). The application of chain end-modified polymers in polymer-filler compound vulcanizates leads to an improvement of dynamic vulcanizate characteristics, ⁷⁵ particularly to reduced vulcanizate hysteresis.

The interaction of a polymer, prepared according to one of the pathways i-v, with filler particles such as silica or carbon black can still be improved using specific backbone modification technologies. Examples of these backbone modifiers can be seen in Figure 2.36. The authors have reported that all backbone-modified polymer vulcanizates have an increased tensile strength and 300%-modulus value compared to the reference compound polymers. The rolling resistance property indicated by $\tan\delta@60\text{ }^\circ\text{C}$ improved for all backbone-modified polymer vulcanizates by 19 to 32% while the $\tan\delta@0\text{ }^\circ\text{C}$ (indicative for wet grip characteristics) deteriorated slightly (3-15%). Overall the largest 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, it was concluded that excellent hysteresis properties of a chain end-modified polymer can be further improved by the application of the backbone modification technique.

Figure 2.35- Polymer preparation and modification pathway⁸⁴

Figure 2.36- Some examples of backbone modifiers⁸⁴

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Chapter 3

The role of material composition in the construction of viscoelastic master curves: silica-filler network effects

Abstract

One of the important aspects in the development of new tire compounds is the correlation between the dynamic mechanical properties of the rubber, measured on laboratory scale, and the actual tire performance. The measuring protocol for dynamic mechanical properties with high precision and good correlation with tire properties is therefore of main concern. In order to predict wet traction, the viscoelastic behavior of the rubber materials at high frequencies (in the MHz range) need to be known. Viscoelastic master curves derived from time-temperature superposition can be used to describe the properties of the materials over a wide frequency range.

In this chapter, the construction of master curves for tread compounds filled with different amounts of silica is discussed. From the vertical shifts as a function of temperature activation energies are derived which apparently are in the linear response region by fulfilling the Kramers-Kronig relations, and their values correspond to physical phenomenon as the underlying principle.

Strain sweep viscoelastic measurements, per definition outside the linear region, lead to much higher activation energies. Because the deformation strains employed for these strain sweep measurements are more realistic for wet traction or skidding phenomena it is concluded that the value of the above measurements in the linear region to predict traction is only limited or a first but still important indication.

3.1 Introduction

A tire interacts with the hard road surface by deforming under load, thereby generating the forces needed for traction, cornering, acceleration and braking. It also provides increased cushioning for driving comfort. Traction, especially under wet conditions, is the most important tire property from a safety point of view. Traction is directly related to energy lost in each deformation cycle: each point in the tire passes through a stress-strain cycle once every rotation¹⁻⁷. Due to the viscoelastic nature of the rubber compound, the deformation leads to energy loss in the form of heat in each cycle. Although it has been stated that the

tread pattern and the roughness of the road surface are as important as the loss properties of the tire tread material in determining the skid properties, the current trend is basically to concentrate on the latter for improvements in performance.

In order to predict wet traction, the viscoelastic properties of the rubber materials at high frequencies, in the megahertz (MHz) range, should be measured. Heinrich et al.⁸⁻¹⁰ have done investigations on the wet skid behavior of different polymers and concluded that neither the glass transition of the polymers alone nor their plateau modulus G_N^0 gives good correlation with wet skid resistance (WSR). A good correlation is only found when relating the WSR to the viscoelastic behavior of the elastomers in the transition region which is typically in the range of 1 kHz-1 MHz.

In practice, measuring dynamic properties is limited by the accessible frequency range of the instrument. However, the modulus at high frequencies is available via the time-temperature superposition principle. According to this principle, the effect of changing the temperature is the same as applying a shift factor a_T to the time scale. The time-temperature superposition for polymeric materials was proposed by Williams, Landel and Ferry in 1955^{11,12} and is generally referred to as the WLF principle. According to this principle, the horizontal shift factor a_T is given by:

$$\log(a_T) = \frac{-C_1(T - T_{ref})}{C_2 + (T - T_{ref})} \quad (3.1)$$

$$T_g < T < T_g + 100^\circ C$$

where T is temperature and T_g is the glass transition temperature. The constants C_1 and C_2 vary with the choice of the reference temperature T_{ref} . If the glass transition temperature is taken as the reference temperature, the two constants have almost universal values for many high diene rubbers: $C_1 = 17.4$ and $C_2 = 51.6$. If $T_g + 50^\circ C$ is taken as T_{ref} , then $C_1 = 8.86$ and $C_2 = 101.6$. These values only differ slightly from one polymer system to the other¹².

The WLF principle has been proven to work well, for practical/engineering purpose, for polymers in their molten state, irrespective of whether they are crosslinked or not, as it is based on the free-volume concept^{12,13}.

It should be taken in to account that time-temperature superposition can break down in the glass-rubber softening region. This break down depends to a great extent on the chemical

structure of the monomer¹⁴. Generally, the viscoelastic behavior of polymers is not adequately understood and there remain many unresolved issues that continue to offer tremendous challenges.

If fillers are added to these polymers, and most particularly reinforcing fillers like carbon black and silica, the WLF-principle does not work properly anymore either. Some overlapping of the curves is then seen in the lower frequency range¹⁵⁻¹⁷. The reason is the additional effect of polymer–filler and even more so filler–filler interactions. The latter is commonly designated as the “filler network”, for which the free-volume concept obviously does not apply. The overlapping in the low frequency region (or vice-versa high temperature region) indicates that the filler network dominates here the dynamic mechanical properties of the filler-rubber composite as the rubber matrix is softer¹⁵. In order to eliminate these overlapping and receive a proper master curve, vertical shifting is necessary.

The filler network manifests itself in various ways, like the need for an additional vertical shift in the creation of dynamic mechanical mastercurves over the common vertical shift accounting for temperature corresponding density differences, in the non-linear Mullins effect¹⁸⁻²⁰ and the Payne effect^{21,22}. An all-inclusive theory relating all these different elements of the behaviour of the filler network does not exist as yet. But all these effects are based on physical principles and therefore should basically respond to temperature variations according to corresponding relatively low activation energies compared to chemically based mechanisms.

The construction of master curves for carbon black and silica reinforced rubbers has been the subject of several experimental as well as theoretical papers already¹⁵⁻¹⁷. It is commonly understood that a silica filler-network is even stronger than a carbon black network^{22,23}. In the present chapter, the construction of master curves based on the dynamic mechanical experiments for a tire tread rubber compound with varied silica filler-loading is discussed. In addition, strain sweep measurements detailing the Payne effect are presented. Activation energies will be derived from the temperature dependence of the vertical shift in the creation of master curves, resp. of the Payne effect and correlated with the material composition.

3.2 Experimental

3.2.1 Materials and Compound Preparation

Blends of oil-extended solution styrene-butadiene rubber (S-SBR) and high-cis polybutadiene (BR) with a weight ratio of 70/30 were used in this study. Compounds have been prepared based on the formulations given in Table 3.1. In the acronym used, 3 stands for 30 phr of BR and 7 for 70 phr of SSBR. S indicates the silica filler and the last number shows the amount of silica: 6 for 60, 7 for 70 and 8 for 80 phr silica. A highly dispersible silica was used as reinforcing filler. The amount of silica was varied between 60 and 80 phr. The amount of coupling agent has been adjusted according to the amount of silica to maintain the same weight ratio. The rest of the ingredients and suppliers are listed in Table 3.1.

The compounds were prepared in a 350 ml Brabender 350S internal mixer Operating at 100 rpm with a filling factor of 0.7. The total mixing time was 9 minutes while the dump temperature was adjusted to approximately 155 °C (by changing the initial temperature). The samples were cured in a Wickert press WLP 1600 at 160 °C to sheets with a thickness of 1.5 mm according to their t_{90} optimum vulcanization time as determined in a rubber process analyzer RPA 2000.

3.2.2 Measurement

Dynamic mechanical analyses were performed in the shear and tension mode in a Metravib DMA2000 dynamic spectrometer. The samples were cut from the cured sheets of the rubber compounds. For producing master curves, time-temperature superposition measurements were performed at different temperatures between -20 °C and 80 °C in steps of five degrees at a dynamic strain of 0.1% and the frequency range of 1-200 Hz. The glass transition temperatures were obtained from temperature sweep measurements in tension mode at a frequency of 1 Hz and dynamic strain of 0.1%. Strain sweep measurements were performed at 10 Hz at different temperatures from 60 to 80 °C.

Table 3.1
Rubber compound compositions (in phr)

Ingredient	Supplier	Sample Code		
		37S6	37S7	37S8
S-SBR		96.3	96.3	96.3
BR		30	30	30
Silic		60	70	80
TESPT ^a	Evonik Degussa GmbH	5.2	6.1	7
TDAE ^b	BP Belgium	6.7	6.7	6.7
Zinc oxide	Sigma Aldrich	2.5	2.5	2.5
Stearic acid	Sigma Aldrich	2.5	2.5	2.5
6PPD ^c	Flexsys	2	2	2
TMQ ^d	Flexsys	2	2	2
Sulfur	Sigma Aldrich	1.4	1.4	1.4
TBBS ^e	Flexsys	1.7	1.7	1.7
DPG ^f	Flexsys	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-di-hydroquinoline

^e Accelerator N-tert-butylbenzothiazole-2-sulphenamide

^f Accelerator diphenyl guanidine

3.3 Results

3.3.1 Master curve via Time Temperature Superposition Measurements: horizontal shift

Time-temperature superposition measurements have been performed on the compounds. It is basically a frequency sweep at different temperatures for a specified dynamic strain. The raw data for the storage modulus of compound 37S7 were presented in Figure 3.1 as an example.

To produce master curves for these filler reinforced compounds, first a horizontal shift is done along the frequency axis. The WLF equation has been used to calculate the horizontal shift factor a_T according to equation (1). T_g+50 °C and the corresponding universal constants were chosen as reference temperature and C_1 and C_2 , respectively. The T_g values for

different compounds filled with different amount of filler were almost the same: -49.5 ± 1 °C. Figure 3.2 shows the storage modulus after applying the horizontal shifting for the 37S7 sample. The master curve is not smooth and some overlapping of the curves at the low frequency region occurs. The physical origin of this overlapping is the superposition of two relaxation processes, the one of the polymer matrix and that of the filler network²⁴.

Figure 3.1- Storage modulus data for compound 37S7 derived from frequency sweep measurements performed at different temperatures between -20 °C and 80 °C in steps of five degrees at a dynamic strain of 0.1%

Figure 3.2- Storage modulus for 37S7 after horizontal shifting along the frequency axis, $T_{ref} = 0$ °C

3.3.2. Vertical shift

In order to obtain a proper master curve, vertical shifts are needed to be applied. For unfilled, non-reinforced polymers the vertical shift is commonly applied to account for the density-change of the polymers with temperature. However, because the filler network greatly overrules these polymer effects, it is common to just include these in the vertical shifting without further detailing. The vertical shifting was done numerically by a MATLAB

program. During vertical shifting, the curve for the reference temperature were kept unchanged and the other isothermals shifted vertically by respective vertical shift factors b_T .

As an example, the storage modulus G' master curve after horizontal and vertical shifting for the 37S7 sample is shown in Figure 3. A nice smooth curve is obtained in this manner.

Figure 3.3- Storage modulus master curve for 37S7, $T_{ref} = 0^\circ\text{C}$

Figures 3.4, 3.5 and 3.6 show the master curves for the storage modulus G' , the loss modulus G'' and the loss tangent $\tan \delta$ of the three different compounds.

Figure 3.4- Storage modulus master curve for the different compounds

Figure 3.5- Loss modulus master curve for the different compounds

Figure 3.6- Loss tangent master curve for the different compounds

By increasing the amount of silica filler from 60 to 80 phr, the storage and loss moduli increase. For the loss tangent $\tan\delta$, a crossover is observed, where in the high frequency region, the lowest filler loading gives the highest $\tan\delta$, but at low frequencies the order is inverted.

It has been stated before that in the high frequency (low temperature) region, unreinforced gum rubber performs best in terms of WSR. In this region, the transition zone, the polymer chains themselves are responsible for the energy dissipation²⁵. By introduction of fillers, the fraction of free polymer chains decreases due to the fact that the polymers near to the filler surface are partly immobilized and act as filler rather than polymer: the occluded rubber concept and/or the concept of a glassy shell around the filler particle^{16,26-28}. Whether it is a real glassy shell or a greatly reduced mobility of the polymer chains attached to the filler particles, in either case it results in decreased damping in the transition zone and consequently decreased $\tan\delta$.

