Influence of molecular properties of SSBR and BR types on composite performance

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\textbf{ABSTRACT}

Modern passenger car tire tread compounds usually consist of a polymer blend of Solution Styrene-Butadiene Rubber (SSBR) and Butadiene Rubber (BR) in combination with a silica/silane system. To further enhance the compatibility between the nonpolar polymer and the polar silica, different functional groups can be introduced at the end or along the polymer chains. The influence of such a polymer functionalization of SSBR and BR on the processing behavior as well as on mechanical and dynamic properties was investigated for silica-filled tire tread model compounds. Silica-filled functionalized SPRINTAN™ SLR 4602 was blended with non-functionalized SPRINTAN™ 363H and functionalized SPRINTAN™ 884 L in three ratios: 90/10, 80/20 and 70/30. The two BRs differ in five analytical properties: molecular weight, vinyl content, cis-content, glass transition temperature ($T_g$) and functionalization. All five properties influence the composite properties in a different way. The functionalization is the dominating influencing parameter in this study. The presence of the functionalization improves the rubber-filler-interaction. This leads to better dynamic and mechanical properties of the model tread compound: The reinforcement index is increased and the tan $\delta$ at 60 $^\circ$C, as lab predictor for the tire rolling resistance, is reduced while the tan $\delta$ at 0 $^\circ$C, as lab predictor for wet grip, is similar to the non-functionalized BR. Furthermore, the $T_g$ of the whole blend compound dominates the dynamic-mechanical behavior, as expected. In the case of BR, the functionalization has the dominating influence on the tan $\delta$, the effect of $T_g$ plays a minor role. These new insights support the development of new functionalized polymers to improve the overall tire performance.

\section{1. Introduction}

In the last years, the European Union (EU) has mandated the reduction of the greenhouse gas emissions, especially carbon dioxide (CO$_2$). Passenger cars are responsible for roughly 13\% of the total CO$_2$ emission in the EU [1], and since the tread of a passenger car tire has a significant influence on the fuel consumption of a car due to its rolling resistance, it is of great importance to develop new tire tread formulations to reduce the carbon footprint. From 2021, the CO$_2$ emission of new passenger cars must be reduced by 27\% compared to 2015 [2]. In the past, Michelin introduced a new silica-silane filler system replacing carbon black in the rubber industry that improves the tire properties including wet grip and rolling resistance [3].

Nowadays, the production of functionalized polymers provides another solution to overcome the problem of interaction between the non-polar polymers with silica. The idea is to increase the compatibility of non-polar polymers with silica to get at least the same level of interaction as with non-polar polymers by using a coupling agent. Therefore, researchers and businesses are developing and testing novel polymers especially made for silica compounds to further enhance the polymer-filler interaction. One example is the production of functionalized Solution Styrene-Butadiene Rubber (SSBRs) [4,5]. This polymer type is produced by anionic solution polymerization initiated by an organo-lithium (Li) catalyst. A unique benefit of this method is the possibility to control the structure of the polymer. Accordingly, it is possible to react the chain-ends of the monomer with a polar group, because the reaction of the chain-ends with another growing monomer chain rarely occurs. Hence, this can significantly change the rheological or chemical properties of the polymer. For instance, chain-end functionalized polymers can be produced which can affect the polymer-filler interaction already in the unvulcanized stage and hence, influence the hysteretic properties of the rubber compound [4]. However, a
co-polymerization of monomers that contain functional groups is difficult due to poor selectivity [6]. Other possibilities are side chain functionalization and the addition of a third functionalized monomer in the main chain. For side chain functionalized SSBR, however, vinyl groups are required to be able to react with the functional groups. Hence, higher vinyl content in SSBR results in higher \( T_g \) [7]. Therefore, the rolling resistance and wear resistance of the tire tread deteriorate due to the lower chain mobility [8].

Various researchers have tested different types of functional groups to optimize the polymer-filler interaction, mainly for SSBR. Studies show that chain-end functionalized polymers with amino or alkoxysilyl groups could in fact improve the dispersibility and interaction of the polymer with silica and hence, the hysteresis loss is reduced. Sone et al. [9] tested these mono-functionalized SBRs along with new bi-functionalized SBRs which contain both an amino- and alkoxysilyl-group. They showed that the use of mono-functionalized SBR with alkoxysilyl and three types of bi-functionalized SBRs lead to a much higher bound rubber content compared to the non-functionalized SBR and two mono-functionalized SBRs with an amino-group. This large difference is caused by the type of interaction. The amino-group forms a reversible hydrogen bond with the silanol group on the silica surface, whereas the alkoxysilyl-group forms a chemical bond with the silanol groups.

