Silane-modified low molecular weight 'liquid' polymers in sulfur cured mixtures of styrene-butadiene copolymers and silica

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ABSTRACT

Silane coupling agents are used in silica filled rubber compounds to increase the filer-polymer interactions and to lower the filler-filer interactions. In addition, silane functionalized polymers can be used. Special types of polymers are low molecular weight 'liquid' polymers. The goal of this paper is to obtain more understanding about the uses and effects of these low molecular weight 'liquid' polymers in combination with silanes and other compound components. Three different silane coupling agents and six different low molecular weight 'liquid' polymers were selected, evaluated and comparatively introduced in mixtures of a SSBR/silica compound. The Payne effect was measured to evaluate the strain dependence of the mixtures. It was used to evaluate the filler-filler interactions and estimate the micro dispersion. This provides information about the interactions and the building of additional networks that comprises the low molecular weight 'liquid' polymer together with the silica, silane and main polymer. Results of dynamic mechanical analysis are discussed. The microstructures and silane-functionalizations show clear dependences on the glass transition temperatures, loss moduli and tan δ values.

1. Introduction

The global emissions of greenhouse gases from trucks and passenger cars are influenced by the deformation energy and friction losses of tires. It is mostly associated with the rolling resistance between the tire tread and the road surface. For this reason, the rolling resistance is considered as one of the most important performance indicators – that is targeted to be reduced – within the tire industry. Furthermore, in the European Union, the tire labelling regulation [1] was established in 2009 and forces the industry to new formulation developments. The rolling resistance is indirectly labeled as fuel efficiency, which is connected to the maximum CO_2 emissions. Additionally, the target emission rates are steadily reduced. This particularly involves the optimization of the important ingredients such as polymers, fillers, silanes, curatives and plasticizers. They are optimized individually or in combination with each other in order to reduce the rolling resistance without losing other important tire properties.

Beside polymers, fillers are considered as the most important ingredients in tire compounds. Carbon black is the established active filler

of rubber goods and tires. This means that the filler contributes to the modulus and improves the mechanical properties, in particular the strength and the stiffness which is indicated by the elastic modulus. A breakthrough in filler technology was the introduction of silica as an alternative active filler in tire tread compounds. This became possible with the "Green tire" technology [2] invented by Michelin in 1992. Green refers herein to the sustainability context and should emphasize the lower carbon footprint. Chemically, carbon black is mostly constituted of hydrocarbon and is hydrophobic. This is also the case for the main polymers used in tires: Natural Rubber (NR), Butadiene Rubber (BR) and Styrene Butadiene Rubber (SBR) that are all hydrocarbon based and therefore naturally interacting through van-der-Waals forces with the carbon black. In contrast, silica has a different chemical constitution. The surface is composed of polar silanol groups that results in a hydrophilic characteristic. Without the addition of other ingredients, the interaction with the polymer is weak, which causes a poor dispersion, phase separation and strong agglomeration/aggregation of the silica particles.

As described, active fillers are used to reinforce an elastomeric

composition and contribute to the elastic modulus. However, this contribution is strain dependent and is different to that from the non-strain dependent crosslinking network formed from the elastomeric polymer. This strain dependence of filler reinforced rubbers was discovered by Payne. The features, called "Payne effect", have been developed into a common understanding for the characterization of the filler-polymer and filler-filler interactions [3,4]. High filler-polymer interactions and low filler-filler interactions can be used as an indication for good micro dispersions without the formation of a dominating filler network [5].

The interaction between silica and polymer can be established by silanes. The silane is composed of a silica active side and a polymer active side which enables the coupling to the respective materials. Therefore, silanes are commonly called silane coupling agents. They are characterized by a dual functionality (bifunctionality) as X3SiRY, X representing the hydrolysable alkoxy group, R stands for the alkyl chain group while Y stands for the organofunctional group [2,3]. Luginsland et al. described a model of rubber reinforcement of silica in the presence of a silane coupling agent [6]. The silica forms a network with strong hydrogen bonding and occluded rubber while the silane couples the silica to the polymer.

To improve the silica-polymer interaction and to reduce the silica network, the silica dispersion became an important field in research and industry. A new generation of silanes (mercaptosilanes) were developed to increase the maximum silica loading and to match with different formulations [6]. The mercaptosilanes consists of a retarding function: The very reactive mercapto group is shielded against the sulfur and CBS to ensure a sufficient hydrophobization [7]. This group is used to protect the mercapto group against a too fast reaction with the vinyl groups of the polymer [8]. In addition, polymers were developed with functional groups to interact directly with the silica surface [9–15].

Another option to improve the rolling resistance is the use of low molecular weight 'liquid' polymers. Braum and Jacobi investigated an epoxidized and silica grafted liquid polybutadiene in silica filled SBR/BR blends [16]. The dispersion and dynamic properties of the compounds were evaluated and correlated to structural parameters of the different liquid polybutadienes such as epoxidation degrees and molecular weight. The approach is a partial or full replacement of the silane coupling agent. The filler dispersion of the compounds with liquid polymers was concluded to be improved – indicated by a reduced Payne effect [16]. In addition to the research, low molecular weight 'liquid' polymers with functional groups are claimed to improve the rolling resistance [17].

An improvement of the rolling resistance from functionalized low molecular weight 'liquid' polymers can be assumed. However, up to now only limited research was carried out to clarify this. Furthermore, their interaction with other compound ingredients and their influence on the filler dispersion is unknown.

Therefore, the goal of the study presented in this paper is to obtain more understanding about the interaction of functionalized and non-functionalized low molecular weight 'liquid' polymers with silica and the base polymer. With this, it should be evaluated if the material contributes or influences the network structures.

Six different low molecular weight 'liquid' polymers, were used with a varying molecular weight and 1,2-vinyl content. Additionally, three of the low molecular weight 'liquid' polymers contains along the chain ethoxysilane groups (Fig. 1)– the other three are unfunctionalized. The liquid polymers were combined with three different silanes and compared to each other. One silane is a common bifunctional silane and the two others are mercaptosilanes with different molecular weights. There were chosen to initiate different interactions with the different liquid polymers.