In the low frequency region, the order in $\tan\delta$ is reversed: the lower the filler content, the lower the $\tan\delta$. At a low frequency, when the polymer is largely outside the transition zone, the major source for energy dissipation is the breakdown and reformation of the filler network. Therefore, a lower $\tan\delta$ is expected for 37S6 for which the filler network is less developed. It is clear that the filler effect at different temperatures or frequency regions is governed by different mechanisms.

In Figure 3.7, the resulting vertical shift factors for the storage modulus for different samples are plotted versus reciprocal temperature: $1/T$. A nearly linear correlation with inverse temperature well above the glass transition temperature is obtained, as indicated by the

lines inserted in the figure. The slopes of these curves can be interpreted as activation energy of the filler network: E_a . Various authors have stated that this activation energy is related to the temperature dependency of glassy shells around the filler particles^{15,16,24,27}. The values of the activation energies for both storage and loss modulus are summarized in Table 3.2.

Figure 3.7- Vertical shift factor from G' vs. $1/T$ at temperatures higher than T_{ref}

In the linear response region, both storage and loss modulus obey the Kramers-Kronig relations²⁹⁻³¹ as the values of the activation energies derived from both are practically the same¹⁵. The differences between the two values of the activation energy are within the error margins of the measurements and calculations.

3.3.3. Strain sweep measurements

In order to compare the behavior of the filler network in large deformations or in the non-linear region, strain sweep measurements at different temperatures from 60 to 80 °C were performed. The results of these measurements for the 37S8 sample are shown in Figures 3.8 and 3.9 for the storage and loss moduli, respectively.

The decrease in elastic modulus upon increasing the strain amplitude, the Payne effect, is commonly related to the filler-filler linkages which are broken under strain. The short-distance forces between filler particles decrease strongly from low strain to high strain values. The breakdown of the filler network by increasing strain amplitude would also release the occluded rubber so that the effective filler volume fraction and hence the modulus decrease³². For this reason the Payne effect is being used as a measure of filler

networking originating from filler-filler interaction as well as filler-polymer interaction, particularly for silica loaded rubber compounds.

Figure 3.8- Variation of storage modulus with strain at different temperatures from 60 to 80 °C for compound 37S8

Figure 3.9- Variation of loss modulus with strain at different temperatures from 60 to 80 °C for compound 37S8

Figure 3.10- Effect of filler loading on the change of the storage modulus with strain at 60 °C

As seen in Figure 3.8, the storage modulus at low amplitudes G'_0 decreases with temperature, whereas the storage modulus at high amplitudes G'_∞ remains more or less

constant. Similarly, in Figure 3.9 the loss modulus shows a temperature dependence for low strain which more or less vanishes at larger strain amplitudes. The peaks in the loss modulus vs. strain amplitude correspond to the strains where the strongest decrease in storage modulus is observed. Figure 3.10 shows the dependence of the Payne effect in storage modulus for different silica filler loadings, obviously being the more for higher loading. And again, for high strains the effect of the amount of filler loading practically vanishes.

The difference between the low strain (0.1%) and high strain (80%) storage modulus, as a measure of the Payne effect, as dependent on temperature can now be used to establish an alternative Arrhenius type activation energy for the silica filler network ^{27,28,33,34}. Figure 3.11 gives an example for the 80 phr-loaded compound, where the natural logarithm of this Payne effect for the storage modulus is plotted against reciprocal temperature. Making use of least square fitting a straight line is drawn through the points in the figure, of which the slope gives the activation energy. This can be applied for the loss modulus as well. The activation energies derived from both, storage and loss moduli, are summarized in Table 3.2. The goodness of fit is shown by the R^2 values, which are reasonably acceptable.

The activation energies are not the same for loss and storage moduli which is pointing to the fact that these Payne effect measurements are per definition outside the linear region. By increasing the amount of filler, the activation energies increase again, similar to what was observed in the linear region due to more pronounced filler network.

Table 3.2

Activation energies derived from vertical shift factors and strain sweep measurements for both G' and G''

	Vertical shift factor		Strain sweep		R^2 (%) (G'/G'')
	Ea (kJ/mol) from G'	Ea (kJ/mol) from G''	Ea (kJ/mol) from G'	Ea (kJ/mol) from G''	
37S6	3.3	3.2	14.9	23.4	93/94
37S7	5.4	5	17.6	29.9	96/97
37S8	8	12.1	21	33.5	95/96

The higher activation energy in case of loss modulus can be attributed to the fact that loss modulus is correlated to the filler-filler contacts which undergo break down and reformation during the dynamic oscillation. Whereas storage modulus is related to virgin, intact filler-filler bonds^{15,17}.

3.4 Comparison between the different methods

In order to compare the previous results, the activation energies derived from both methods, the vertical shift factor and strain sweep measurements, are shown in Figure 3.12. By increasing the filler loading all the activation energies increase. The values of the activation energies are much higher for the results derived from the Payne effect measurements compared to those derived from the vertical shifting.

Fritzsche et al.¹⁶ have done similar measurements on carbon black filled S-SBR samples and reported similar results. They concluded that in the activation energy derived from the vertical shift, the temperature dependence of filler-filler bonds plays the main role, while the dynamics on the surface of the filler is basically neglected. Therefore the values of activation energies from the vertical shift factors are lower.

Typical activation energies for physically based mechanisms are of the order of 10 (kJ/mol), whereas chemically based processes are of the order of 60-80 (kJ/mol). Along with this reasoning the activation energies obtained from the vertical shifting exercise point at phenomena which are essentially still physical of origin.

The much higher activation energies derived from the Payne effects, but still closer to the physical than to the chemical based processes, indicate that the viscoelastic response of the compounds at such high strains cannot simply be considered as reversible physical phenomena. There is more involved than reversible rearrangement of the filler-network, or vice-versa reversible chain-rearrangement of the crosslinked polymer network. The amounts of energy loss in case of the Payne-effect related large deformations are substantial because of irreversible effects, whether physical or maybe even partly chemical of nature.

The present study was triggered by the need to predict WSR of tires from viscoelastic data of rubber materials measured on laboratory scale equipment. The question may now be raised how large the deformations are of in particular the tire tread compounds during skidding or acceleration traction. Though opinions differ³⁵⁻³⁷ the 7–8 % strain is more physically

reasonable than 0.1 % strain. It implicitly puts a limit to the value of viscoelastic master curves for WSR-simulation of tire compounds. Equipment which can measure at such high deformations and high frequencies do not exist, resp. it may be questioned whether such machines are feasible from a construction standpoint. For the moment, tire designers have to make with the limited means available to combine the results from viscoelastic master curves for small deformations with separate observations on e.g. Payne effects for large deformations and make the best estimate on basis of both.

Figure 3.11- Logarithmic magnitude of Payne effect from storage modulus as a function of reciprocal temperature $1/T$ for compound 37S8.

Figure 3.12- Activation energies derived from the Payne effect and vertical shift factor for both G' and G'' versus silica filler loading.

3.5 Conclusions

In order to predict wet skid performance of tire tread compounds, their viscoelastic properties at very high frequencies, in the MHz range and at high deformations need to be determined. However, it is practically not possible to perform such measurements on current dynamic mechanical spectrometers. Most commonly the construction of master

curves on basis of the WLF principle is then employed for small strain values in the linear region where the WLF principle is valid.

To produce a proper master curve for a silica-reinforced tire tread compound, both horizontal and vertical shifting need to be applied for the time-temperature superposition. The horizontal shift is based on the WLF principle, making use of the same universal constants as if the compounds were non-reinforced and with adjustment of the T_{ref} vs. T_g somewhat to compensate for the small T_g -shift with different filler loadings. The vertical shift can be considered as a thermally governed process related to the filler particles as they interact with each other (filler network), and as they are connected to the polymer chains (the filler-polymer interaction). The vertical shift factors for three tire tread compounds with resp. 60, 70 and 80 phr silica filling, show Arrhenius type behavior when plotted against $1/T$ for the high temperature or vice-versa low frequency range of the master curve. In the high frequency or vice-versa. low temperature region of the master curve, which is considered to be representative for the wet skid performance of tires, the loss tangent value decreases with an increase in the amount of filler. It indicates that the presence of filler negatively influences the damping properties of the polymer network. The activation energies derived from the vertical shift factors for both the storage moduli G' and the loss moduli G'' at strain deformation of 0.1% are almost equal, and in the range of physical processes. It also means that the Kramers –Kronig relations are fulfilled in this linear response region.

Strain sweep measurements performed at different temperatures with strains between 0.1 and 100% on the same three compounds give the activation energies which are 3-5 times higher than for the vertical shifting operation. Furthermore, the values derived from the loss modulus G'' are much higher than those derived from the storage modulus G' . As mentioned before, this has been related to different behavior of storage and loss modulus. Activation energy associated with storage modulus arises from virgin, intact filler-filler bonds and the other from damaged filler-filler bonds which break down and reform during dynamic deformation. However, these energies still do not reach by far the level of typical chemical processes. But as the deformations involved in these Payne measurements are more representative of what happens in real wet traction or skidding of tires, it demonstrates that the value of low deformation master curves is only limited from the perspective of predicting these phenomena on basis of laboratory testing.

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Chapter 4

Stress-based viscoelastic master curve construction for model tire tread compounds

Abstract

The viscoelastic master curves for tire tread compounds filled with different amounts of silica are prepared through constant-stress-based measurements in a Mettler Toledo DMA instrument. This method of measurement allows for higher strain values than in the linear regime as applied in the previous Chapter 3, more representative for skidding phenomena of tires. Furthermore, the necessity of sample glueing is eliminated in this special instrument. The vertical and horizontal shift factors are calculated and compared to the ones derived from the strain-based measurements in Chapter 3. The effect of filler networking on the dynamic mechanical properties in the different behavioral regions are also studied.

4.1 Introduction

In Chapter 3 the viscoelastic properties of the tire tread compounds with different filler loadings at a very wide frequency range were evaluated through time-temperature superposition measurements in a Dynamic-Mechanical Analyzer (DMA) instrument. The viscoelastic master curves produced therefrom were used to describe the behavior of the compounds in different frequency zones. The measurements were performed at a constant strain value of 0.1%, which is practically in the linear response regime. Such low strain values are far below the real strains occurring during actual performance of tires on the road, particularly during traction or wet skidding, which is the main subject of the present chapter. The actual dynamic strain values on the road during skidding is estimated to be between 6 and 8% at ambient temperature: see Chapter 3.

An important difficulty of high-strain measurements is the need to glue the rubber samples to the sample holders, which could be a root for error per se. In order to decrease the errors originating from sample preparation, the measurements were repeated in a Mettler-Toledo DMA instrument which provides the opportunity of testing the samples without applying the glue. Besides, the accessible strain range is much broader in this instrument.

As was explained before, the viscoelastic master curves can be obtained by performing time-temperature superposition measurements and shifting the resulted data horizontally and vertically in order to get the final master curves. In the present chapter the viscoelastic data obtained from constant-stress-based time-temperature superposition measurements in a Mettler-Toledo DMA instrument were treated in a computer program which is able to deliver the final master curves. In order to obtain these, the viscoelastic graphs were shifted manually in horizontal and vertical directions. Horizontal (a_T) and vertical (b_T) shift factors were collected and compared with the values obtained in the strain-based DMA measurements from the previous chapter. The activation energy of the filler network (E_a) are derived from the vertical shift factors and compared with the ones presented in Chapter 3.

4.2 Experimental

4.2.1 Materials and compound preparation

Blends of oil-extended solution styrene-butadiene rubber (S-SBR) and high cis Polybutadiene (BR) with a weight ratio of 70/30 were used in this study. The compounds were prepared based on the formulations given in Table 4.1. A highly dispersible silica was used as reinforcing filler. The amount of silica was varied between 60 and 80 phr. An unreinforced/unfilled compound was prepared as the Reference compound. The amount of TESPT coupling agent was adjusted to the amount of silica to maintain the same weight ratio as the compound 37S8, and the amount of sulfur was adjusted according to the amount of coupling agent in the system to keep the same molar concentration of sulfur in all the compounds. Finally, the ratio between silica and DPG was also kept constant in all the compounds. The remaining ingredients are as listed in Table 4.1. The suppliers are as listed in Table 3.1, Chapter 3.

The compounds were prepared in a 350 ml Brabender 350S internal mixer operating at 100 rpm with a fill factor of 0.7. The total mixing time was 9 minutes, while the dump temperature was adjusted to approximately 155 °C (by changing the initial temperature). The samples were cured in a Wickert press WLP 1600 at 180 °C to sheets with a thickness of 1 mm according to their t_{90} optimum vulcanization time as determined in a Rubber Process Analyzer RPA 2000 from Alpha Technologies.