The researchers proved that there is a correlation between abrasion loss and bound rubber content – the higher the bound rubber the lower the abrasion loss. The SBRs with a grafted alkoxysilyl group that can create a chemical bond, have a much higher wear resistance.

Besides, the hysteresis loss was also affected by the structure of the end-chain functionalized SBRs. They measured the viscoelastic hysteric loss \( \tan \delta \) of the uncured compounds at 3% strain and at 50 °C and proved that this \( \tan \delta \) decreases when a functional group is added to the chain-end of the polymer. Remarkably, the two bi-functionalized SBRs with both polar groups at one chain-end show remarkably low \( \tan \delta \) values, even compared to the bi-functionalization where the groups are placed at both sides of the main chain. Besides that, the Payne effect of the bi-functionalized SBR showed the lowest \( G' \) values and hence, the best filler micro-dispersion. This was also confirmed by transmission electron microscopy (TEM) measurements [9].

Maghami et al. [10] tested two functionalized SBRs, namely SPRINTAN™ SLR 4602 (SBR-4602) and Buna VSL VP PBR 4003. The first polymer is chain-end modified and the second one has carboxyl groups along the entire main chain for improved polymer-filler interaction. The polymers show both a high chemically bound rubber content compared to the non-functionalized reference compound, which means that they have a high polymer-filler interaction. Noticeably, the two functionalized SBRs show a lower hardness, tensile strength and elongation at break related to those properties of the non-functionalized reference compound. Nevertheless, the \( \tan \delta \) at 60 °C (as passenger car tire rolling resistance indicator [12]) of the cured modified polymers were around 15% lower than the unmodified polymer, as measured at 6% strain. Moreover, the results of the rebound resilience test show the same behavior. The results of the rebound test are exactly the opposite to the values of \( \tan \delta \). Hence, it shows that the addition of functional groups at the non-polar polymer chain improves the compatibility with the polar silica. Therefore, the functionalization of SSBR leads to a lower rolling resistance of the passenger car tire tread [11].

Another example to functionalize polymers is the production of high cis-1,4-butadiene rubber (BR) using a neodymium catalyst [4,5]. Positive 1,4 addition allows the addition of functional groups at the polymer chain-ends, a characteristic that is not possible by using Ti-, Ni- or Co as catalyst. However, the fraction of added functional groups at the chain-ends is low compared to SSSBRs synthesized by living anionic polymerization because of the different polymerization mechanisms. Nevertheless, chain-end functionalized BR improves the tangent delta and wear resistance through interaction with the reinforcing agent [7].

In general, it can be concluded that functionalized polymers increase the affinity with the polar silica particles which results in a better filler micro-dispersion and hence, the hysteretic properties are improved.

In the present work, the effect of functionalization of the polymer on the in-rubber properties of silica-filled composites was studied in detail. Hence, different types of (functionalized) BRs and SSSBRs were blended in various ratios including the silica-silane system. The Mooney viscosity, Payne effect and macro filler dispersion of the compounds were analyzed to investigate the effect of the functional groups grafted on the polymer chain.

In addition, the dynamic and mechanical properties like hardness and tensile strength of the various SSBR/BR blends are discussed. Moreover, the effect of functionalization of the polymer on the dynamic mechanical properties of the passenger car tire tread compounds was investigated. Therefore, the \( \tan \delta \) at 0 °C and 60 °C were analyzed which are known to be lab indicators for the wet grip and rolling resistance of the tire [12]. In this way, it can be shown if the functionalization of polymers can improve the expected overall tire performance. Furthermore, the influence of two different molecular structures of BR on the tire tread performances was evaluated.

2. Materials and methods

2.1. Compound formulation and mixing regime

2.1.1. Ingredients

In this research, one SSBR and two types of BR from Trinseo Deutschland GmbH are used: the SSBR SPRINTAN™ SLR 4602 (SBR-4602) and the BRs SPRINTAN™ 363H (BR-363) and SPRINTAN™ 884 L (BR-884). The functionalized polymers can chemically interact with the silica, the SSBR as well as the BR-884 are chain-end functionalized. The characteristic properties of these polymers are shown in Table 1.