2. Experimental

2.1. Raw materials

The following raw materials were used: Solution polymerized styrene-butadiene copolymer with 15% bound styrene (SSBR), SPRIN-TAN™ SLR 3402 supplied by Trinseo and high dispersible silica, ULTRASIL® 7000, supplied by Evonik. Three different organosilanes were chosen to trigger different interactions with the other components. They are shown in Table 1. Because of their long chemical names, they will be henceforth assigned by the product name and synonyms: Si 266 (Si-A), NXT (Si–B) and Si 363 (Si–C). The antioxidants were N-phenyl-N′-1,3-dimethylbutyl-p-phenylenediamine (6PPD), supplied from Sigma Flexsys and Antiozonant paraffinic wax, supplied from Sasol. Additives used for vulcanization include zinc oxide, stearic acid and sulfur, all supplied from Sigma Aldrich. The accelerator combination used in the formulations is n-cyclohexyl-2-benzothiazolesulfenamide (CBS) and tetrabenzylthiuram disulfide (TBzTD), both supplied from Flexsys. As a plasticizer, an aromatic oil, Treated Distillate Aromatic Extract (TDAE), VIVATEC 500, supplied from Hansen & Rosenthal was used. The low molecular weight polybutadienes were provided from Kuraray and are listed in Table 2. They are segmented in two groups: 1. three silane-modified types and 2. three unmodified types. They contain different molecular weights, 1,2-vinyl contents and degrees of the functionality. The naming of the different liquid polymer types is as following: the "L" e.g. in Si-L-BR-4 (Table 2) refers to liquid or low molecular weight polymer; "BR" refers to the type of polymer butadiene, "Si" refers to the functionality with silane and the last number refers to the different silane modified and unmodified types. The "grafted type" means the triethoxysilyl-group is along the polymer chain. The "terminated type" means the triethoxysilyl-group is at the chain end.

2.2. Preparation of rubber compounds

Table 3 shows the SSBR/Silica based model formulation. The liquid polymer is added additionally to the formulation.

The compounds were mixed in three stages. The first two steps where executed in a Brabender internal mixer with a mixing chamber size of 350 mL. The fill factor was set at 70%. The mixing procedures of the first mixing stage includes the following steps: 1. at 0:00 (minute:second) polymer addition, 2. at 1:00 (minute:second) addition of 50% of the silica, silane and TDAE and low molecular weight polymer, 3. At 3:20 (minute:second) addition of the remaining 50% silica, 4. At 6:20 (minute:second) addition of the zinc oxide, stearic acid, wax and 6PPD. Discharge at 7:00 (minute:second). The starting temperature of the
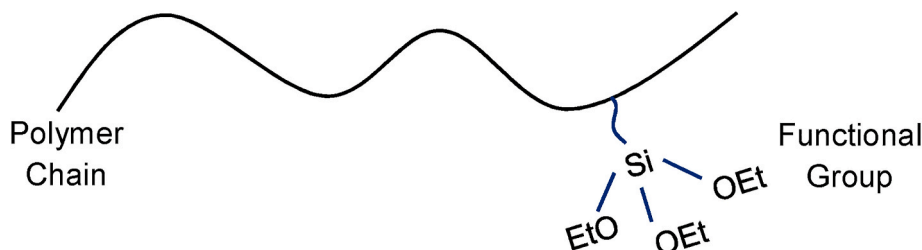

Fig. 1. Structure (schematic) of silane grafted low molecular weight 'liquid' polymer.

Table 1
Main properties of the silanes [18,19].

Synonym	Product Name/Chemical Name	Chemical Structure	Molecular Weight (M_N, g/mol)
Si-A	**Si 266** [18] bis(triethoxysilylpropyl) disulfide		480
Si–B	**NXT** [19] 3-Octanoylthio-1-propyltriethoxysilane		365
Si–C	**Si 363** [18] 3-Mercaptopropyl-di (tridecan-1-oxy-13-penta (ethyleneoxide))ethoxysilane		987.5

Table 2
Main properties of the different liquid polybutadienes [20].

Synonym	Product Name	Functionality (Si/Chain)	Molecular Weight (M_N, g/mol)	1,2-vinyl[a] (mol%)	T_G (°C)	Viscosity (Pa*s at 38 °C)
L-BR-1	L-BR-361	–	5500	High	−60	3.5
L-BR-2	L-BR-302	–	5500	Low	−85	0.6
L-BR-3	LBR-305	–	30,000	Low	−95	40
Si-L-BR-4	–	2.0 (Grafted)	6000	High	−50	5.3
Si-L-BR-5	–	0.9 (Terminated)	5500	High	−50	3.3
Si-L-BR-6	–	3.8 (Grafted)	35,000	Low	−88	86

[a] Vinyl Content: Low 10–40%, High 40–70%.

Table 3
Formulation of the SSBR/Silica model compound.

Formulation	Reference Formulation	Liquid Polymer Formulation
SSBR	100	100
Silica	80	80
Silane Coupling Agent	6.4	2.8–13.2[a]
TDAE	25	25
Liquid Polymer	0	15 or 7.5
Zinc Oxide	3	3
Stearic Acid	2	2
Sulfur	1.5	1.5
Accelerator	2.0 CBS	2.0 CBS
	0.2 TBzTD	0.2 TBzTD
Antidegradants	1.5 6PPD	1.5 6PPD
	1.5 Wax	1.5 Wax

[a] Different silanes: Si-A, Si–B, Si–C, content in phr adjusted according to the total ethoxysilane concentration of the reference formulation (isomolar).

mixer was 50 °C. The targeted temperature at the end of the mixing was 140 °C of the compound to ensure a sufficient silanization between the silica surface and the silane coupling agent or the silane-modified liquid polymer. The second mixing step was applied to homogenize the compound, 16 h after the first mixing stage. After every mixing step the compound was sheeted out on a two-roll mill. The third mixing step was carried out on the same two-roll mill. The amount of accelerators and sulfur were recalculated according to the mass of the compound after the second mixing stage.

The compounds were cured on a Wickert laboratory press at 160 °C and 100 bar, according to the t_{90} value of the specific compound. The cured specimens measured 100 mm in length and width and 2.0 mm in thickness.