Table 4.1
Rubber compound compositions (in phr)

Ingredient	Sample Code			
	37S8	37S7	37S6	unfilled
S-SBR	96.3	96.3	96.3	96.3
BR	30	30	30	30
Silica	80	70	60	0
TESPT^a	5.25	6.13	7.0	0
TDAE^b	6.7	6.7	6.7	6.7
Zinc oxide	2.5	2.5	2.5	2.5
Stearic acid	2.5	2.5	2.5	2.5
6PPD^c	2	2	2	2
TMQ^d	2	2	2	2
Sulfur	1.4	1.6	1.8	3.1
TBBS^e	1.7	1.7	1.7	1.7
DPG^f	2	1.75	1.5	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-di-hydroquinoline

^e Accelerator N-tert-butylbenzothiazole-2-sulphenamide

^f Accelerator diphenyl guanidine

4.2.2 Measurements

Constant-stress-based dynamic mechanical analyses were performed in the shear mode in a Mettler Toledo DMA/SDTA861e which allows for measurements from 0.001 to 1000Hz frequency in the temperature range from -150 up to 500 °C. This instrument provides the opportunity of shear testing without applying glue on the surface of the samples, so eliminating the errors coming from this. Time-temperature superposition measurements were performed at different temperatures between -40 °C and 80 °C in steps of ten and twenty degrees. The measurements were performed under maximum 0.5 and 2 N forces, which means that the strains vary with the modulus-variations of the samples in the

temperature-range applied. The samples were cylinders with 6 mm diameter and 1mm thickness.

Horizontal and Vertical shiftings were done manually using a proprietary computer program provided by Lanxess. An arbitrary reference temperature (in this case 0°C) was chosen and the shift factors and WLF constants C_1 and C_2 (see Chapter3, equation 3.1) were obtained. In this specially designed software there is a possibility to take either the reference temperature and WLF constants as fixed values, or treat them as variables to be calculated by manual shifting of the curves. The Reference Temperature was fixed at 0°C, in order to be able to compare the data with those from Chapter 3.

4.3 Results and discussion

Time-Temperature Superposition (TTS) measurements are basically frequency sweeps performed at different temperatures. Constant-stress-based TTS measurements were performed at two constant force values: 0.5 and 2 N. Strain values can then be calculated from shear modulus and shear stress as follows:

$$\begin{aligned}\tau &= G\gamma \\ \tau &= F/A \\ G &= \sqrt{G'^2 + G''^2}\end{aligned}\tag{4.1}$$

In which γ is the shear strain, G is the complex shear modulus and τ is the Shear Stress which is derived from force, F , and the surface area under shear, A .

Strain values at the whole frequency region for different compounds are presented in Figure 4.1. As is seen, the strain values are large in low frequency/high temperature region and can reach a high value of 6% in case of the unfilled compound at 0.5N force and up to 24% at 2N. By increasing the frequency the strain level decreases and approaches zero in the MHz region. As explained before, high strain values are desirable for predicting wet grip behavior of the compounds when used in tires.

Figure 4.1- Strain values vs. frequency for different compounds

Storage and loss moduli and loss tangent mastercurves can be seen in Figures 4.2 and 4.3. The procedure to produce the master curves is the same as was explained in Chapter 3, 3.3.1. The frequency sweep data at different temperatures (raw data) were shifted horizontally by choosing the curve at 0°C as the reference. The WLF constants C_1 and C_2 , were calculated for this reference temperature, see Table 4.2. The horizontal shift factors for all the compounds are shown in Figure 4.4. As seen, the WLF constants and horizontal shift factors for all the compounds are very similar. In the constant-strain measurements in Chapter 3, the same horizontal shift factors could be used for all the compounds irrespective of their filler content, under the assumption that the WLF constants depend only on the reference (glass transition) temperature of the polymers, which does not change by introducing fillers into the system. This is again confirmed by the present constant-stress measurements, in which the horizontal shift factors are almost the same for all compounds. So basically the shift factors from the unfilled compound can also be applied to the filled/reinforced compounds.

The master-curves for the low stress, 0.5 N, measurements are reasonably good for G' as well as G'' , but worse than the constant-strain measurements in Chapter 3. However, for the high stress, 2 N measurements the quality of the vertical shifting is substantially worse for the G'' . Therefore this also shows in the $\tan\delta$ mastercurves.

Figure 4.2- Storage(G') and Loss(G'') moduli and $\tan \delta$ mastercurves for the measurements at 0.5N

Figure 4.3- Storage(G') and Loss(G'') moduli and $\tan \delta$ mastercurves for the measurements at 2N

Introducing fillers into the compounds grossly increases the storage and loss moduli¹⁻³. By increasing the amount of filler from 60 to 80 phr, both moduli increase. This is in fact experienced in both methods: constant-strain as well as constant-stress. In the loss tangent,

$\tan\delta$, graph, some crossovers are observed, as was already seen in constant-strain measurements in Chapter 3. In the low frequency/high temperature regime, gum rubber has the lowest $\tan\delta$. By introducing fillers into the system, the loss tangent increases. As was explained before in Chapter 3, in this low frequency region, when the polymer is far above the glass transition temperature, the major source for energy dissipation is the breakdown and reformation of the filler network ⁴. Therefore, a lower $\tan\delta$ is expected for the unfilled compound in which there is no filler network. By increasing the frequency or moving towards lower temperatures, a crossover occurs. In the following region, the polymer chains themselves are responsible for the energy dissipation ⁴. Therefore, the highest $\tan\delta$ is observed for the unfilled compound. By the introduction of fillers the fraction of free polymer chains decreases due to the occluded rubber and/or the glassy shell around the filler particle ⁵⁻⁷, which results in decreased damping in the transition zone and consequently decreased $\tan\delta$ for the highly filled compounds.

Table 4.2- WLF constants for the measurements at different forces

	0,5N		2N	
	C ₁	C ₂	C ₁	C ₂
37S6	8,85	92,5	9,25	81,77
37S7	9,78	85,37	8,91	82
37S8	8,87	98,11	9,27	92,94
unfilled	8,87	91,56	8,73	89,03

Figure 4.4- Horizontal shift factors from G' for the different compounds

The vertical shift factors for the storage modulus of the different samples are plotted versus reciprocal temperature in Figure 4.5. The vertical shift can be considered as a thermally governed process related to the filler particles as they interact with each other in the filler network, and as they are connected to the polymer chains: the filler-polymer interaction. Similar to what was observed in Chapter 3, part 3.3.2, a linear correlation with inverse temperature well above the glass transition temperature is obtained, as indicated by the trendlines inserted in the figure. The slopes of these curves can be interpreted as activation energy of the filler network: E_a , which is related to the temperature dependency of glassy shells around the filler particles^{5,8-9}.

Figure 4.5- Vertical shift factors from G' for the different compounds

The activation energy values derived from the storage modulus vertical shifts are presented in Table 4.3. Clearly, by increasing the amount of filler the activation energy increases, due to the fact that a stronger filler network is formed in the compounds. Comparing the measurements performed at different applied forces/stresses, the activation energies are somewhat lower when higher force/stress is applied on the samples.

Looking at the different measuring methods, the activation energy is much lower for the constant-stress measurements than for the constant-strain. This is quite surprising in view of the much higher activation energies obtained for the strain sweep, Payne effect measurements in Chapter 3, compared with the constant-strain measurements executed there in the essentially linear regime. However, to compare all the different testing

conditions and how these interfere with the behavior of the filler-filler network becomes a matter of conjecture. As documented by Fröhlich et al.^{10,11} the major part of the Payne effect, the maximum energy dissipation due to the continuous breakdown and reformation of the filler network measured at a low frequency of typically 1.6 Hz and high temperature of 60 °C takes place at appr. 7% strain, between strains of appr. 0.5 – 20%. These strains are factually of the same order as observed for the present constant-stress measurements at 2N load, as presented in Figure 4.1 at low frequency. This can also be derived from the Payne effect measurements presented in Figure 3.10 in Chapter 3, executed at 10 Hz frequency and also 60 °C. As the present experiments were additionally executed at a lower temperature than the 60 °C, the question may be posed: how the filler-filler networks in the samples react to the different ranges of strains, frequencies and temperatures employed throughout the present series of constant-stress measurements. Time-temperature superposition as developed by Boltzmann is well documented and works well for pure polymers¹². The additional presence of the filler-filler network is an enormous complicating factor. In that respect, the constant-strain dynamic experiments in Chapter 3 were a degree easier to interpret because at least one of the three variables: strain, frequency and temperature, was kept constant. Be it, that the strain applied there was so small to be in the essentially linear regime where the filler-filler network stayed more or less in-tact, but unfortunately not representative for the strains experienced by a skidding tire.

As a last point may be mentioned, that using the present Mettler Toledo DMA/SDTA861e there was no need to use a glue the samples to the sample holders, which may have facilitated the energy transfer from the instrument to the samples, resulting in lower energy required for breaking down the filler network. It is felt, however, that that is most probably only a minor effect.

Table 4.3- Activation energy values derived from storage Modulus(G') vertical shifts for both constant-strain-based and constant-stress-based TTS measurements

	Ea (KJ/mol)		
	Constant-stress		Constant-strain
	0,5N	2N	
37S6	1,05	0,8	3.3
37S7	1,33	1,02	5.4
37S8	2,92	2,2	8

4.4 Conclusions

To produce a proper master curve for a silica-reinforced tire tread compound, both horizontal and vertical shifts need to be applied for time-temperature superposition measurements. The horizontal shift factors can either be derived from the WLF theory or by manually shifting of the different modulus-curves obtained at different temperatures. It was confirmed that the horizontal shift factors are the same for unfilled and filled compounds. The vertical shift factors show an Arrhenius type behavior when plotted against $1/T$ for the high temperature or vice-versa low frequency range of the master curve. The activation energy of breaking the filler-network is lower when higher stress is applied on the sample. It is also lower than what was obtained for the constant-strain-based measurements in the linear regime in Chapter 3.

The reason for that is puzzling, particularly in view of the highest activation energy obtained in Chapter 3 for the high-strain Payne Effect measurements. It must be concluded that the simultaneous variation of strain, frequency and temperature in the present constant-stress-based experiments is an enormous complicating factor, making decoupling of the various polymer-based and filler network-based phenomena practically impossible, or would require much more study. A small additional effect may be a higher efficiency of energy transfer from the instrument to the sample, because no glue was needed between the samples and sample holders.

4.5 Acknowledgement

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Chapter 5

New functionalized SBRs in the tire tread compound: interactions with silica and zinc oxide

Abstract

Unlike carbon black, silica is polar and naturally not compatible with non-polar hydrocarbon elastomers. This lack of interaction or compatibility between the filler and the elastomer typically causes lower properties compared to carbon black filled compounds. A common approach to deal with this problem is to utilize 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 give improved compatibility of elastomers with fillers such as silica. In this chapter, 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 green tire tread compound will be discussed and compared to the reference compound which contains unmodified s-SBR as the main polymer. The results show the significant potential of two of these modified SBRs to reduce 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 which catalyzes the vulcanization process. However, in silica filled compounds, ZnO may interfere with the silanization process²⁴ 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 'green tire' tread compound, a series of compounds have been prepared, in which ZnO addition in a later stage was compared to conventional mixing. The dynamic and mechanical properties of the final compounds are discussed.

5.1 Introduction

With the introduction of silica technology in passenger car tire tread applications, the filler-polymer interactions have become of key importance. 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 7mol% of epoxidation groups in main chains results in a reduction of around 4 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. ⁶ prepared a series of functionalized s-SBRs using some coupling agents and chain-end and backbone modifiers; the polymer preparation and modification pathway were shown in Chapter 2, Figure2-6. Using chain end modified polymers in polymer-filler compound vulcanizates leads to an improvement of dynamic vulcanizate characteristics,⁴ particularly to a reduced vulcanizate hysteresis. 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 $\tan\delta@60^\circ\text{C}$, which used as rolling resistance indicator, improved for all backbone-modified polymer vulcanizates by 19 to 32%, while the $\tan\delta@0^\circ\text{C}$ (wet grip indicator) deteriorated slightly (3-15%) ⁵. Overall a predominantly rolling resistance indicator (or $\tan\delta@60^\circ\text{C}$) 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 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 ^{12,13}: 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. 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 5.1.

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 ¹⁶. 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: Scheme 1. Then the released zinc ion reacts with the accelerator to form an active accelerator complex.

Figure 5.1- General scheme for sulfur vulcanization¹⁵

The exact activation role of ZnO is very much dependent on the type of accelerator present in the system. Figure 5.2 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 nature¹⁷⁻¹⁹.