The functionalized SBR-4602 is blended with both the unfunctionalized BR-363 and functionalized BR-884 in three ratios: 90/10, 80/20 and 70/30 (Table 2).

To reinforce the compounds, precipitated silica in combination with a bifunctional organosilane and carbon black were used in all blends. The silica ULTRASIL® 7000 GR (U7000GR, granules as dosage form) is a highly dispersible filler, with a specific surface area (CTAB [13]) of 160 m²/g. Since silica is hydrophilic and the used polymers are hydrophobic an additional coupling agent (bis(triethoxysilylpropyl)disulfide, TESPED) was used for the chemical bonding between rubber and silica to enhance the polymer-filler interaction.

A constant amount of Treated Distillate Aromatic Extracted (TDAE) oil was used in all compounds. The compounds were sulfur (S) cured with zinc oxide (ZnO) and stearic acid as activators for the vulcanization reaction. Besides, tetrasooyl thiuram disulfide (TMTD) and N-cyclohexyl-2-benzothiazyl-sulfenamide (CBS) were added as primary accelerators and N,N’-Diphenylguanidine (DPG) as secondary accelerator. The compounds were protected against oxygen and ozone by using polymerized 1,2-dihydro-2,2,4- trimethylquinoine (TMQ), N,(1,3-Dimethylbutyl)-N’-phenyl-p-phenylenediamine (6PPD) and wax. The

| Table 1 | Typical polymer characteristics. |
|---------|--------------------------------|
| Rubber  | SBR-4602 | BR-363 | BR-884 |
| Functionalized | Yes | No | Yes |
| Molecular mass ratio | 1 (low) | 1.5 (high) | 1.3 (medium) |
| Styrene, % | 21 | | |
| Vinyl, % | 63 | 0.7 | 12 |
| 1,4-cis, % | – | 96.6 | 30–37 |
| trans, % | – | 2.7 | 35–40 |
| ML 1 + 4 (100 °C), MU | 63 | 63 | 68 |
| Thickness, mm | | | |
| Slope* | –0.85 | –0.51 | –0.67 |
| Density, g/cm³ | 0.93 | 0.91 | 0.90 |
| \( T_g \) in °C | –25 | –107 | –92 |

*a Slope of the Mooney-relaxation curve to describe the viscoelastic behavior of the polymers. The closer the value to 0 the more elastic the material.
3

final compound formulations for these four series are given in Table 3.

2.1.2. Mixing process

All compounds were mixed in a 390 ml Brabender Plasticorder 350 S internal mixer (Brabender GmbH & Co. KG, Duisburg, Germany) including tangential rotors (N-rotor geometry) using a three-stage mixing procedure as described in Table 4.

In the first stage, the polymers were added together with the silica/ silane system and the protecting agents. The fill factor and chamber temperature of the mixer were set to 0.75 and 50 °C respectively. The rotor speed was set to 100 rpm. When the internal temperature of the mixer reached 140 °C, the rotor speed was reduced manually to keep this temperature for the optimum silanization reaction. After each mixing stage, the dump temperature of the compounds was measured. Finally, the compounds were re-mixed on a laboratory two-roll mill to achieve a homogeneous filler distribution. During the full process, the viscosity of the compound drops due to the high temperature which reduces the effective dispersive mixing [14]. Therefore, the rubber sheets were stored for 24 h before they were used for the next mixing stage.

In the second stage, the cold compound was re-mixed in the internal mixer and the secondary accelerator DPG was added. The higher compound viscosity results in more effective dispersive mixing again. The fill factor and chamber temperature of the mixer was set to 0.70 and 50 °C, respectively. The fill factor was reduced by 5% due to the material loss in each mixing stage. Besides, the initial rotor speed is set to 100 rpm. The final silanization temperature of 140 °C in the mixer was kept constant by adapting the rotor speed manually. Hence, the remaining silane can react with the silica. DPG was added as an accelerator already in the first stage to shield the silica surface additionally to reduce the absorption possibility of the main accelerators CBS and TBzTD in the final mixing stage [15].