The liquid polymer and silane coupling agent were added according to the total number of silane groups in the compound. The reference formulation contains Si-A. For the liquid polymer containing compounds, the individual concentrations are indicated in the legend in each figure from Fig. 2 to Fig. 12. For example, "L-BR-1_15/Si-A_6.4" contains 15 phr of L-BR-1 (L-BR-361) and 6.4 phr of Si-A (Si266).
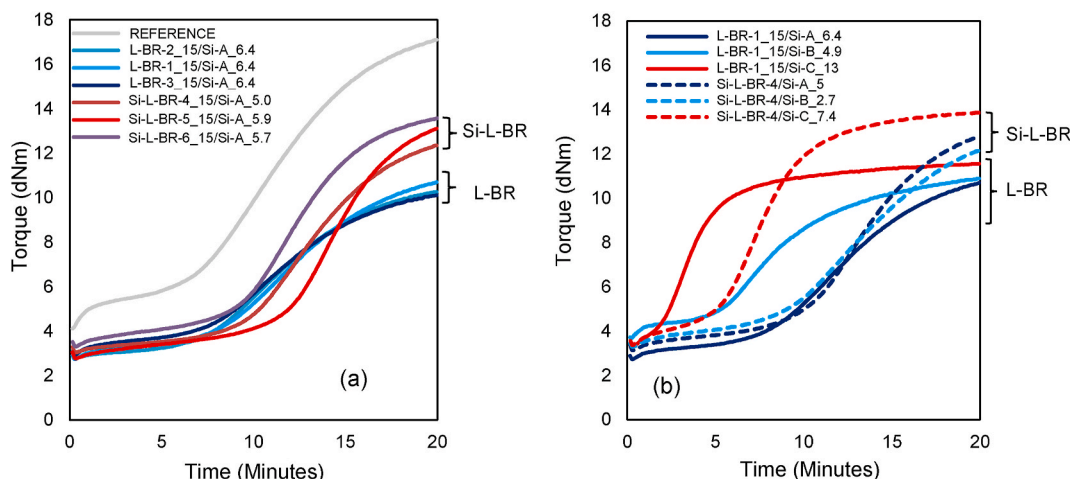

Fig. 2. Curing Curves of the SSBR/Silica compounds at 160 °C, at frequencies of 1.667 Hz, with different Liquid Polymers (a) and different Silanes (b).

2.3. Rheological and mechanical properties

The compound's curing kinetics were determined with an Alpha Instruments Rubber Process Analyzer RPA 2000, dynamic mechanical rheological tester according to ASTM D5289. The increase in torque at 160 °C and 0.5% strain was measured over a time period of 20 min. The frequency applied was 1.667. The optimal vulcanization time (t_{90}) of the compounds was determined. The curing.

The tensile properties of cured compounds were determined by using a Zwick Z020 tensile tester according to ISO-37.

The Shore A hardness was measured by using a Zwick hardness tester according to ASTM D-2240.

The Mooney Viscosity was measured by using a Mooney viscometer, ViscTech from TechPro, according to ASTM 1646. The values represent the ML (1 + 4)100 °C.

The Payne effect was measured on the uncured compounds by using the RPA 2000 in order to investigate the filler-filler interactions. The storage modulus at 0.56% and 100% strain were measured at the temperature of 100 °C and a frequency of 0.5 Hz.

The dynamic measurements of the cured compounds were performed using a DMA2000 dynamic spectrometer. For storage (E′) and loss modulus (E″) as function of temperature, measurements were performed between −80 °C and 80 °C with a heating rate of 2 °C per minute at a dynamic strain of 0.1%, static strain of 1% and a frequency of 10 Hz. An indication of abrasion resistance (tan δ at −50 °C), wet grip performance (tan δ at 0 °C) and rolling resistance (tan δ at 70 °C) can be determined from the data.

2.4. Solubility and swelling

2.4.1. Crosslink density

The Crosslink Density (CLD) was determined by a swelling test. To remove low-molecular soluble substances (e.g. residues, decomposition products, fatty acids, antioxidants etc.) prior to the swelling, the samples were extracted with acetone and subsequently with tetrahydrofuran for 3 days in each solvent, followed by 3 days drying in a vacuum oven. Then, approximately 0.4 g of these pre-treated samples were swollen to equilibrium in toluene for 7 days at ambient temperatures. After that, the samples were dried to constant weight for 3 days at 50 °C in a vacuum oven. The CLD was calculated according to the Flory-Rehner equation [21] (Equation (1)):

$$\nu = - \frac{\ln(1 - V_r) + V_r + xV_r^2}{V_0 \left(V_r^{\frac{1}{3}} - \frac{2V_r}{f} \right)} \tag{1}$$

ν is the CLD per unit volume (mol/cm^3), V_r is the volume fraction of the rubber in a swollen sample, V_0 is the molar volume of the solvent (in case of toluene = 106.9 cm^3/mol), f is the functionality of the structural unit of the polymer ($f = 4$, assumption for the formation of tetra-functional units) and χ is the Flory-Huggins polymer-solvent interaction parameter. For an SBR/toluene system, χ is 0.378 as reported by George et al. [22]. The above-mentioned Flory-Rehner equation is only valid for non-filled systems. For systems with fillers, especially when different filler compositions are introduced, the volume fraction of the filler should be corrected according to Kraus [23]. However, in the present investigation the filler content and the filler system are the same for all compositions. The crosslink densities were calculated without the Kraus correction.

3. Results and discussion

3.1. Curing characteristics, crosslinking density and payne effect

3.1.1. Curing characteristics

Fig. 2a shows the cure curves of different silane functionalized liquid polybutadienes versus non-functionalized liquid polybutadienes containing compounds. They are combined with bis(triethoxysilylpropyl) disulfide (Si-A). Fig. 2b shows the cure curves of different silanes with one non-functionalized liquid polybutadiene (L-BR-1) versus one silane functionalized liquid polybutadiene (Si-L-BR-4). Between repeated measurements the maximum variation is±0.21 dNm.

The sulfur vulcanization is accomplished by zinc oxide as activator and CBS as an sulfonamide accelerator and TBzTD as thiuram-type accelerator. The accelerators act as catalysts by breaking the sulfur chain and turning them into reactive sulfuric intermediates, while the zinc oxide herein convert the accelerators [8].