Figure 5.2- Formation of polysulfidic MBTS via a complex with zinc¹¹¹

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 complex¹².

ZnO does not react with sulfenamide accelerators themselves like N-cyclohexylbenzothiazole-2-sulfenamide (CBS) and N-tert-butylbenzothiazole-2-sulfenamide (TBBS)^{20,21}. 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 5.3, and then the complex formation continues as described before.

Figure 5.3- 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 agent²²⁻²⁴. Reuvekamp et al.²⁴ 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. 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 till 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 5.4²⁴.

Figure 5.4- Possible reaction between silica and ZnO ²⁴

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 chapter, 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.

5.2 Experimental

5.2.1 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. Buna VSL VP PBR 4003 (Lanxess, Leverkusen, Germany) is statistically modified along the entire polymer main chain with COOH-groups with a concentration of 35 [meq./kg]. SPRINTAN SLR-4630 (Styron, Schkopau, Germany) is partially Si-coupled and contains a non-staining stabilizer ²⁵. Properties of these elastomers and their suppliers are as shown in Table 5.1. All other ingredients and suppliers are as listed in Table 3.2. Four compounds (Ref, CS8, P8 and S8) were prepared based on the formulations given in Table 5.2. In the compound CS8, an extra amount of oil was added to compensate for the lack of oil in this elastomer compared to the other two.

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

minutes while the dump temperature for the first two stages was adjusted to 155 ± 5 °C by changing the initial temperature (as explained in Table 5.3).

In order 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 Ist stage of mixing was eliminated and added later on in the IIIrd stage with the curatives. Two of the new SBR types which showed promising improvement of 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.

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.

Table 5.1
Different SBR types used in this study

SBR Type	SLR 4630	SLR 4602	PBR 4003	Buna VSL 5025-2 HM
Supplier	Styron	Styron	Lanxess	Lanxess
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 Visc. ML1+4 [MU]	55	65	53	62
Oil content (TDAE) [phr]	37.5	0	37.5	37.5

Table 5.2
Rubber compounds composition (phr)

Ingredient	Compounds Code			
	S8	CS8	P8	Ref.
S-SBR	96.3	70	96.3	96.3
BR	30	30	30	30
Silica	80	80	80	80
TESPT	7	7	7	7
TDAE	6.7	33	6.7	6.7
Zinc oxide	2.5	2.5	2.5	2.5
Stearic acid	2.5	2.5	2.5	2.5
6PPD	2	2	2	2
TMQ	2	2	2	2
Sulfur	1.4	1.4	1.4	1.4
TBBS	1.7	1.7	1.7	1.7
DPG	2	2	2	2

Table 5.3
Mixing procedure

Ist Stage	
Rotor speed:	110 RPM
Initial temp.:	50 °C
Min.	
Add polymers	
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
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 curatives (mixed together)
3.0	Dump @ ~ 100 °C

5.2.2 Measurements

A rubber process analyzer RPA 2000, Alpha Technologies, 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 0.833Hz, at 160°C and for 30 minutes.

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 crosshead 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. Additionally, samples immersed in toluene were treated under ammonia atmosphere in order to separate 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 wet traction: see Chapter 2. 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:

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

where F_y is the side force and F_z is the normal load on the wheel sample. The Higher the SFC the better is the Wet grip expected.

5.3 Results and discussion

In order to protect the intellectual properties of Apollo Vredestein, all data presented in this chapter are relative, normalized to the Reference compound values.

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 in 5.2.2. Ammonia splits the adsorptive physical bonds between rubber and silica, therefore only the covalently bound elastomer portion remains attached to the filler.

Figure 5.5 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. 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.

Figure 5.5- Bound rubber content (total and chemically) in the different compounds

Relative hardness values of the cured compounds are given in Figure 5.6. As is clearly seen, the hardness values of all the compounds are lower than the reference one, the one with early addition of ZnO. Using functionalized polymers, generally, results in lower hardness values than the reference compound, with compound CS8 showing the lowest one. Omission of ZnO in the 1st stage of mixing also has a diminishing effect on the hardness values compared to the conventionally prepared compounds, and this may affect the other properties of the compounds such as the SFC or tensile properties. In order to avoid possible misconceptions, a series of compounds with adjusted hardness values have been prepared, and will be reviewed in Chapter 6.

Figure 5.6- Hardness values of the cured compounds

Tensile properties of the compounds are presented in Figure 5.7. 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 5.7- Relative tensile properties of the compounds

Figure 5.8 shows the relative $\tan\delta@60^\circ\text{C}$ values of the compounds. It is commonly accepted that $\tan\delta$ 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 made therefrom. Lower $\tan\delta$ indicates lower hysteresis, which results in less energy dissipation³². 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 to the Ref. compound. 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 network^{26,27}. Besides, some authors suggest that slippage of polymer chains on the filler particle surface is a source of energy dissipation, too²⁸. Either mechanisms work well in interpretation of obtained results. Polar functionalized SBRs (compounds CS8 and P8) show a lower loss tangent, while Si-coupled SBR (compound S8) shows a bit higher $\tan\delta$ value compared to the Ref. 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, something which does not occur in case of Si-coupled SBR (compound S8). In addition, when strong interactions occur between silica particles and polymer chains - which is indicated by Bound Rubber test results, see Figure 5.5 - 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 $\tan\delta@60^\circ\text{C}$ for the two.

Figure 5.8- Relative $\tan\delta@60^\circ\text{C}$ values for different compounds

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 compound too, the decrease is much larger in case of compound CS8-Z and reaches 39% relative to the Ref. 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 to their conventionally mixed compounds (CS8 and P8), again it can be concluded that mercapto functionalities are more reactive towards ZnO and/or more eager to react with silica particles than the carboxyl functionalities.

Rebound resilience tests confirm the loss tangent data, see Figure 5.9. 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 to the Ref., 11% and 3%, respectively. The Rebound value of the compound S8 remains almost unchanged compared to the Ref. compound, like it showed little change in the $\tan\delta@60^\circ\text{C}$ as well. Absence of ZnO during the early stages of mixing by itself already brings about more than 6% increase in the rebound resilience value in case of the reference compound, but the highest value in rebound resilience is found for the compound CS8-Z with 15% increase, all corresponding with the lowest $\tan\delta$ value.

Figure 5.9- Relative rebound resilience data measured at 70°C

Figure 5.10 represents the relative storage modulus data as a function of strain for the different compounds with ZnO present in the Ist stage of mixing. The difference between the storage moduli at low strain and high strain is defined as the Payne effect^{33,34}. As it is seen, compound CS8 has the lowest Payne effect value, thus the best filler dispersion and or lowest filler-filler interactions. Compounds P8 and S8 show lower Payne effects compared to 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 Ist and IInd 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 indeed in case of the reference compound: Figure 5.11 (a). Incorporation of functionalized polymers into the compound recipe helps diminish the filler network even more; these results can be seen in Figures 5.11 (b) and (c).

Figure 5.10- Relative storage modulus versus strain measured at 80°C for the different compounds with ZnO present during mixing

The LAT100 results of the three compounds with and without ZnO present in the Ist stage of mixing are shown in Figures 5.12 and 5.13(a) to (c). The principle of the LAT100 measurements is explained in Chapter 2, 2.3.6. Measured value is the side force coefficient, 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 5.6, the hardness of the compounds CS8, P8 and S8 are all 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 crosslink density may influence the material properties as well. To avoid misunderstandings related to hardness changes, a series of compounds with adjusted hardness values have been prepared and tested, the results of which are presented in Chapter 6.

Figure 5.11- Relative storage modulus versus strain measured at 80°C for the different compounds with and without ZnO added in Stage I: (a) Ref. (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 side force coefficient values. Therefore, the same traction performance on the wet road is expected for these compounds if implemented in tires. It indicates that 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 ²⁹, where compounds with the same Payne effect values, hence similar filler-filler interactions show different LAT100 behavior. 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 contributed to this effect, too.

Figure 5.12- Relative Side Force Coefficient (SFC) vs. temperature

Figure 5.13- Relative side force coefficients measured at different temperatures for the different compounds with conventional and late addition of ZnO: (a) Ref. (b) P8 (c) CS8

5.4 Conclusions

Silica has a polar structure and is not compatible with the hydrophobic rubber by nature. Adding functional groups in the polymer chains may help in improving the compatibility between these two important ingredients of tire tread recipes. In this chapter, the effect of three different functional SBR types in the formulation of a green tire tread was studied. It has been demonstrated that grafting polar groups, carboxyl (-COOH) or mercapto (-SH) onto the polymers, works well in increasing the affinity between the elastomers and the silica filler, while the 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 with mercapto-functionalities. It is commonly accepted that a lower loss tangent arises from better filler dispersion / less filler-filler interactions and less slippage of polymer chains on the filler particle surface or a combination of these two mechanisms. Lower slippage can be due to stronger interactions arising between polar silica particles and polar moieties on the polymer chains. In addition, alkaline ZnO may be attracted to acidic polymer moieties, therefore less obstructing the silanization process leading to better filler dispersion, again. Lower filler-filler interactions were further confirmed via Payne effect measurements, which show the smallest decrease in storage modulus vs. strain for the compound containing mercapto moieties.

Bound Rubber tests were performed in order to prove the filler-polymer interactions. The chemically bound rubber part was much higher for all functionalized elastomer compounds, especially for the two compounds containing polar functionalities confirming the lowest filler-filler interaction.

The LAT100 test results show that there is not much difference in the side force coefficient (SFC) values of the different compounds, where the effect of hardness changes should not be neglected, of course. This implies a comparable wet grip performance on the road. However, the mechanical properties of the compounds with polar functionalities on the SBR are slightly lower than the properties of the reference compound.

As zinc oxide is intruding into the silanization reaction, and this may become more critical when functional polymers are present in the system, three compounds were prepared with ZnO added at a later stage of mixing at the same time as the curatives to investigate the

effect of ZnO in the functionalized polymer compounds. The results show that ZnO indeed has a significant influence on the loss properties and filler dispersion of the compounds. Compound CS8-Z, in which a dithiol modified SBR was used and ZnO was added at a later stage, has the largest improvement with 39% decrease in the loss tangent value at 60°C compared to the reference compound. The rebound resilience data for these compounds show the same trend, where the compound CS8-Z has the highest rebound resilience increase (15%). This decrease in hysteresis makes this material prone for application in tire treads, as it is expected to result in a reduced rolling resistance.

The Payne effect data show that absence of ZnO during the early stages of mixing helps in lowering the filler-filler interactions: Lower Payne effect values were obtained for all the compounds with ZnO added later on. The side force coefficients measured on a LAT100 as indication for the wet skid resistance were independent of the time of ZnO addition. The same SFC value in presence and absence of ZnO can be interpreted in a way that more developed silanization does not play a particular role in the friction properties of the compounds. Therefore, the same wet road performance as the conventionally processed compounds is expected for these compounds. However, it should be kept in mind that the reduced hardness observed for the compounds based on the functionalized elastomers may have affected these results. This will be discussed in the next chapter.

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Chapter 6

Effect of hardness-adjustments on the dynamic and mechanical properties of tire tread compounds

Abstract

In technical practice, the alteration of a rubber formulation is usually made in such a way as to keep the hardness of the rubber product constant. This is, because a specific hardness of the rubber product sets the limit to its practical applications. As was mentioned in Chapter 5, adding zinc oxide in a later stage of mixing, shows very 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. In this chapter compounds of the ZnO-study with adjusted Hardness are prepared through oil adjustment and/or change in the vulcanization system. Dynamic and mechanical properties of these compounds are studied and compared with the original data without Hardness adjustment.

6.1 Introduction

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 compound ¹, influences the other properties of the compound ²⁻³, 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 tire ². 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 level ⁴. Figure 6.1 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 in Chapter 5, 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 of the ZnO-series with adjusted hardness values were prepared and their dynamic and mechanical properties evaluated.

Figure 6.1- Wet traction vs. Durometer hardness for several tread and butyl rubbers ⁴

6.2 Experimental

6.2.1 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 according to the formulations given in Table 5.1. Two type of functionalized SBRs were used in this study: SPRINTAN SLR-4602 (Styron, Schkopau, Germany) and Buna VSL VP PBR 4003 (Lanxess, Leverkusen, Germany). Their characteristics can be found in Chapter 5, 5.2.1 and Table 5.1. A highly dispersible silica was used as reinforcing filler, and the compound containing regular S-SBR BUNA VSL 5025-2HM (Lanxess, Leverkusen, Germany) was taken as the reference. All other ingredients and suppliers are as listed in Table 3.2. 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, as was discussed in Chapter 5). In order to adjust to the same hardness as the Reference compound, either the amount of oil in the formulation was changed (compounds P8-Z-oil and CS8-Z-oil) or the curing system was changed from Semi-Efficient to Conventional (compounds P8-Z-curatives and CS8-Z-curatives). In a Conventional cure system, the accelerator to sulfur ratio is rather low compared to the Semi-Efficient one and the resulting crosslinked network will be mainly polysulfidic of nature. On the other hand, in this system, a higher crosslink density is expected due to the higher amount of sulfur present; and a higher crosslink density leads to increased hardness ⁵.