In the third stage, the cold compound was shortly mixed with the vulcanization system inside the internal mixer. The fill factor and chamber temperature of the mixer were set to 0.65 and 50 °C, respectively. The fill factor was reduced by 5% due to the material loss in each mixing stage. Besides, the initial rotor speed was kept constant at 60 rpm. The rotor speed is relatively low to ensure a low temperature inside the mixer to prevent pre-scorch. As mentioned before, the compound was re-mixed on the two-roll mill to achieve a well dispersed and distributed compound. During storage, the smaller silica clusters inside the final compounds could re-cluster forming a more intensive filler-filler network. This is based on the finding from literature [22], that even in the case of a maximal silanization reaction 75% of all silanol groups remain unreacted. This leads to an increase in the viscosity of the rubber with increasing storage time.

2.1.3. Vulcanization

The vulcanization behavior of the compounds was measured at a frequency of 1.67 Hz and 0.5° strain at 160 °C for 20 min in the Rubber Process Analyzer (RPA) of ALPHA Technologies (Hudson, Ohio, USA). Hence, t95 was determined which is the time where 95% of the maximum cure torque is reached. To evaluate the hardness and tensile properties, the raw mixture was vulcanized in a two mm thick rectangular mould in the Wickert WLP 1600 (Landau, Germany) hydraulic press at 100 bar and 160 °C according to the determined optimum cure time t95.

For the rebound test samples, the compounds were vulcanized in a circular mould with a diameter of 29 mm and a thickness of 12.5 mm. The cure time was set to t95 + 5 min extra to ensure complete curing of the entire sample.

2.2. Composite properties

The term composite properties is used here as description for filler containing rubber raw mixtures and vulcanizates.

The test methods to measure the rheological properties, filler dispersion, mechanical and dynamic properties are explained in detail in the following paragraphs.

2.2.1. Mooney viscosity

The Mooney viscosity of the rubber samples are measured in the Mooney Viscometer 2000 of ALPHA Technologies. The measurement is performed in accordance with the Mooney ML (1+4) program of the ISO 289-1 standard at a temperature of 100 °C [16].

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### Table 2

| Compound         | Ratio                  |
|------------------|------------------------|
| SBR-4602/BR-363  | 100/0, 90/10, 80/20, 70/30 |
| SBR-4602/BR-884  | 232.6                  |

### Table 3

| Ingredients     | [phr] |
|-----------------|-------|
| Rubber          | Vary  |
| SBR-4602        | Vary  |
| BR-363          | Vary  |
| BR-884          | –     |
| Filler          | 80/80 |
| N330 carbon black | 5/5   |
| TESPD           | 5.8/5.8 |
| Activators      | 2/2   |
| ZnO             | 2     |
| Stearic Acid    | 2     |
| Oil             | 26/26 |
| TDAE            | 26/26 |
| Anti-ox/oz      | 1.5/1.5 |
| TMQ             | 2/2   |
| 6PPD            | 2/2   |
| Wax             | 2/2   |
| Curatives       | 2/2   |
| DPG             | 2/2   |
| TBzTD           | 0.2/0.2 |
| CBS             | 1.6/1.6 |
| Sulfur          | 2/2   |
| Total           | 232.6/232.6 |

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* Table 2 shows the varying contents.
2.2.2. Payne effect measurement
The Payne effect (difference of the complex modulus $G^\prime$ at lower and higher strains $\Delta G$) of the uncured and cured rubber samples were measured using the identical RPA as for the evaluation of the vulcanization kinetics (see section 2.1.3). For both samples, the Payne effect is measured twice sequentially. This should eliminate the flocculation effect of the silica particles during storage as explained before. Otherwise, the measured shear modulus at lower strains would be significantly higher which would lead to an increase in $\Delta G$. The test is performed at 1 Hz and 60 °C with 1 min delay between sweeps. The Payne effect for the unvulcanized mixtures is measured from 0.56 to 100% strain. For the Payne effect of the vulcanized composites, the strain is set from 0.56 to 40% strain due to force limitations of the device. The Payne effect was used as an indicator to predict the micro-dispersion as recently discussed in the literature [23].

2.2.3. Optical microscopy
The Olympus BX51 M optical microscope (Tokyo, Japan) was used to investigate the macro filler dispersion of the silica inside the compounds. This microscope has an optical magnification of $5 \times$ which was used in combination with the Olympus MPLFLN 10x/0.30 objective. For the analysis, a stripe from vulcanized tensile sheet (2 mm thickness) was cut using a razor blade. The freshly cut surface was analyzed to identify filler agglomerates bigger than 6 μm.