The different pairings initiate different curing speeds and maximum torques. One reason is the difference in the filler flocculation. It is a measure for the degree of the hydrophobation of the silica, the re-agglomeration of silica aggregates caused by the differences of the silane coupling agents and liquid polymers. Silica filled compounds tend to flocculate in the early stage of curing caused by temperature exposure [24,25]. This can be clearly observed in the cure curve of the reference compound by a slight but clear increase in torque in the early minutes of the curing. At this stage, no stable crosslinking network is established which hinders a re-agglomeration. The second influence on the curing speed is the activation of the sulfur by CBS and the reaction of silane with the silica and polymer. In particular, a clear difference is visible for the two different types of the silanes used in this investigation, the bifunctional type silane, Si-A and the two mercaptosilanes (Si–B and Si–C). The third influence comes from the different liquid polymers.

In both graphs of Fig. 2 higher maximum torque values are plotted for all silane-functionalized liquid polybutadiene containing compounds versus the non-functionalized types. This indicates that an additional network is generated. Beside the known silica-silane-polymer and polymer-polymer networks [6], most probably an additional network with the silica and the Si-L-BR is generated which will be connected to the main polymer though entanglements and crosslinking units. The latter will be limited but particularly true for the high molecular version that consists of enough double bonds.

The different non-functionalized L-BR's, shown in Fig. 2a, are showing slight different cure curves according to their microstructure. Compared to the reference without plasticizer, the torque levels (minimum and maximum torques) are reduced. One reason is due to the additional plasticization as they are added additionally to the formulation as shown in Table 2 Another reason is the effect of the reduction of the average molecular weight of the polymer. The use of a low molecular weight polymer reduces an ideal crosslinking network [26]. It is mainly because of the lower statistical probability to create crosslinking units between the main and liquid polymers.

The molecular weight shows different result for the curing profiles. For example, the low molecular Si-L-BR-4 shows a clear increase in the maximum torque compared to the two non-functionalized counter types, L-BR-1 and L-BR-2. However, the increase is comparably low. The high molecular weight Si-L-BR-6 shows a higher increase in torque compared to its counter type, L-BR-3. The increase is also true for the silane group position: The low molecular weight and end-terminated type, Si-L-BR-5 shows a higher maximum torque as the grafted version, Si-L-BR-4. The differences of the vinyl contents are very small for the torque evaluation and only shows a slight higher torque for L-BR-1 (the 1,2-vinyl rich version). However, the small increase for the 1,2-vinyl – in parallel along with a higher cis-content – can be expected [8].

Another interesting observation is the difference in curing speeds: the low molecular versions Si-L-BR-4 and Si-L-BR-5 show a delayed increase in torque. A slow curing progress in the first half of the total curing time and a rapid increase within the second half. The creation of the additional network, involving the Si-L-BR is competing with the silane coupling agents for the creation of the silica-silane-polymer and polymer-polymer networks. The total molecular weight as average of the compound ingredients is reduced due the dilution with the comparably much low molecular weight polymers. It takes some sub-

sequential reactions steps before a real network is generated.

The curing curves of the mercaptosilanes (Si–B and Si–C) compared to Si-A are shown in Fig. 2b. Even though they consist retarding groups, the curing speed is faster than that for the bifunctional silane (Si-A). The compound comprising Si–C shows further a higher reactivation speed than Si–B and also a higher maximum torque. It has to be taken into account that the concentration of Si–C was significantly higher (13 phr.) to closely match with the silane groups of the reference compound (Si-isomolar).

Compared to the non-functionalized L-BR, the introduction of the Si-L-BR together with the mecaptosilanes reduces the initial curing speed but results in higher maximum torques due to a delayed acceleration. The end torque value of the Si–C is more significant increased as the Si–B. An interesting result is that the Si-A and Si–B show relative similar curing kinetics when each is combined with the Si-L-BR-4. This can be attributed to the triethoxysilyl group of the liquid polymer which dominates the reaction in each pairing (Si-L-BR/Si-A and Si-L-BR/Si–B). With the non-functionalized L-BR-1, the curves of Si–B and Si–C are different and show a faster curing speed.

In general, the highly reactive mercapto group can react with sulfur and CBS, the triethoxysilyl group can couple with the silica and the thiol group of the mercaptosilane can react with the 1,2-vinyl group of the polymer. – When Si-L-BR is present in the system, even more reactions are possible: The Si-L-BR's can create an additional network between the silica, silane, liquid polymer and polymer that reduces the proportion of the conventional networks, the Polymer-Polymer and Silica-Silane-Polymer networks. It is particular true and more significant for the mercaptosilanes as their reactivity is faster for the compound containing the non-functionalized materials.

3.1.2. Crosslinking density

Together with the curing kinetics, the CLD provides a more complete discussion about the liquid polymer's and silane's influences. Fig. 3a shows the CLD of the different L-BR's and Si-L-BR's containing compounds with bis(triethoxysilylpropyl)disulfide (Si-A). The variation of the single measurements is in the range of $\pm 1.96 * 10^{-5}$ mol/cm³.

Comparing the low molecular weight types, the CLD changes according to the introduced functionalization: Compared to the unmodified countertypes of L-BR-1 and L-BR-2, the end-terminated Si-L-BR-5 shows an increased CLD and the grafted Si-L-BR-4 shows a decreased CLD. Compared to the non-functionalized types, however, the increase of the CLD with the high molecular weight types is more pronounced than for the low molecular weight types.

The end-functionalized, Si-L-BR-5 and the high molecular weight type, Si-L-BR-6 show a relative higher CLD. This can be explained by a generation of an additional network, which incorporates liquid polymer, the silica and the main polymer. Otherwise, if the liquid polymer is only

connected to the silica, higher extractions would be measured which would result in lower CLD values. In particular this seems to be true for the high molecular weight version. This is based on the consideration that a longer polymer chain increases the possibility that this chain is connected to another polymer chain via sulfur bridges. The result of the low molecular weight type (Si-L-BR-4) is more differentiated: as previously shown in Fig. 2, the maximum torque increases compared to the unmodified version, which indicates that the final network strength is increased. As previously discussed, an additional network is competing for the limited silane groups and the limited free sulfur for the creation of the silica-silane-polymer and polymer-polymer network. As this network involves a lower molecular weight material it can be assumed that the network creates less crosslinking units and therefore shows a lower CLD [26].