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. 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 (as explained in Table 5.3, Chapter 5).

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 an Alpha Technologies Rubber Process Analyzer RPA 2000.

6.2.2 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 $\tan\delta$ @ 60°C were measured after precuring the compounds according to their t_{90} 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.

Table 6.1

Rubber compounds formulations (phr)

	Ref.	Ref-Z	P8-Z	P8-Z-oil	P8-Z-curatives	CS8-Z	CS8-Z-oil	CS8-Z-curatives
SBR BunaVSL 5025-2	96,3	96,3						
BR	30	30	30	30	30	30	30	30
PBR 4003			96,3	96,3	96,3			
SLR-4602						70	70	70
Silica	80	80	80	80	80	80	80	80
TESPT	7	7	7	7	7	7	7	7
TDAE oil	6,7	6,7	6,7	-	6,7	33	15	33
Zinc oxide	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
6PPD	2	2	2	2	2	2	2	2
TMQ	2	2	2	2	2	2	2	2
Sulfur	1,4	1,4	1,4	1,4	2,5	1,4	1,4	2,5
DPG	2	2	2	2	0,36	2	2	0,36
TBBS	1,7	1,7	1,7	1,7	0,3	1,7	1,7	0,3

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: see Chapter 2. Wheel samples were made by compression molding at 170°C for 11 minutes in a special mold using the Wickert laboratory vulcanization press WLP 1600. Testing conditions were as explained in 5.2.2, Chapter 5.

6.3 Results and discussion

In order to protect the intellectual properties of the company Apollo Vredestein, all data presented in this chapter are relative, normalized to the Reference compound values.

The cure characteristics of the eight compounds are shown in Figure 6.2. As is clearly seen, changing the curing system totally changes the cure behavior of the compounds. The marching modulus seen for the two compounds with the conventional cure system (P8-Z-Curatives and CS8-Z-Curatives), demands much longer cure time to reach a steady level if at all, meaning much higher t_{90} -values to a level of being impractical. The natural acidity of silica, due to the large number of hydroxyl groups on its surface, can lead to physisorption of the basic molecules added for the vulcanization. In particular, accelerators can be adsorbed because they often contain basic amine functions. According to the literature ⁶ a silica surface can adsorb 1.84 DPG molecules per nm^2 , i.e. 2.9×10^{20} molecules per gram of silica with a specific surface of $160 \text{ m}^2/\text{g}$. This reaction will cause a decrease of cross-linking efficiency as well as a change in the cross-link structure. Moreover, as a result of blocking active sites due to the adsorption, one can also observe a reduced ability to create the filler network ^{7,8}. It seems that the amount of DPG used in these two compounds (P8-Z-Curatives and CS8-Z-Curatives) was not sufficient to neutralize the remaining silanol groups on the silica surface, left after the silanization reaction. With the insufficient amount of DPG (as in the present case) proper vulcanization will not be achieved. By increasing the amount of DPG this problem would have been solved. Unfortunately, there was not enough time to repeat this part of the investigation. The test results for these two compounds with the current formulations are presented (to obtain an idea how these undercured compounds perform), but it should be emphasized that they are not reliable and useful.

The relative Hardness values of the compounds are presented in Figure 6.3. Clearly, decreasing the amount of oil and changing the cure system have 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 6.4. 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.

Figure 6.2- Cure characteristics (RPA rheograms) of the compounds at 160°C

Figure 6.3- Relative Hardness value 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 6.5. 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.

Figure 6.4- Relative mechanical properties of the compounds

Relative loss tangent values measured at 60°C are presented in Figure 6.6. 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 dissipation¹¹. The compounds containing SPRINTAN SLR-4602 polymer show the lowest $\tan\delta$ -values @

60°C as already seen and discussed in Chapter 5, 5.3. 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 values ¹². 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. In a conventional vulcanization system crosslinks are more polysulfidic rather than monosulfidic, therefore a more flexible segmental mobility in the vulcanizates exists ⁵. In any case, the energy loss will increase. 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 $\tan\delta@60^\circ\text{C}$ data: Figure 6.7. The higher the rebound resilience, the more elastic the compound and therefore the lower the hysteresis, which favors lower Rolling Resistance. As was shown and discussed in Chapter 5, 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.

Figure 6.5- Relative volume loss of the different compounds

Figure 6.6- Relative $\tan\delta@60^\circ\text{C}$ values for different compounds

Figure 6.7- Relative rebound resilience data measured at 70°C

The relative storage modulus data as a function of strain, or Payne effect for the different compounds are presented in Figure 6.8. 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, as was already discussed in Chapter 5. 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.

Figure 6.8- Relative storage modulus versus strain measured at 100°C for the different compounds

Figure 6.9 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. The compounds with the conventional cure system exhibit doubtfully lower SFC values. Measuring the hardness values of the LAT100 test wheels revealed that the wheels made of the two compounds with different cure system (P8-Z-Curatives and CS8-Z-Curatives) have a markedly lower hardness value compared to those measured on the cured sheets: Figure 6.10. Given the slow curing behaviour of these two compounds as observed at 160°C in the rheometer, Figure 6.2, even though the LAT100 test wheels were vulcanized at 170°C, the cure time of 11 minutes must have been too short to obtain sufficient vulcanization. Therefore new LAT100 test wheels from these compounds were prepared and vulcanized for longer time: 18 minutes at 170°C, to get to a higher hardness value of the LAT100 test wheels; however it was not very helpful, see Figure 6.11. Anyhow, the LAT100 test was repeated for these new samples. The results are presented in Figure 6.12. As seen, the SFC increases when the samples with the conventional cure system are cured for longer time,

indeed confirming the undercure of the first samples. 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.

Figure 6.9- Relative side force coefficients measured at different temperatures for the different compounds

Figure 6.10- Relative Hardness values of the compounds and the LAT100 test wheels

Figure 6.11- Relative Hardness values of the LAT100 test wheels(cured for 11 and 18 minutes) compared to the Hardness of the their sheet samples

Figure 6.12- Relative SFC values for the new longer cured LAT100 wheel samples

6.4 Conclusions

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, either some amount of oil was removed from the formulation or the vulcanization system was changed from Semi-Efficient to Conventional. However, lately it was revealed that the applied conventional cure system with low amount of DPG was not suitable for these silica-filled compounds, and the compounds remained

undercured. The cure curves confirm that changing the vulcanization system to Conventional leads to a very different behavior; both compounds with the Conventional vulcanization system show impractical marching modulus and have much higher t_{90} values. Consequently, the results of the two compounds with Conventional cure system were not reliable and useful.

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. As expected and already explained in Chapter 5, the CS8-Z series compounds show the lowest $\tan\delta$ @ 60°C. Higher Hardness led to a small increase in $\tan\delta$ @ 60°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, as already discussed in Chapter 5, 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.

6.5 References

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Chapter 7

Influence of oligomeric resins on traction and rolling resistance of silica-filled tire tread compounds

Abstract

This study concerns the silica-reinforcement of synthetic rubber compounds for passenger tire treads with the objective to gain a better insight into the beneficial effects of oligomeric resins, derived from natural and synthetic monomers, on the major tire performance properties: Rolling Resistance and (Wet) Skid Resistance. It highlights the relationship between the performances of various oligomeric resins in different concentrations on the dynamic mechanical behavior of the silica reinforced passenger car tire tread compounds. Three types of resins were tested: a polyterpene, a terpene-phenolic and a pure vinyl-aromatic hydrocarbon resin. Dynamic Mechanical Analysis (DMA) was used, in addition to Mooney viscosity, tensile and hardness tests to assess the behavior of these resins in the rubber and to characterize the processibility of the compounds. The DMA results show that the resins and rubber compounds are compatible at the resin quantities used. The $\tan\delta$ loss properties versus temperature were used as an indication for wet skid and rolling resistance. Introduction of resins in the system leads to a shift to higher temperatures in the $\tan\delta$ peak, which can be an indication for improved wet skid performance of the tire compound. In addition, a reduction in $\tan\delta$ @ 60°C is observed which is attributed to reduced interactions between filler particles. These results are more confirmed through Payne effect data, where all the resin containing compounds show lower storage moduli compared to the compound without resin. The latter data are promising for improved rolling resistance performance.

7.1 Introduction

The ever increasing demands on tire performance account for a continuous effort to raise the overall level of the so-called “Magic Triangle of Tire Technology”: the balance between Rolling Resistance (RR), Traction or Wet Skid Resistance (WSR) and Wear or Abrasion Resistance. This is partly, but not only, triggered by governmental influences like the recent tire labeling regulation issued by the European Union ¹, or similar regulations in the USA, Japan and elsewhere. These requirements on RR and WSR are often conflicting, as improvement in one characteristic usually causes a decrease in the other. A compromise

between these characteristics is therefore always aimed for. It has recently been demonstrated that oligomeric resins have a beneficial influence on this balance, particularly on the WSR with no or even a small positive influence on the RR of passenger tires, based on synthetic rubbers with silica reinforcement²⁻⁵.

Oligomeric resins represent a class of materials used for a very broad range of purposes. For a classification of the variety of these products the reader is referred to the overview given by Kim et al.⁶. Resins can be obtained from different sources: extracted from trees or purposely produced from hydrocarbon monomers. These resins are commonly divided into four main groups: the naturally derived rosin acids and terpenes, and the synthetic C₅- and C₉-based hydrocarbons; various after-treatments are also applied.

It has become common practice to use laboratory scale dynamic mechanical testing to predict or simulate real tire performance. In particular, the dependence of the loss factor ($\tan\delta$) on temperature at a frequency of typically 10Hz can be used for such purpose⁷⁻⁹. The range between +40°C and approximately +70°C and frequency of 10Hz represents the operating conditions of a tire and under these conditions the loss factor can be used as an indication for the RR. As an indication of traction or WSR, the loss factor $\tan\delta$ around 0°C till approximately +30°C may be employed. However this is not the confirmed and accurate method to predict the WSR of the tire. Heinrich et al.¹⁰⁻¹² have done investigations on the wet skid behavior of different polymers and concluded that neither the glass transition of the polymers alone nor their plateau modulus, G_N^0 , gives a good correlation with wet skid resistance (WSR). A good correlation is only found when relating the WSR to the viscoelastic behavior of the elastomers in the transition region which is typically in the range of 1kHz-1MHz. Yet due to the limited capability of the measuring instruments, this high frequency range is often not accessible and $\tan\delta$ in the low temperature range may be taken as a primary indication for wet skid performance, see Chapter 3, 3.1.

The objective of the present study was to elucidate the mechanistic role of such oligomeric resins on the WSR and RR of silica-reinforced passenger tire treads based on synthetic rubbers. Three oligomeric resins were selected, representing the classes of natural resins: poly-terpene resin (resin A) and a phenolic modified terpene resin (resin B) and a pure vinyl-aromatic hydrocarbon resin (resin C). The oligomeric resins were used as admixtures in low

quantities: 2, 4 and 6 phr, in substitution of the corresponding amounts of extender oil in silica-reinforced tread compounds with a SBR/BR rubber blend. The influences of the oligomeric resins on the filler-filler and rubber-filler interactions and their effect on the processing characteristics of these compounds were investigated, as well as their influence on the dynamic and mechanical properties of their vulcanizates. These results are compared with those obtained for a compound containing no resin.

7.2 Experimental

7.2.1 Materials and compound preparation

Blends of oil-extended solution styrene-butadiene rubber (S-SBR) and high-cis polybutadiene (BR) with a weight ratio of 70/30 were used in this study. A highly dispersible silica was used as reinforcing filler. The three types of oligomeric resins investigated were provided by Arizona Chemical B.V. All three types are from the SylvatraxxTM product line: the naturally derived oligomeric poly-terpene resin (resin A); the phenolic modified oligomeric terpene (resin B); the pure vinyl-aromatic hydrocarbon resin (resin C). The characteristic properties of the resins are given in Table 7.1. Compounds were prepared based on the formulation given in Table 7.2, a common “Green Tire” silica-reinforced passenger car tire tread¹³. In the acronyms employed the first letter represents the type of oligomeric resin, A, B and C, and the number represents the concentration in phr of oligomeric resins used. Reference compound is the one containing no resin. The amount of coupling agent bis(tri-ethoxy-silyl propyl)tetrasulfide (TESPT) was held constant throughout the study to represent the commonly accepted optimum amount¹⁴. The other ingredients are as listed in Table 7.2 and introduced somewhere else (Chapter 3, Table 3.1).