2.2.4. Shore A hardness
The Shore A hardness of the vulcanized rubber compounds was measured according to the ISO 868 standard [17]. For the test sample, three strips of 2 mm thick vulcanized sheets were stacked together. The hardness is measured three times and the average value is used for the evaluation.

2.2.5. Stress-strain behavior
The tensile stress-strain behavior of the vulcanized rubber samples was analyzed using the Zwick Tensile Tester Z1.0 (ZwickRoell, Ulm, Germany). As test specimens, type 2 dumbbells were used according to the ISO 37 standard [18]. The tensile machine operates at a crosshead speed of 500 mm/min and a pre-tension of 0.1 N is applied. The average of five dumbbells were used for the analysis. The following parameters were analyzed: modulus at 100% strain (M100) in MPa, modulus at 200% strain (M200) in MPa, modulus at 300% strain (M300) in MPa, Tensile Strength at the maximal possible strain ($\sigma_b$) in MPa and elongation at break ($\varepsilon_b$) in %.

2.2.6. DIN abrasion
The abrasion loss was analyzed according to the DIN ISO 4649 [19].

2.2.7. Rebound
The resilience of the vulcanized compounds is measured using the ZwickRoell 5109 Rebound Resilience Tester. The resilience test is performed at room temperature (23 °C) as well as at 60 °C according to ISO 4662 standard [20]. As mentioned before, the test specimens have a diameter of 29 mm and a thickness of 12.5 mm. For the measurement at room temperature, the front as well as the rear of the specimens are tested. To measure the rebound resilience at elevated temperature, the oven is first pre-heated at 60 °C for half an hour. Subsequently, the test samples are heated at 60 °C for 1 h. For this measurement conditions, only the front of the specimens was tested due to the rapid cooling and therefore, two test samples are used per compound.

2.2.8. Dynamic mechanical analysis (DMA)
The Dynamic Mechanical Analysis (DMA) of the vulcanized rubber samples is performed in tension mode in the DMA GABO EPLEXOR of Netzsch Gerätebau GmbH (Selb, Germany) with a force-measuring head of 150 N according to DIN 53513 [21]. The test specimens are 50 mm long and 10 mm wide with a thickness of 2 mm. Before testing, the samples are pre-heated for 5 min at the starting temperature. A static strain of 3% and dynamic strain of 2% is applied to the sample at a constant frequency of 2 Hz. The measurement starts at a temperature of −70 °C and rises until 75 °C with a heating rate of 2 K per minute.

3. Results and discussion
The two types of BR differ in five analytical properties: molecular weight, vinyl content, cis-content, glass transition temperature ($T_g$) and type of functionalization (see Table 1). All five characteristics can influence the composite properties in a different way. The higher molecular weight ($M_w$) of BR-363 should lead normally to a worse processability, but to better mechanical composite properties. The higher vinyl content of BR-884 should result in a higher coupling efficiency to silane causing improved wet grip indicator. The higher cis content of BR-363 should lead to a higher coupling efficiency to silane. The higher $T_g$ of BR-884 should improve wet grip indicator but degrade the rolling resistance indicator. The functionalization of BR-884 should enable an additional chemical coupling to silica resulting in greater reinforcement but also a higher compound viscosity. The question thus remains: which of these various factors has the greatest contribution on the overall performance balance?

3.1. Mooney viscosity
Fig. 2 displays the Mooney viscosities of the investigated SBR/BR blend based silica compounds (see Fig. 1). The expectation was that the viscosity, taken here as an indicator for the processability, is influenced by the molecular weight and the functionalization. The Mooney viscosity increases with decreasing BR-363 content but increases with increasing BR-884 content, compared to the pure SSBR compound. This observation shows that the functionalization dominates the behavior while the influence of the different molecular weights is of minor importance. The presence of the functional groups in BR-884 causes a chemical coupling during the mixing to the silica which leads to an increase in the compound Mooney viscosity.

3.2. Cure behavior
The cure behavior is shown in Fig. 3. The torque $S_{\text{max}}$ is increasing in both blend systems with increasing content of BR. The higher torque values are achieved for the BR-363 type. The torque is the indicative of the crosslinking density caused by polymer-polymer and silica-silane-polymer coupling and contains also a filler-filler network contribution. In non-miscible blends, the vulcameter torque is also affected by the phase morphology and filler localization [25]. As there is no functionalization in BR-363 it can be expected that the silica dispersion is worse, which results in a stronger filler-filler network. As already mentioned above, the blends of SSBR with BR-884 show an increase in torque with increasing BR content. This might be caused by the additional coupling possibilities of the functional groups of BR with the silica, resulting in a higher filler-polymer coupling.