The CLD of the reference compound with SSBR is $\nu = 4.1 * 10^{-4}$ mol/cm³. It is a plausible value and comparable to ranges obtained in other investigations of SSBR and BR [26–28]. Statistically, this measurement can be connected to the molecular weight of the polymer chain, M_N and the average molecular weight of the network chain between crosslinks, M_{CS} according to equation (2) [29].

$$\nu = \frac{\rho}{2}\left(\frac{1}{M_{CS}} - \frac{1}{M_N}\right) \tag{2}$$

Assuming a molecular weight of the SSBR of 150,000 g/mol (the real value is not disclosed from the manufacturer) the average molecular weight between two crosslinks can be calculated to $M_{CS} = 1220$ g/mol. Approximately every 30th double bond has reacted. Adding the unmodified liquid polymers, this value increases to app. $M_{CS} = 1610$ g/mol. In this case only every 40th double bond has reacted. Considering further that the observed low molecular weight versions consist of approximately 100 double bonds per molecular chain with an average molecular weight of 5500 g/mol, then two to three crosslink units can be created for each liquid polymer chain, statistically speaking. For the high molecular versions of the liquid polymers – with approximately 550 double bonds per chain, an average molecular weight of 30,000 g/mol – this can increase to fourteen crosslink units per chain.

From this statistical standpoint it is highly probable that the liquid polymer is integrated in or at least partially connected to the main polymer network. The molecular weight still allows a minimum of connections per chain. In case of the low molecular weight types (5000 g/mol to 6000 g/mol), two to three crosslink units per chain are created in average. In case of the high molecular weight type (30,000 g/mol) around fourteen crosslink units per chain are created which makes a full integration in the main polymer-polymer network even more likely.

Fig. 3b shows the CLD for the three different types of silanes and the low molecular weight, grafted-functionalized Si-L-BR-4. When the L-BR incorporates the silane-functionalization, the mercaptosilane Si–B-
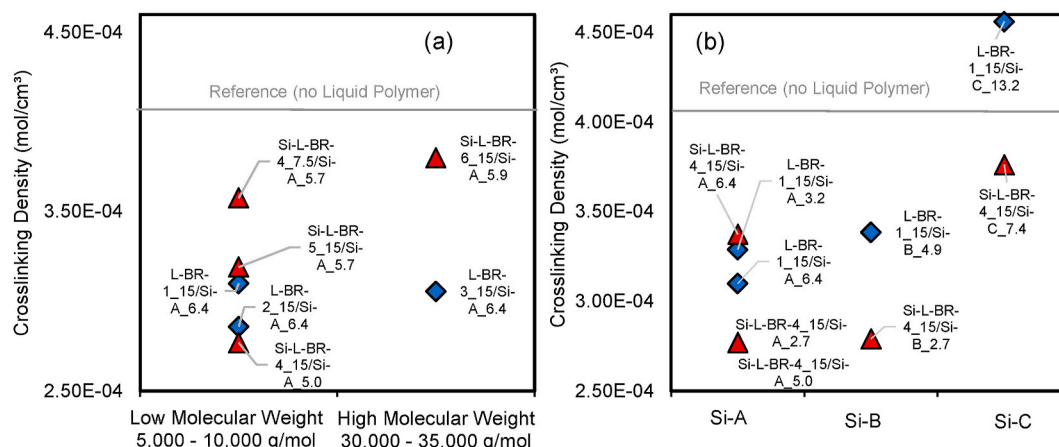

Fig. 3. CLD of the SSBR/Silica compounds with different Liquid Polymers (a) and different Silanes (b).

containing compound shows the same tendency as those with Si-A: The CLD is reduced compared to the unfunctionalized L-BR-1. However, the other mercaptosilane, Si–C, shows a significant increase in CLD.

The molecular weight of Si–C is relatively high. The rheometer torque and CLD are also similar to the silane-functionalized Si-L-BR without mercaptosilane. It can be assumed that the Si–C is reacting with the Si-L-BR-4 – or conversely, that it results in a strong increased CLD compared to the versions comprising Si-A and Si-B. The mercapto group of Si–C can also react with the triethoxysilyl group from the Si-L-BR-4 or its double bond. The latter is more likely for the higher molecular and higher 1,2-vinyl type liquid polymers because it is known from literature that a high 1,2-vinyl and high a cis-content has a higher reactivity with a thiol group [8,30]. This is also confirmed by the strong CLD increase of the non-functionalized L-BR's with both mercaptosilanes. The 1,2-vinyl content of the main polymer is 63% and therefore significant in the interaction.

3.1.3. Mooney Viscosity

Fig. 4 shows the Mooney viscosity values of the investigated compounds separated for low and high molecular weight (a), and the different silanes (b). Between repeated measurements the maximum variation is ± 1.0.

Generally, compared to the reference without any liquid polymer, the addition of the liquid polymers reduces the Mooney viscosity of the compounds. The direction is in accordance with the maximum torques presented in Fig. 2. The Si-L-BR's shows higher values than the non-functionalized L-BR's.

3.1.4. Payne effect

The cure curves and CLD provide information about the generation of the final network and indicates the contribution of an additional network, created by the different liquid polymers. The Payne effect measurement on the uncured compounds delivers further information about the filler-filler and filler-polymer interactions [3,4]. Figs. 5 and 6 show the Payne effects values, the differences of the modulus at low (0.56%) and at high strain (100%). The values provide additionally an indication of the micro dispersion [5,31] and enables a further estimation of the compound's performance. Between repeat measurements the maximum variation is±2.8 kPa.

Fig. 6a shows the Payne effects for the different uncured compounds that contain the varying L-BR's and Si-L-BR's with Si-A containing compounds. Compared to the non-functionalized types, the silane-functionalization of the low molecular weight types reduce the Payne effect. The high molecular weight types, shows an inverse tendency.