Compounds were prepared in a 350 mL Brabender 350S internal mixer using a three stage mixing procedure, as presented in Table 5.3, chapter 5. The oligomeric resins to be added were physically mixed with the extender oil, ½ silane, TMQ and 6PPD in the first mixing stage prior to adding them together to the mixer. After cooling down, the first stage master batch was returned to the mixing chamber for a second stage. This was done to ensure a high level of coupling reaction between the silane and the silica¹⁵. After a maturation time of approximately 24 hours, the second stage master batch was returned to the mixing chamber and mixed with the curatives till a temperature of 100 °C at 75 rpm for 3 minutes.

Table 7.1

Characteristics of Resins used in this research

Resin code	A	B	C
Main Designation	Polyterpene (100% cyclo-aliphatic)	Terpene phenolic	Aromatic hydrocarbon
Main Components	Terpene	Terpene +Phenol	Styrene+ α -Methyl Styrene
Mn [g/mol]	630	563	723
PDI*	1.6	1.3	1.6
T_g [°C]	72	60	43
Softening point [°C]	120-126	112-118	80-90
Density [kg/m³]	1.05	1.01	1.064
Viscosity** [mPa.s]	10000	3400	650
Hydroxyl value [mg KOH/g]	-	50	-

* Poly Dispersity Index

**at 150°C

Samples were vulcanized in a Wickert press WLP 1600 at 100 bar and 160 °C to sheets with a thickness of 1.5 and 2 mm, applying their ($t_{90} + 2$) minutes optimum vulcanization time, as determined in a Rubber Process Analyzer RPA 2000 of Alpha Technologies, according to the procedure as described in ISO 3417.

7.2.2. Measurements

Mooney viscosity measurements were performed with an Alpha Technologies Mooney 2000VS, at 100°C, according ISO 289-1. Payne effect and Dynamic temperature sweep tests of the vulcanized compounds were performed respectively in shear and tension mode, in a Metravib DMA2000 dynamic spectrometer. The samples were cut from the vulcanized sheets of the rubber compounds. For temperature sweeps, measurements were performed between -80 °C and +80 °C with 5°C/min rate at a dynamic strain of 0.1%, static strain of 1% and a frequency of 10 Hz. Strain sweep measurements (Payne effect) of the vulcanizates were performed at constant frequency of 10 Hz at 90 °C, with strain amplitudes ranging from

0.1 to 100%. Hardness of the vulcanized compounds was measured with a Zwick 3150 Shore A Hardness Tester. Tensile and tear strength measurements were performed in tensile mode in a Zwick/Roell Z1.0 tensile tester, according to ISO 37.

Table 7.2

Compounds Compositions (phr) and properties

Ingredient		Compound sample code									
		Ref.	A-2	A-4	A-6	B-2	B-4	B-6	C-2	C-4	C-6
S-SBR		96.3	96.3	96.3	96.3	96.3	96.3	96.3	96.3	96.3	96.3
BR		30	30	30	30	30	30	30	30	30	30
Silica (1165MP)		80	80	80	80	80	80	80	80	80	80
TESPT		7	7	7	7	7	7	7	7	7	7
TDAE		6.7	4.7	2.7	0.7	4.7	2.7	0.7	4.7	2.7	0.7
Zinc oxide		2.5	2.5	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	2.5	2.5
6PPD		2	2	2	2	2	2	2	2	2	2
TMQ		2	2	2	2	2	2	2	2	2	2
Resin		0	2	4	6	2	4	6	2	4	6
Sulfur		1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
TBBS		1.7	1.7	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	2	2
Properties											
Mooney viscosities	ML(1+4) at 100 °C	70	69	70	72	72	76	77	72	74	75
Tensile Strength	[MPa]	17.1	17.6	17.8	20.1	20.6	20.3	20.1	20.7	20.4	20.8
Elongation @ break	[%]	387	349	367	435	428	444	468	465	422	434
M ₁₀₀	[MPa]	2.1	2.6	2.2	2.2	2.2	2.2	2.0	1.9	2.5	2.3
M ₃₀₀	[MPa]	12.2	14.4	13.6	12.3	12.6	12.1	10.8	11.1	13.9	12.8
Hardness	[Shore A]	61	61	61	62	60	61	62	60	61	62
T _g	[°C]	-42	-45	-40	-42	-45	-42	-40	-51	-42	-40

7.3 Results and discussion

Mixing behavior of the compounds containing various resins significantly changed relative to the non-resin containing Reference compound, particularly at the end of the first mixing stage. Figure 7.1 shows typical mixing fingerprints for the three compounds containing 4 phr of the various oligomeric resins, in comparison to the non-resin containing Reference

compound. After 2 minutes of mixing, when all the silica, silane and the oil/resin are added to the mixture, the torque level of the compounds containing resins B and C progressively deviate from the Reference one. Resin A shows either the same or a bit lower torque value than the Reference. When the concentration of oligomeric resins is changed, similar behavior is observed. This difference in mixer torque could be a consequence of the partial replacement of the low viscosity extender oil by the higher viscosity oligomeric resins; however, the effects are opposite of what might have been expected on basis of the natural viscosities of the respective resins (Table 7.1), with Resin A having remarkably high and Resin C a very low viscosity. Table 7.2 lists the Mooney viscosities for the various finished compounds; these confirm the earlier observations: Resin A shows approximately the same Mooney viscosity as the Reference. Resins B and C show a mutually comparable progressive increase in Mooney viscosity with increasing loading in comparison with the Reference compound. It is clear that the viscosity of the resins themselves cannot account for this effect.

Figure 7.1- Fingerprint of 1st Stage masterbatch mixing of the reference and 4 phr resin-containing compounds.

It is well known for the present silica technology that an in-situ reaction of the coupling agent with the silica surface needs to take place during mixing, in order to make the polar

silica particles hydrophobic and to provide a reactive surface which later-on during vulcanization can chemically couple with the rubber polymer chains. The efficiency of this silanization is a crucial factor in this technology and can positively or negatively be influenced by the conditions during mixing¹⁶. The Mooney increase can be taken as a first indication that the addition of the resins enhances somewhat the hydrophobation/compatibilization of the silica achieved by the coupling agent TESPT. The more common way to judge this is by the so-called Payne effect discussed later.

The mechanical properties after vulcanization are also presented in Table 7.2. Oligomeric resin addition has virtually no effect on the hardness value. The small increase seen in the hardness value of the compounds with 6phr resin (regardless of the type of resin), could be the consequence of the replacement of some of the plasticizing oil softener by the less softening resins. The M_{300} values within the Resin groups A and B show a decreasing trend; Resin C shows no trend. The tensile strength though increases rather significantly with oligomeric resin content. Resins B and C give a high reinforcing contribution to the tensile strength already at 2 phr additions, without further increase at higher resin loadings. Similarly the elongation at break is increased already at 2 phr loading, but does not further increase at higher loadings. Resin A, on the other hand, shows a steady increase in tensile strength and -after an initial decrease - elongation at break, even up to 6 phr loading. This might indicate a limit in the solubility of the resins in the compound, where Resins B and C apparently reach their limit at around 4 phr, while Resin A dissolves homogeneously till 6 phr in this type of compound.

Driven by filler-filler interaction and mediated by matrix viscosity and polymer-filler interaction, filler aggregates can establish contacts thus leading to a denser solid network. This filler network contributes to the overall storage modulus reinforcement for rubber compounds and affects the viscoelastic properties. Contrary to a polymer network, the effect of filler reinforcement diminishes upon deformation due to breakage of filler-filler contacts and induces a non-linear viscoelastic response even when small deformations are applied. The storage modulus (G') strain dependence and the difference between low-strain and high-strain G' is normally referred to as Payne effect^{17,18}. The short-distance forces between filler particles decrease strongly from low strain to high strain values. The breakdown of the filler network by increasing strain amplitude would also release the

occluded rubber so that the effective filler volume fraction and hence the modulus decrease¹⁹. For this reason the Payne effect is used as a measure of filler networking originating from filler-filler interaction as well as filler-polymer interactions, particularly for silica loaded rubber compounds. Payne effect measurements of the storage modulus performed on the optimally vulcanized compounds are presented in Figure 7.2. The lower the difference between low and high strain modulus, the lower the filler network development which can be attributed to better silanization. It signifies reduced interaction between the filler aggregates themselves, possibly (but not necessarily) more interaction/bonding between the fillers and the polymer chains and a better filler dispersion. All resins clearly show a positive effect on the silanization efficiency relative to the Reference, as all their G' vs. strain data are lower than the Reference compound. Resins B and C are even better than Resin A. And as to the effect of concentration, all three resins seem to reach saturation at a concentration of around 4 phr. Similar results were obtained with the loss modulus versus strain. As reduced filler-filler interaction and increased filler-polymer interaction is the essence of less hysteresis and consequently lower RR of tire treads, these reduced Payne effects may anticipate improvements in RR²⁰.

In order to assess the influence of these resins on RR in detail, the results of $\tan\delta$ against temperature are presented in Figure 7.3 for the temperature range of 30 – 80 °C. With the exception of sample C-6, which shows erratic behavior, and despite the scatter in the data, all compounds containing Resins B and C clearly show a reduction in $\tan\delta$ relative to the Reference, particularly at 60 °C. The effects for Resin A are less pronounced.

Figure 7.2- Payne effect of reference compound and resin containing compounds

Figure 7.4 shows the $\tan\delta$ data in the temperature range representative for WSR: 0 – 30 °C. Here a clear positive effect of higher $\tan\delta$ values indicates a higher and thus improved WSR of tire treads made from these compounds. The largest relative improvements found for $\tan\delta$ are around 35% for the samples B-4 and C-2. All curves converge at 30 °C to correspond with cross-over at around 40 °C, as seen in Figure 7.3. A closer look at the $\tan\delta$ data at sub-zero temperatures, -25 – 0 °C, also sometimes referred to as relevant for Ice Grip properties of tire treads, is presented in Figure 7.5. It shows the increases in $\tan\delta$ as well as an increase in the peak heights themselves. The effects are again most prominent for Resins B and C relative to Resin A.

Figure 7.3- $\tan \delta$ against temperature in the temperature range of 30 – 80 $^{\circ}\text{C}$ for all of the compounds

Figure 7.4- $\tan \delta$ against temperature in the WSR range for all the compounds

Figure 7.5- $\tan\delta$ of different resins in the ice grip temperature range

To summarize, the preferred compounds regarding RR and WSR are Resins B and C rather than Resin A. In view of saturation or limited solubility effects, quantities of ± 4 phr of all types of resins seem sufficient to achieve more or less optimal results.

The results as presented clearly indicate the potential of oligomeric resins as admixtures to silica-reinforced tire tread compounds, to impart at the same time improvements in WSR and RR, without any significant effect on other properties. A slight increase in hardness was noticed upon addition of the resins, which in commercial tire production could give reason to compound composition adjustments. But in the context of the present study this was not considered appropriate as it might have obscured the effects seen and made the interpretation difficult.

Overall Resin C and Resin B gave the best results, compared to the reference compound. This obviously has something to do with the mutual compatibility of the resins with the polymers. From a phenomenological perspective the chemical nature of the resins come in effect: the vinyl-aromatic base of Resin C or the phenolic modification of Resin B are closer in structure to the styrene-butadiene than the polyterpene structure of Resin A. This might explain the better compatibility. In case that the components are mutually not compatible/soluble, the T_g 's do not merge and keep their individual values and two T_g -peaks would remain visible in the $\tan\delta$ vs. temperature diagram, at least when the quantities of both components are sufficiently high. This is not the case in the present study. Except for the compounds with 2phr resin content, which have a bit lower T_g and by considering the accuracy of the measurements and the standard deviations, all the other compounds have almost the same T_g values compared to the Reference, as given in Table 7.2. It can be taken as a sign of good/sufficient solubility at the low amounts added. It can be concluded that the resin containing compounds are homogeneous and compatible²¹.