3.3. Payne effect measurement (uncured)
The SBR-4602/BR-363 blends show the lowest $G^\prime$ values at low strain of the uncured compound in the second sweep (Fig. 4). In this blend system, the $G^\prime$ value at low strain is decreasing with increasing BR content. The opposite trend is true for the SBR-4602/BR-884 blends: Here, the $G^\prime$ value at low strain increases with increasing BR content. This is related to the functionalization of BR-884: This BR can chemically bond to the silica already during the mixing, therefore, polymer-silica bonds are created during the mixing, shifting the starting $G^\prime$ to higher values.

The presence of increasing amounts of functionalized BR relative to SSBR leads to a shift towards higher $G^\prime$ values indicating the presence of
a more readily available functionalization in BR-884. Both BR-884 and SBR-4602 are functionalized, but the impact of the functionalized BR on $G^*$ is more pronounced and therefore the functionalized BR provides more sites for polymer-silica bonding. If the functionalized SSBR is blended with the non-functionalized BR-363, the possibility to form these polymer-silica bonds during mixing is reduced. This leads to a continuous reduction in the $G^*$ at low strain with increasing BR-363 content.

### 3.4. Macro-dispersion measurement

Fig. 4 shows optical microscopy images from two selected vulcanized composites with a relative bad silica macro dispersion for both samples and slight advantages for the BR-363; vice versa the findings from Payne
effect. The higher molecular mass of BR-363 may have the highest effect, by causing higher shear energy during the mixing process.

3.5. Payne effect measurement (cured)

Fig. 5 shows the Payne effect of the cured compounds. For both blend systems, G⁺ at low strain is decreasing with increasing SBR content. This could be an indication that the SSBR with its bulky aromatic styrene groups leads to a better micro-dispersion of the silica, causing a weaker filler-filler network. Furthermore, the SBR-4602/BR-363 blend system shows higher G⁺ values at low strains in comparison to the SBR-4602/BR-884 blend system. It seems that the functionalized BR covers the silica in a more effective way results in a better hindrance of the formation of filler-filler network.

The G⁺ value at high strains delivers hints on the efficiency of the silica-silane-polymer coupling. There are different influencing factors: a higher cis- and vinyl-content should lead to a more effective coupling as well as the presence of functionalization. The BR-363 has a much higher cis-content, the BR-884 the higher vinyl-content as well as a functionalization. In this case, all three properties seem to contribute in a similar way to the final result, the cis-content being slightly less important than the others.

3.6. Dependence of Payne effect on SSBR content

Fig. 6 shows the dependence of the Payne effect on the SSBR content. The Payne effect for uncured samples depends on the SSBR content and on the type of BR (as explained above). The Payne effect for cured samples decreases with increasing SSBR content and is lower for BR-884. This is an effect of the functionalization.

3.7. Shore a hardness

The Shore A hardness values given in Table 5 show a reduction of hardness for the SBR/BR-blends versus the SBR-4602 based composite, but do not allow a clear differentiation between the different BR blend partners. These results do not correlate with the findings from vulcanization torque, where the torque increases for both SBR/BR blend variations with rising BR content vs. the single SBR-4602 composite. This can be explained by the fact that the hardness is a static measurement where the filler content is rather the dominating factor in comparison to the crosslinking density. On the contrary the vulcanization measurement is done while a dynamic oscillating strain is applied. A changing filler network as well as filler-polymer interactions have to be taken into account. Therefore, a direct correlation cannot be expected.

3.8. Stress-strain behavior

Fig. 7 and Table 6 show the stress-strain behavior of the different SBR/BR blend compounds. The presence of BR in general leads to a decrease in the moduli at higher strain which was expected due to its poorer mechanical properties in comparison to SSBR. In the case of BR-884 this reduction is less pronounced. The expectation was that the higher molecular weight of BR-363 should result in higher moduli at higher strain. However, the functionalization of BR-884 and therefore improved interaction with silica has a stronger reinforcing effect on the stress-strain properties than the molecular weight. This result shows the importance of the functionalization: The presence of a functional group at the polymer chain leads to a chemical interaction with the silanol group of the silica. This interaction delivers an additional contribution to the three-dimensional network normally formed by the sulfur bridges between the polymer chains and the silica-silane-polymer coupling. As a conclusion, it can be said that an improved rubber-filler interaction dominates the reinforcing effect whereas the differences in molecular weight seem to be less determining.