This is in contrast to the previous discussion for the torque and CLD measurement. It was assumed that the higher values for the silane-modified types are caused by the generation of an additional network,
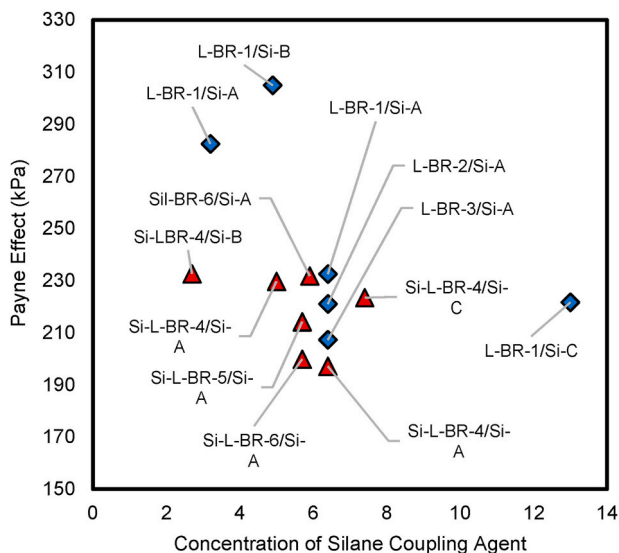

Fig. 5. Payne effect for the different L-BR and Si-LBR in relation to the concentration of the Silane Coupling Agent.

involving the liquid polymer, silica and the main polymer. This would lead to the assumption of improved filler-polymer interactions and reduced filler-filler interactions. However, from the Payne effect measurement of the uncured compounds, the high molecular weight type creates more filler-filler interactions.

Fig. 5 shows the Payne effects for the uncured compounds filled with different silanes. Lower Si-A contents (3.2 phr with L-BR-1 and 2.7 phr with Si-L-BR-4) lead to more pronounced effects comparing the silane-modified and non-modified L-BR. An Increase in the silane concentration to 5.0 phr shows a small effect, and another further increase to 5.7 phr shows almost no effect. It can be assumed, that the silane coupling agent rivals with the silane-modified liquid polymer for the reactive silanol groups on the silica surface.

This result confirms that the siliane-functionalized liquid polymer is acting effectively and can partially replace the silane coupling agent.

In combination with Si–B (Fig. 6b), a significant reduction of the Payne effect is shown for the Si-L-BR-4 compared to the non-functionalized liquid polymer, L-BR-1. For Si–C, no further reduction with these combinations were measured - Si-L-BR-4 compared to L-BR-1. The results of the high molecular weight liquid polymer (Si-L-BR-6) shows an analogy to the low molecular weight liquid polymer (Si-L-BR-4) together with a high molecular weight mercaptosilane (Si–C) pairing: a high maximum torque and high CLD (assuming a strong additional
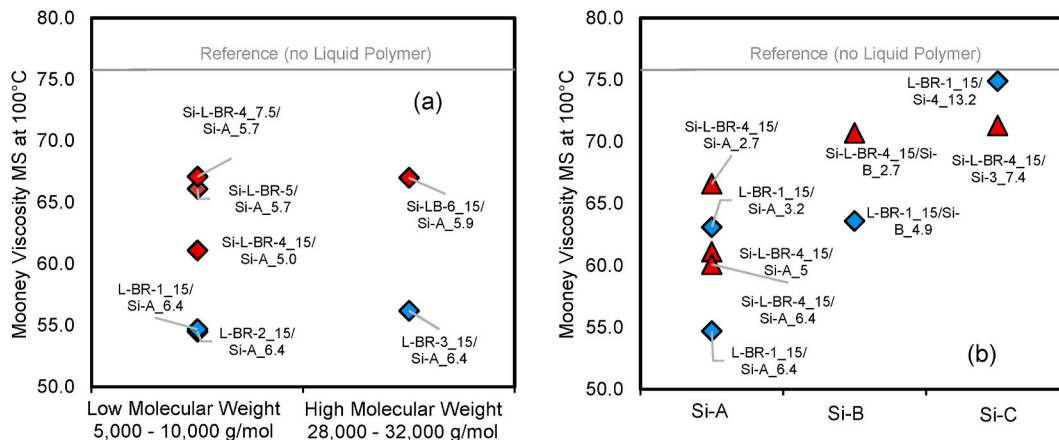

Fig. 4. Influence of different L-BR and Si-LBR (a) in combination with different Silanes (b) on the Mooney Viscosity.
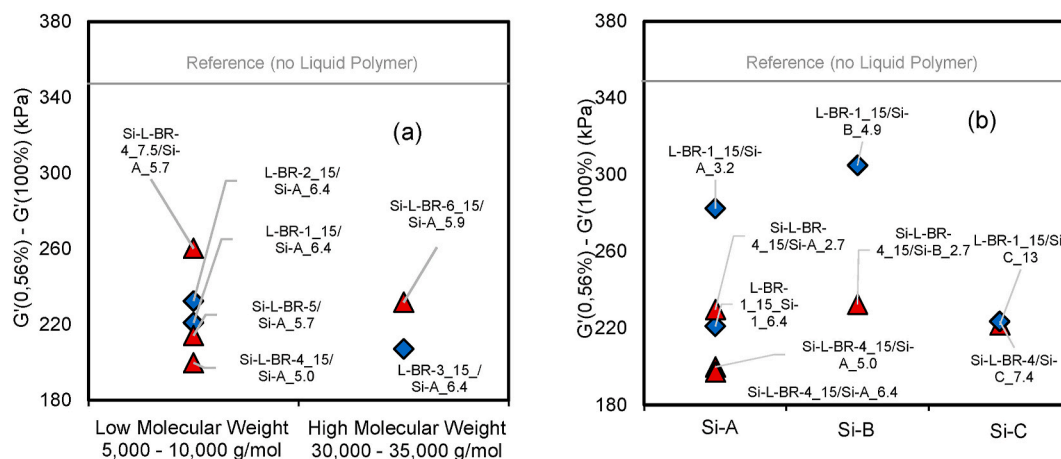
Fig. 6. Payne effect for the different L-BR and Si-LBR (a) in combination with different Silanes (b) on the Payne effect.

network) but a worse Payne effect (assuming a higher filler network). One possibility is that this effect is derived from a difference of 1,2-vinyl contents. The thiol groups of the mercaptosilane Si–C shows a predominated effect in the reaction with the 1,2-vinyl-rich polybutadiene [30,31]. The L-BR-1 and Si-L-BR-4 can react together according to Fig. 7 (D). It is particular plausible as the CLD (Fig. 3) is significant higher for these types.