Another explanation, also covering the increase in the peak height of $\tan\delta$ as well as the lower $\tan\delta$ at the RR-range in higher temperatures, is related to the enhancement of the silanization of the silica by the oligomeric resins, as referred to before. The degree of silanization by the coupling agent TESPT and later the chemical bonding of rubber chains to the modified filler surface leads to the creation of a significant amount of immobilized rubber molecules, or at least heavily restricted in their segmental motions; sometimes also

called a glassy layer around the filler particles²²⁻²⁴. This has been reported in other works as well^{9,20,25}. Scurati et al.²⁵ have investigated the filler-filler and filler-polymer interactions in rubber compounds and claimed that hysteresis is greatly dependent on the degree of filler network at all temperatures. Compounds with lower filler networking give higher $\tan\delta$ peak values. In the glassy state, it is the polymer that mainly dictates the compound loss properties, while at temperatures far above the T_g , it is the filler network that governs the reinforcement. A system with a less developed filler network has lower high-temperature loss tangent and less strain dependence compared to a system with a more developed filler network. This plays a particularly important role in silica reinforcement, as this chemical bonding is a prerequisite for silica to work as reinforcing filler, in contrast with the more traditional carbon black, where this bonding is mainly physical of nature and therefore less strong. If filler particles are not attached to the polymer matrix, like in the case of carbon blacks, the energy loss contributions are significantly higher and this leads to relatively higher compound hysteresis.

Apparently, the presence of the oligomeric resins enhances this immobilization of rubber molecules on the silica filler. This raises the hydrodynamic volume of the filler particles, which then can account for the viscosity increases as observed²⁶. However, it also improves the silica dispersion and thereby releases more of the rubber molecules occluded in the void spaces of the silica aggregates. The Payne effect data support this phenomenon in the sense, that the mutual interactions between the filler aggregates are reduced. This raises the effective volume fraction of rubber in the compounds, which enhances the rubber elastic performance of the compounds versus the “dead, non-elastic” contribution of the filler, as is reflected in the lower $\tan\delta$ in the RR temperature range, but also in the increased $\tan\delta$ peak. Similar observations and analyses has been reported by others, e.g. as a result of functionalization of the polymers²⁷⁻²⁹, or by variation of the type and chemical structure of the coupling agent used instead of TESPT^{29,30}. It would require more fundamental in-depth studies, however, to confirm this further in detail.

7.4 Conclusions

Addition of low amounts of low molecular weight oligomeric resins of natural and/or synthetic origin bears the potential to enhance the (wet) skid resistance and at the same

time reduce the rolling resistance of silica-reinforced passenger tire treads based on synthetic rubbers. In the specific polymer matrix used for this investigation, the vinyl-aromatic based hydrocarbon resin and the phenolic-modified terpene resin perform better than the poly-terpene resin. The overall performance of the resins depends on the particular rubber formulation and the selection of rubbers which explains the necessity of a large variety of oligomeric resins derived from various monomers. Addition of 2 to 6 phr resin to the compounds to replace the same amounts of extender oil, has little influence on vulcanization behavior, hardly raises the hardness, but has a strong positive influence on tensile strength and elongation at break. The Payne-effect improvements resulting from the addition of the oligomeric resins indicate a reduced filler-filler interaction of the silica filler and tighter silica-rubber interaction, as obtained by enhancement of the silanization by the coupling agent TESPT. It results in a stronger immobilized rubber shell around the silica particles and more rubber released from occlusion in the void spaces of the silica aggregates. It improves the “elastic” performance of the compounds: reduced hysteresis, and consequently gives indication for lower RR of tire treads made thereof, versus increases in the $\tan\delta$ temperature and peak-height in the glass-transition region, indicative for higher (wet) skid resistance of tire treads.

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Chapter 8

Summary

With increasing the global concern for fossil fuel consumption, automotive industry moves toward more efficient vehicles. Tires are of great importance in this respect, as the tire compound material in contact with the road surface and under the cyclic deformation dissipates energy due to its viscoelastic nature. On the other hand the friction between the road and the tire surface is required for a safe drive. These two contrary characteristics of the tire need a compromise to deliver a secure and efficient ride. Regarding the environmental issues, since July 1st, 2012, all the tire manufacturers in Europe are obliged to provide an efficiency label for their tires indicating three characteristics which includes fuel efficiency (related to Rolling Resistance (RR) performance) and safety (related to Wet Skid (WS) performance). Present thesis deals with these two important aspects of the tire; RR and WS, investigating on a green tire tread material. In this regard **Chapter 2** reviews the current state of the knowledge on the relationship between the viscoelastic properties of the rubber compound used in the tire tread and these two important tire characteristics and the methods to measure them are summarized. In addition, an overview on the new generation of the Styrene Butadiene Rubbers (SBRs) and their preparation method is included in this chapter. Loss factor ($\tan\delta$) is a determining parameter in analyzing the tire tread material performance. It has been accepted that the $\tan\delta$ value of a tread compound measured at a temperature around 60°C and a frequency of 10Hz can be representative of the Rolling Resistance performance of a tire made thereof. However for Wet Skid performance the situation is a bit different. In order to predict Wet Skid, the viscoelastic properties of the rubber materials at high frequencies, in the megahertz (MHz) range, should be measured which is not feasible with the current laboratory facilities. Nonetheless Viscoelastic master curves derived from time-temperature superposition (TTS) can be used to describe the properties of the tread materials over a wide frequency range. **Chapter 3** presents the procedure to produce the viscoelastic mastercurves for several compounds filled with different amounts of silica and the behavior of the filler network at the different frequency regions is evaluated. Activation energy of the filler network is calculated from the Arrhenius relationship of the vertical shift factor at the high temperature / low frequency

range of the mastercurve. The activation energies derived for both the storage moduli G' and the loss moduli G'' are almost equal confirming that in the linear response region (strain deformation of 0.1%) the Kramers –Kronig relations are fulfilled. However the activation energies derived from the strain sweep measurements are 3-5 times higher and the values derived from the loss modulus G'' are much higher than those derived from the storage modulus G' which arises from the fact that storage modulus deals with the virgin, intact filler-filler bonds and the loss modulus with the damaged filler-filler bonds which break down and reform during dynamic deformation. Anyhow these energies are still far from the level of typical chemical processes. An important realization derived from these investigation was that in the high frequency / low temperature region of the mastercurve, which is considered to be representative for the wet skid performance of the tires, the $\tan\delta$ value decreases with an increase in the amount of filler. It indicates that the presence of fillers negatively influences the damping properties of the polymer network. However the complication is that such low strain values (0.1%) are far below the real strains occurring during actual performance of tires on the road, particularly during traction or wet skidding. Considering this difficulty and in order to produce the mastercurves at higher strain conditions, the same series of the compounds were tested in a different Dynamic Mechanical Analyzer (DMA) instrument, the one which enables performing the tests under constant stress. The results were presented in **Chapter 4**. TTS measurements were performed at two constant force values: 0.5 and 2 N. The calculated strain values are large in low frequency/high temperature region and can reach a high value of 6% in case of the unfilled compound at 0.5N force and up to 24% at 2N. By increasing the frequency the strain level decreases and approaches zero in the MHz region. In the high frequency region of the mastercurve, the highest $\tan\delta$ is observed for the unfilled compound confirming the negative effect of the fillers on the Wet Skid performance of the tire, which was observed in the strain-based measurements too. The activation energy of filler network is also calculated from the vertical shift factors. The values are lower than what was observed in strain-based measurements. The interpretation is too complicated and would require much more study.

With the introduction of silica technology in passenger car tire tread applications, the filler-polymer interactions have become of key importance. Besides the silane coupling agents and control of the silanization process, a polymer functionality can play an essential role in

the polymer-filler interactions. In the last years many researches has been focused on the functionalization of the common elastomers used in the tire formulation, basically Styrene Butadiene Rubber SBR and Butadiene Rubber BR. 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. The results of the investigation on the effect of three different 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 are shown in **Chapter 5**. The results show the significant potential of two of these modified SBRs to reduce rolling resistance of tire treads made thereof, while no major change in wet grip occurs. The largest improvement, a decrease of 16% in loss tangent at 60°C, was achieved for the compound with mercapto-functionalities. It is commonly accepted that a lower loss tangent arises from better filler dispersion / less filler-filler interactions and less slippage of polymer chains on the filler particle surface or a combination of these two mechanisms. Lower slippage can be due to stronger interactions arising between polar silica particles and polar moieties on the polymer chains. In addition, alkaline ZnO may be attracted to acidic polymer moieties, therefore less obstructing the silanization process leading to better filler dispersion, again. Lower filler-filler interactions were further approved via Payne effect measurements, which show the smallest decrease in storage modulus vs. strain for the compound containing mercapto moieties. Higher filler-polymer interactions is confirmed through Bound Rubber test. Additionally, the interference of Zinc oxide (ZnO), as a well-known activator in sulfur cure systems, with the silanization process and the polar moieties on the polymer chains is explored in this Chapter. Three compounds were prepared with ZnO added at a later stage of mixing at the same time as the curatives, to investigate the effect of ZnO in the functionalized polymer compounds. The outcome is that ZnO indeed has a significant influence on the loss properties and the filler dispersion of the compounds. The largest improvement, 39% decrease in the loss tangent value at 60°C compared to the reference compound, was achieved for the compound CS8-Z in which a dithiol modified SBR was used. This decrease in hysteresis makes this material prone for application in tire treads, as it is expected to result in a reduced rolling resistance. Adding ZnO to the compound in a later stage of mixing favors the Rolling Resistance of the tires made thereof, but bring along lower hardness values which can affect other properties

of the compounds, such as tire traction. In order to avoid misinterpretations, compounds were prepared with adjusted hardness levels and their dynamic and mechanical properties were presented in **Chapter 6**. In order to adjust the Hardness level of these compounds to the Reference one, either some amount of oil was removed from the formulation or the vulcanization system was changed from Semi-Efficient to Conventional. However, lately it was revealed that the applied conventional cure system with low amount of DPG was not suitable for these silica-filled compounds, and the compounds remained undercured. Consequently, the results of the two compounds with Conventional cure system were not reliable and useful. Adjusting the Hardness value by removing 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 from LAT100 test, 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. But Overall the excellent performance of the dithiol modified polymer in the tread formulation, as already discussed in Chapter 6, does not change much by changing the Hardness value of its compound as it performs at a large distance better than the other polymers used. The effect of oligomeric resins derived from natural and synthetic monomers on the viscoelastic behavior of the silica-reinforced tire tread compounds and their potential to improve passenger car tire performance is discussed in **Chapter 7**. Three oligomeric resins were selected: the naturally derived oligomeric poly-terpene resin; the phenolic modified oligomeric terpene and the pure vinyl-aromatic hydrocarbon resin. The results show that adding low amounts of low molecular weight oligomeric resins bears the potential to enhance the Wet Skid resistance and at the same time reduce the Rolling Resistance of the silica-reinforced passenger tire treads. In the specific polymer matrix used for this investigation, the vinyl-aromatic based hydrocarbon resin and the phenolic-modified terpene resin perform better than the poly-terpene resin. The Payne-effect improvements seen for all the resin containing compounds signifies reduced interaction between the filler aggregates, possibly (but not necessarily) more interaction/bonding between the fillers and the polymer chains and a better filler dispersion. Better performance of the vinyl-aromatic based hydrocarbon resin and the phenolic-modified terpene resin can be attributed to the mutual compatibility of the resins

with the polymers. From a phenomenological perspective the chemical nature of the resins come in effect: the vinyl-aromatic base of Resin C or the phenolic modification of Resin B are closer in structure to the styrene-butadiene than the polyterpene structure of Resin A.

Samenvatting

Vanwege de toenemende wereldwijde bezorgdheid over het verbruik van fossiele brandstoffen beweegt de automobiellindustrie zich in de richting van efficiëntere voertuigen. Banden spelen in dat verband een grote rol, aangezien het banden compound-materiaal in contact met het weg-oppervlak energie dissipeert onder cyclische deformatie vanwege z'n viscoelastische aard, hetgeen resulteert in rol-weerstand. Aan de andere kant is wrijving vereist tussen de weg en het banden-oppervlak voor een veilige wegligging: (natte) slip-weerstand of tractie. Deze twee conflicterende karakteristieken van een band vereisen een compromis teneinde een veilige en zekere wegligging te verkrijgen. Betreffende de duurzaamheids-aspecten zijn sinds 1 juli 2012 alle banden-distributie punten in Europa verplicht om een efficiency label voor hun banden ter beschikking te stellen, welke drie karakteristieken aangeeft, omvattende brandstof efficiëntie (gerelateerd aan Rolweerstand (RR)) en veiligheid (gerelateerd aan Natte Slip-Weerstand (WS)) en banden-lawaaai; het laatste punt valt buiten het doel van dit proefschrift.