3.9. Dynamic-mechanical behavior and tire performance indicator

The dynamic properties of the compounds may primarily depend on the Tg (Table 1). To proof this, the Tg values of the blends were calculated according to the Fox equation (Equation (1)) [24]:

\[
\frac{1}{Tg_1} = \frac{w_1}{Tg_{1,w}} + \frac{w_2}{Tg_{2,w}}
\]

Where w₁, w₂: weight fraction of polymer 1 and 2.

\(Tg_{1,w}, Tg_{2,w}: Tg\) of polymer 1 and 2.

Fig. 8 compares the rebound values at 25 °C and at 60 °C with the calculated Tg values.

There is a clear dependence with the rebound decreasing with increasing Tg. This phenomenon can be expected, as lower Tg indicates a higher elasticity at temperatures distant from the glass transition. Therefore, the Tg appears to be the dominating factor for the rebound.

The DMA loss factor tan δ vs. temperature curves (see Fig. 9) show the same dependency: The damping performance is influenced by Tg, a higher SSBR content leads to a shift of the tan δ maximum to higher temperatures; clear differences between the shapes of the peaks were found for the blend partners BR-363 and BR-884: the blends with higher amount of BR-363 (left) show a broader and lower tan δ-maximum than the blends with BR-884 (right).

The comparison of the Tg measured by DMA and the calculated Tg by the Fox equation on basis of DSC measurements for the raw polymers shows a good correlation but the absolute values are different (see Fig. 10).

The tire performance indicator (Table 7) tan δ at 0 °C for the wet grip shows that the wet grip performance seems to be improved with increasing SSBR content. In comparison, the different BR types do not have any significant influence. This finding does not fit to the expectation that the higher vinyl content and Tg of BR-884 would lead to a better wet performance indicator. One important aspect has to be considered: BR is added only with amounts of 10–30 phr. This means that the SBR phase is still the dominating one, the contribution of BR might not be clearly visible due to too low amounts. On top of this, an addition of 10
phr BR means that 10 phr of SBR is replaced. The SBR itself contains as well partly BR. To observe really a clear effect, the applied changes might be too small.

The tire performance indicator $\tan \delta$ at 60 °C for the rolling resistance shows the expected tendency: An increase in SSBR content leads to higher $\tan \delta$ values at 60 °C (with the exception of the BR-363-sample with a blend ratio of 90/10), indicating a worse rolling resistance. The blends with BR-884 show an even lower rolling resistance indicator than those with BR-363. These results demonstrate again that the functionalization dominates the performance of the analyzed systems in comparison to the influence of the molecular weight and compound $T_g$.

4. Conclusion

Silica-filled functionalized SBR-4602 rubber compounds were blended with non-functionalized BR-363 and functionalized BR-884 in three ratios: 90/10, 80/20 and 70/30. The two types of BR differ in five analytical properties: molecular weight, vinyl content, cis-content, glass transition temperature ($T_g$) and functionalization. All five characteristics influence the composite properties.

The compound Mooney values are higher for the SSBR compositions comprising BR-884 as blend partner. The increased viscosity is the result of the silica-efficient BR grade functionalization and this trend was also reflected by the unvulcanized composites’ Payne effect. The SBR-4602/BR-884 samples show advantages in stress-strain behavior vs. BR-363 as blend partner. The rebound (25 °C) showed clear decrease with rising compound $T_g$ by rising SSBR content in the blend, but no clear differences between the blend partners BR-363 and BR-884. The DMA rolling resistance indicator $\tan \delta$ at 60 °C for the rolling resistance shows the expected tendency: An increase in SSBR content leads to higher $\tan \delta$ values at 60 °C (with the exception of the BR-363-sample with a blend ratio of 90/10), indicating a worse rolling resistance. The blends with BR-884 show an even lower rolling resistance indicator than those with BR-363. These results demonstrate again that the functionalization dominates the performance of the analyzed systems in comparison to the influence of the molecular weight and compound $T_g$.