Fig. 7 shows schematically the reaction of the non-modified liquid polymer with the main polymer. In case of the sulfur vulcanization (A), the co-reaction between the liquid and main polymer has a higher statistical probability for the high molecular weight types. Therefore, more crosslink units will be created. This is confirmed by the higher torque and CLD measurement. Another – lower – probability is the reaction of the liquid polymers with each other. It is less probable as less liquid polymer is less present than the high molecular weight polymer. Considered further if only the liquid polymer would be in the compound, – which is not the case – then much more crosslink units would be necessary to create a real network. However, before it is created, it takes some sub-sequential reactions steps. The molecular weight increases. Longer, branched molecules starts to connect and finally form the network. This is visible by the lower curing speed, in particular for the low molecular weight types. The differences of the 1,2-vinyl contents (B)

depend on the use and combination with the mercaptosilanes. The higher 1,2-vinyl contents show a higher probability to react with the thiol-groups resulting in a faster curing maximum torque.

Fig. 8 shows schematically the possible reactions between the silane (exemplary for Si-A) and the silane-functionalized liquid polymer. Four possible reactions can occur that correspondingly creates additional networks: 'main polymer'–'liquid polymer'–silane (A), 'main polymer'––'liquid polymer'–silane–silica (B), 'main polymer'-'liquid polymer'-silica (C) and silica– ('main-polymer') –'liquid polymer'–silane–silica (D). (A) and (B) are no networks but may modify the existing networks between siliane, silica and main polymer. However, they may cause a hydrophobization of the silica and reduce the filler-filler interactions. (C) can be considered as an additional network. (D) is an extended additional network. The different to the other cases – and the connections without liquid polymer – is the long and flexible distance between silica and main polymer. Another interesting fact is that it couple between two silica clusters. This may lead also to a worse micro dispersion. It is confirmed by the same Payne effect (Si-L-BR-4_Si–C) or higher Payne effect (Si-L-BR-4_Si–B).

The reactions occur in parallel with different statistical probabilities according to the microstructures of the liquid polymers, the types of silane and the concentrations. It is possible that the silane-modified
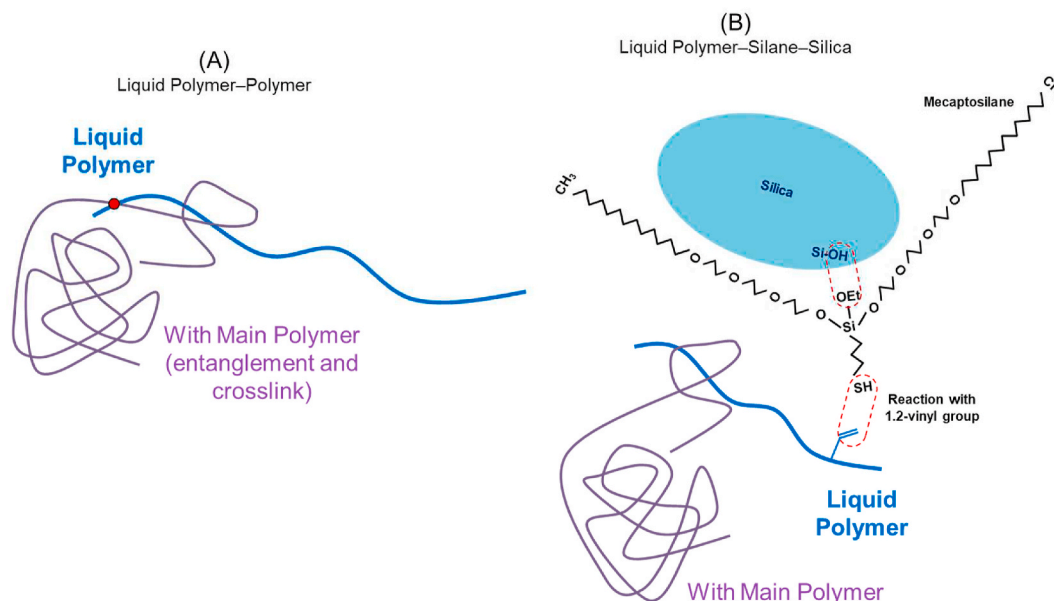