Het huidige proefschrift behandelt twee belangrijke aspecten van de band: RR en WS, onderzocht aan de hand van een zogenaamd "Green Tire" loopvlak materiaal, met silica gebruikt voor versterking van de banden rubber. In dit verband wordt in **Hoofdstuk 2** een overzicht gegeven van de huidige stand van de kennis betreffende het verband tussen de viscoelastische eigenschappen van rubber compounds gebruikt in banden loopvlakken en deze twee belangrijke banden karakteristieken, en worden de methodes samengevat om deze te meten. Daarnaast wordt in dit hoofdstuk een overzicht gegeven van een nieuwe generatie Styreen Butadiëen Rubbers (SBRs) en hun bereidingswijzen. De dynamisch mechanische verlies-factor ($\tan\delta$) is een belangrijke parameter in de analyse van het functioneren van het banden-materiaal. Het is algemeen aanvaard, dat de $\tan\delta$ -waarde van een loopvlak-compound gemeten bij een temperatuur rond 60°C en een frequentie van 10Hz beschouwd kan worden als representatief voor het Rol-Weerstand gedrag van een band daaruit gemaakt. Echter, voor het Natte Slip-gedrag is de situatie gecompliceerder. Om het Natte Slip-gedrag te voorspellen moeten de viscoelastische eigenschappen van de rubber materialen gemeten worden bij hoge frequenties, in het megahertz (MHz) gebied en bij relatief grote deformaties, wat niet mogelijk is met huidige laboratorium apparatuur.

Desondanks kunnen viscoelastische master curven afgeleid van Tijd-Temperatuur Superpositie (TTS) gebruikt worden om de eigenschappen te beschrijven van de loopvlak-materialen over een breed frequentie-gebied. **Hoofdstuk 3** geeft de procedure om viscoelastische mastercurven te verkrijgen voor verscheidene compounds gevuld met verschillende hoeveelheden silica versterkende vulstof, en verder wordt het gedrag van de vulstof netwerken bij verschillende frequenties geëvalueerd. De activerings-energie van het vulstof-netwerk wordt berekend aan de hand van de Arrhenius-vergelijking voor de verticale verschuivings-factor in het hoge temperatuur / lage frequentie gebied van de mastercurve. De activerings-energieën afgeleid voor zowel de opslag- G' als de verlies-moduli G'' zijn vrijwel gelijk, hetgeen bevestigt dat in het lineaire response-gebied (rek-deformatie van 0,1%) aan de Kramer-Kronig relaties wordt voldaan. Echter, de activerings-energieën afgeleid uit de variabele rek metingen zijn 3-5 maal zo hoog en de waardes afgeleid met de verlies-modulus G'' zijn veel hoger dan die verkregen uit de opslag-modulus G' . Dit vindt z'n oorsprong in het feit, dat de opslag-modulus betrekking heeft op maagdelijke, intacte vulstof-vulstof bindingen, en de verlies-modulus met de beschadigde vulstof-vulstof bindingen, die breken en zich opnieuw vormen gedurende dynamische deformatie. In ieder geval liggen deze activerings-energieën nog ver beneden het niveau voor typische chemische processen. Een belangrijke gevolgtrekking van dit onderzoek was dat in het hoge frequentie / lage temperatuur gebied van de mastercurven, dat representatief geacht wordt voor de Natte Slip-Weerstand van de banden, de $\tan\delta$ -waarde afneemt bij toename van de hoeveelheid vulstof. Het geeft aan, dat de aanwezigheid van versterkende vulstoffen zoals silica de dempings-eigenschappen van het polymere netwerk negatief beïnvloedt. Evenwel, een complicerende factor is dat de lage rek-waardes (0,1%) ver beneden de werkelijke rekken liggen welke optreden gedurende het actuele gedrag van banden op de weg, met name gedurende tractie of Natte Slip. Met het oog op deze moeilijkheid en teneinde masterecurven te produceren bij hogere rek-condities is dezelfde reeks compounds nogmaals onderzocht in een ander Dynamic Mechanical Analyzer (DMA) instrument, een die testen bij constante spanning mogelijk maakt. De resultaten worden weergegeven in **Hoofdstuk 4**. TTS metingen zijn verricht bij twee constante kracht-waardes: 0,5 and 2 N. De berekende rek-waardes zijn groot in het lage frequentie / hoge temperatuur gebied en kunnen een hoge waarde bereiken van 6% in geval van het onge vulde compound bij 0,5N kracht en wel 24% bij 2N. Door de frequentie te verhogen neemt het rek-niveau af en

tendeert naar nul in het MHz gebied. In het hoge frequentie gebied van de mastercurven wordt de hoogste $\tan\delta$ waargenomen voor het onge vulde compound, hetgeen het negatieve effect van vulstoffen op het Natte Slip gedrag van de band bevestigt, zoals eerder waargenomen in de constante rek-gebaseerde metingen. De activerings-energie van het vulstof netwerk wordt wederom berekend uit de verticale verschuivings-factoren. De waardes zijn lager dan waargenomen voor de constante rek-gebaseerde metingen. De interpretatie hiervan is erg ingewikkeld en vereist daarom veel meer onderzoek.

Bij gelegenheid van de invoering van silica technologie in personenwagen banden-loopvlak toepassingen zijn vulstof-polymeer interacties van eminent belang geworden. Naast de silaan coupling-agents en controle van het silaniserings-proces kan de functionaliteit van het polymeer een essentiële rol vervullen in de polymeer-vulstof interacties. In de afgelopen jaren zijn veel ontwikkelingen toegespitst op functionalisering van de gebruikelijke polymeren voor banden-formuleringen, voornamelijk Styreen Butadieen Rubber SBR en Butadieen Rubber BR. Het doel is verlaging van de hydrofobe karakteristieken van de koolwaterstof polymeren en hen meer verdraagzaam maken met hydrofiele silica, resulterend in betere silica dispersie en verbeterde polymeer-vulstof interacties. De resultaten van onderzoek naar het effect van drie verschillende gefunctionaliseerde SBR's: één gemodificeerd langs de keten met carboxylaat-eenheden; één gemodificeerd met dithiol-groepen en één gedeeltelijk Si-gekoppeld, op de dynamische en mechanische eigenschappen van een silica-versterkt banden loopvlak compound worden gepresenteerd in **Hoofdstuk 5**. De resultaten demonstreren de significante mogelijkheid van twee van deze gemodificeerde SBR's om de RolWeerstand van banden loopvlakken daaruit gefabriceerd te verlagen zonder een duidelijke verandering in de Natte Slip-Weerstand. De grootste verbetering, 16% verlaging van de mechanische verliesfactor gemeten bij 60°C, werd bereikt voor het compound met mercapto-functionaliteiten. Het is algemeen aanvaard, dat een lagere verliesfactor ontstaat door een betere vulstof-dispersie / minder vulstof-vulstof interacties en minder afglijden van polymeer-ketens van het oppervlak van het vulstof-deeltje, of een combinatie van deze twee mechanismen. Minder afglijden kan het gevolg zijn van sterkere interacties tussen polaire silica deeltjes en polaire eenheden op de polymeer-ketens. Daarnaast kan alkalisch ZnO worden aangetrokken door zure groepen op het polymeer, waardoor het silaniserings-proces minder wordt gestoord, hetgeen op z'n beurt

weer leidt tot een betere vulstof-dispersie. Lagere vulstof-vulstof interacties zijn verder aangetoond via Payne-effect metingen, die de minste daling in opslag-modulus vs. rek lieten zien voor het compound dat mercapto-eenheden bevatte. Hogere vulstof-polymeer interacties zijn daarnaast bevestigd door Bound Rubber testen. Bovendien wordt in dit hoofdstuk de onderlinge wisselwerking tussen zinkoxide (ZnO), als algemeen bekende activator in zwavel vernettings systemen, en het silaniserings-proces en de polaire eenheden op de polymeer-ketens onderzocht. Drie compounds werden aangemaakt met ZnO toegevoegd in een laat stadium van de menging, gelijktijdig met de vulkanisatie-middelen, om het effect van ZnO in de gefunctionaliseerde polymeer compounds te onderzoeken. Het blijkt dat ZnO inderdaad een significante invloed uitoefent op de verlies-eigenschappen en de vulstof-dispersie van de compounds. De grootste verbetering, een afname van 39% in de verliesfactor bij 60°C ten opzichte van het referentie-compound werd verkregen voor compound CS8-Z waarin een dithiol-gemodificeerd SBR is gebruikt. Deze verlaging in hysteresis maakt dit materiaal geschikt voor toepassing in banden loopvlakken, aangezien het verwacht wordt te resulteren in een verlaagde RolWeerstand. Het toevoegen van ZnO aan het compound in een laat stadium van de menging komt de RolWeerstand van banden daaruit gemaakt ten goede, maar gaat gepaard met lagere hardheids-waardes, die andere compound-eigenschappen mogelijk kunnen beïnvloeden, zoals banden tractie. Teneinde verkeerde interpretaties te vermijden zijn daarnaast compounds aangemaakt met aangepaste hardheids-niveaus, waarvan de dynamische en mechanische eigenschappen zijn weergegeven in **Hoofdstuk 6**. Om het hardheids-niveau van deze compounds aan te passen aan het referentie-compound, werd hetzij een weinig olie verwijderd uit de formulering, hetzij het vulkanisatie-systeem veranderd van Semi-efficiënt naar Conventioneel. Echter, aan het einde bleek dat het toegepaste conventionele vulkanisatie systeem met laag gehalte aan Di-Phenyl Guanidine (DPG) niet geschikt was voor deze silica-gevulde compounds en dat de compounds in feite onder-ge vulkaniseerd waren gebleven. Dientengevolge waren de resultaten voor de twee compounds met het conventionele vulkansatie-systeem niet betrouwbaar, noch bruikbaar. Aanpassen van de hardheids-waarde door weglaten van wat olie verhoogt de interne frictie tussen de vulstof-deeltjes danwel tussen vulstoffen en polymeer ketens. De Payne-effect test resultaten bevestigen hogere vulstof-vulstof interacties in de compounds met lagere hoeveelheid olie. Kijkend naar de Side Force Coefficient (SFC) waardes van de LAT100 testen lijkt het erop, dat het verwijderen van wat

olie uit de formuleringen leidt tot een kleine toename in de frictie coëfficiënt van de compounds. In ieder geval zijn de veranderingen in SFC-waardes zeer klein en binnen een band van 3-7%, en derhalve niet echt significant in de werkelijke banden-praktijk. Maar over het geheel genomen verandert het uitnemende gedrag van het dithiol-gemodificeerde polymeer niet veel in de loopvlak-formulering door verandering van de hardheids-waarde van z'n compounds, aangezien het veel beter functioneert dan de andere gebruikte polymeren.

Het effect van oligomere harsen afgeleid van natuurlijke en synthetische monomeren, op het viscoelastisch gedrag van de silica-versterkte banden loopvlak compounds, en hun potentieël om de personenwagen-banden prestaties te verbeteren wordt besproken in **Hoofdstuk 7**. Drie oligomere harsen werden uitgekozen: een oligomere poly-terpeen hars op natuurlijke basis: A; een fenol-gemodificeerde oligomere terpeen: B; en een zuivere vinyl-aromatische koolwaterstof hars: C. De resultaten tonen aan dat het toevoegen van kleine hoeveelheden laag-moleculaire oligomere harsen de mogelijkheid biedt om de Natte SlipWeerstand te verbeteren bij gelijktijdige verlaging van de RolWeerstand van silica-versterkte personenwagen banden-loopvlakken. In de specifieke polymere matrix gebruikt voor dit onderzoek voldoen de vinyl-aromatische koolwaterstof hars en de fenol-gemodificeerde terpeen hars beter dan de poly-terpeen hars. De Payne-effect verbeteringen waargenomen voor alle harsen-bevattende compounds indiceert een verlaagde interactie tussen de vulstof-aggregaten, mogelijk (maar niet noodzakelijkerwijs) meer interactie/binding tussen de vulstoffen en de polymeer ketens, en een betere vulstof-dispersie. Het betere gedrag van de vinyl-aromatische koolwaterstof-hars en de fenol-gemodificeerde terpeen hars kan worden toegeschreven aan onderlinge verdraagzaamheid van de harsen met de polymeren. Vanuit een fenomenologisch gezichtspunt speelt de chemische aard van de harsen een rol: de vinyl-aromatische hars C of de fenolische modificatie van hars B lijken qua chemische structuur meer op de styreen-butadiëen dan de polyterpeen structuur van hars A.

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**Though the way is full of perils, and the goal is far out of sight, there is no road to which
there is no end: do not despair.**

«Hafez»

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