### Table 5

| Rubber          | SBR-4602/BR-363 | SBR-4602/BR-884 | SBR-4602 |
|-----------------|-----------------|-----------------|----------|
| Blend Ratio     | 70/ 80/ 90/     | 70/ 80/ 90/     | 100/0    |
| Shore A hardness| 60 ± 59 ± 56 ± | 57 ± 58 ± 57 ± | 64 ± 1   |

Fig. 6. Payne effect versus SBR content for uncured and cured samples.

### Table 6

| Compound        | Blend | $M_{100}$ [MPa] | $M_{200}$ [MPa] | $M_{300}$ [MPa] | $M_{300}/100$ [MPa] | $\sigma_b$ [MPa] | $\varepsilon_b$ [%] |
|-----------------|-------|-----------------|-----------------|-----------------|---------------------|-----------------|-------------------|
| 70/ 363         | 2.0 ± | 5.4 ±           | 11.1 ±          | 5.4 ±           | 21.1 ±              | 447             |                   |
| 30              | 0.1   | 0.2             | 0.2             | 0.2             | ± 0.5 ±            | ± 10            |                   |
| 4602/363        | 2.1 ± | 5.8 ±           | 11.8 ±          | 5.7 ±           | 19.9 ±              | 436             |                   |
| 80/ 20          | 0.2   | 0.2             | 0.2             | 0.2             | ± 0.5 ±            | ± 10            |                   |
| 90/ 10          | 2.2 ± | 6.4 ±           | 13.0 ±          | 6.0 ±           | 20.0 ±              | 407             |                   |
| 70/ 363         | 2.1 ± | 5.9 ±           | 12.3 ±          | 5.9 ±           | 20.8 ±              | 423             |                   |
| 30              | 0.1   | 0.2             | 0.2             | 0.2             | ± 0.5 ±            | ± 10            |                   |
| 4602/884        | 2.1 ± | 6.3 ±           | 12.9 ±          | 6.0 ±           | 19.9 ±              | 403             |                   |
| 80/ 20          | 0.2   | 0.2             | 0.3             | 0.3             | ± 1.0 ±            | ± 20            |                   |
| 90/ 10          | 2.2 ± | 6.6 ±           | 13.4 ±          | 6.2 ±           | 20.5 ±              | 405             |                   |
| 70/ 363         | 2.1 ± | 6.3 ±           | 12.9 ±          | 6.0 ±           | 19.9 ±              | 403             |                   |
| 30              | 0.1   | 0.2             | 0.2             | 0.2             | ± 0.5 ±            | ± 10            |                   |
| Ref.            | 2.4 ± | 7.1 ±           | 14.1 ±          | 5.8 ±           | 20.4 ±              | 389             |                   |

Fig. 7. Stress-strain behavior.
resistance lab predictor tan δ (60 °C) showed a remarkable advantage (lower values) for the composites comprising BR-884 at BR contents > 20 phr.

In summary, the functionalization is the dominating influencing parameter in this study. The presence of the functionalization improves the rubber-filler-interaction. This leads to better dynamic and mechanical properties of the model tread compound: The reinforcement index is increased and the tan δ at 60 °C, as lab predictor for the tire rolling resistance, is reduced while the tan δ at 0 °C, as lab predictor for wet grip, is similar to the non-functionalized BR. Furthermore, the T_g of the whole blend compound dominates the dynamic-mechanical behavior, as expected. In the case of BR, the functionalization has the dominating influence on the tan δ, the effect of T_g plays a minor role.

| Compound | Blend | tan δ at 0°C | tan δ at 60°C |
|----------|-------|--------------|---------------|
| 4602/363 | 70/30 | 0.259        | 0.0117        |
|          | 80/20 | 0.429        | 0.0124        |
|          | 90/10 | 0.524        | 0.0110        |
| 4602/884 | 70/30 | 0.353        | 0.0107        |
|          | 80/20 | 0.422        | 0.0110        |
|          | 90/10 | 0.527        | 0.0112        |
| Ref.     | 100/0 | 0.726        | 0.0130        |

Table 7: Performance of various SBR/BR blends on tire performance indicators as determined by DMA.

Fig. 9. DMA temperature sweep curve as tire performance indicators.

Fig. 10. Comparison of the T_g calculated by Fox and measured by DMA.

Declaration of competing interest

The authors have no affiliation with any organization with a direct or indirect financial interest in the subject matter discussed in the manuscript.

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