Fig. 7. Reaction of the liquid polymer with the main polymer, through sulfur vulcanization (A) and with the mercaptosilane (B).
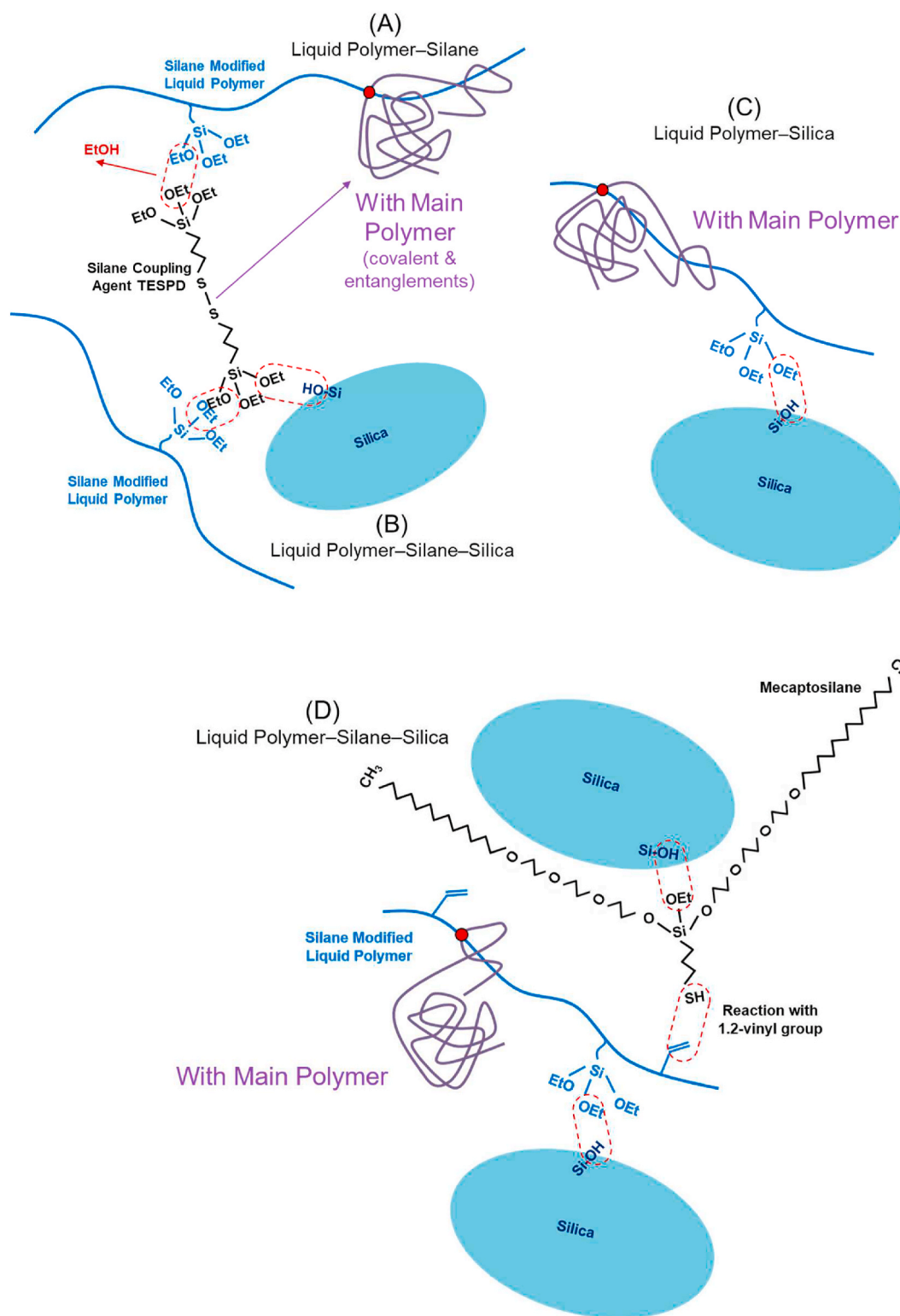
Fig. 8. Possible Reactions between the low molecular 'liquid' polymer, silane coupling agent and silica.

liquid polymer with the bifunctional silane (Si-A) creates connections of (A), (B) and (C). Moreover, the high molecular weight version (Si-L-BR-6) will be effectively integrated into the polymer network, as shown and discussed in *Crosslink Density*. It is therefore a plausible assumption that in this case more connections of (A) and (B) are created. While, in case of the how molecular type, Si-L-BR-4, the polymer chains can move more freely with a higher possibility to connect both, the silica and the main polymer. More connections of (C) will be created, consequently resulting in an additional network. In case of the mercaptosilanes, Si-B and Si-C, (D) can be assumed as the most probable reaction. The silane groups of both materials react with the silica. The thiol group of the silane react with the 1,2-vinyl groups of the liquid polymer.
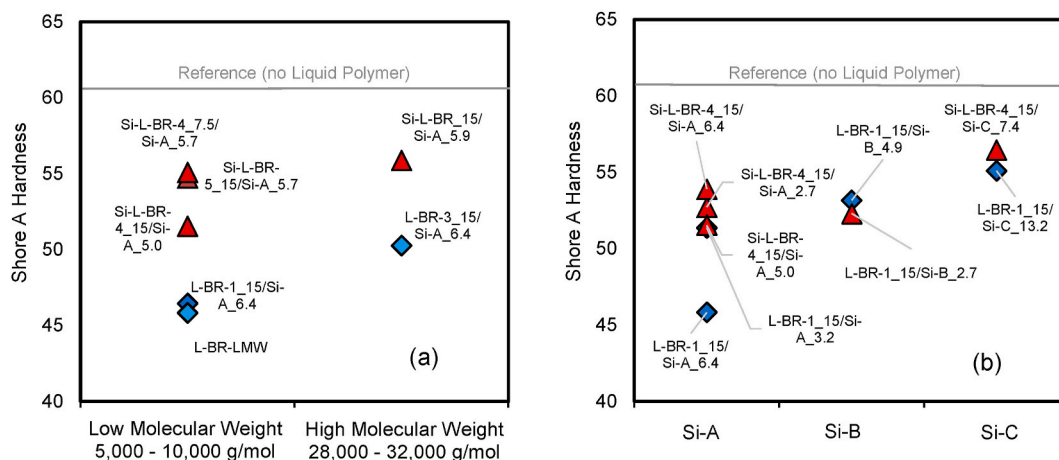
Fig. 9. Shore A Hardness of the different L-BR and Si-LBR (a, b).

3.2. Mechanical properties

3.2.1. Hardness

Fig. 9 shows the Hardness results of the investigated compounds separated for low and high molecular weight (a), and the different silanes (b). The variation of the single measurements is in the range of ±1.6 Shore A.

Compared to the reference without any liquid polymer, the addition of the liquid polymers reduces the hardness of the compounds. The direction is in accordance with the maximum torques presented in Fig. 2. The Si-L-BR's shows higher values than the non-functionalized L-BR's. This is associated with the creation of an additional network, supported by the silane group as discussed in the previous chapter.

Generally, higher CLD values show higher Shore A hardness values as shown in Fig. 10. It is, however, differentiated for the type of the liquid polymer and type of silane. The silane-modified liquid polymers, show higher hardness values but a lower CLD. The same tendency is true for the mercaptosilane, Si-C. The highest hardness, however, but still relatively low compared to the significant high CLD values. As previously explained, it is derived from the reaction between the Si–C's thiol group with the 1,2-vinyl group of the liquid polymer, resulting in a higher CLD.

The silane coupling agent concentrations show no clear tendency as shown in Figs. 9 and 11. As shown in the previous segments, in
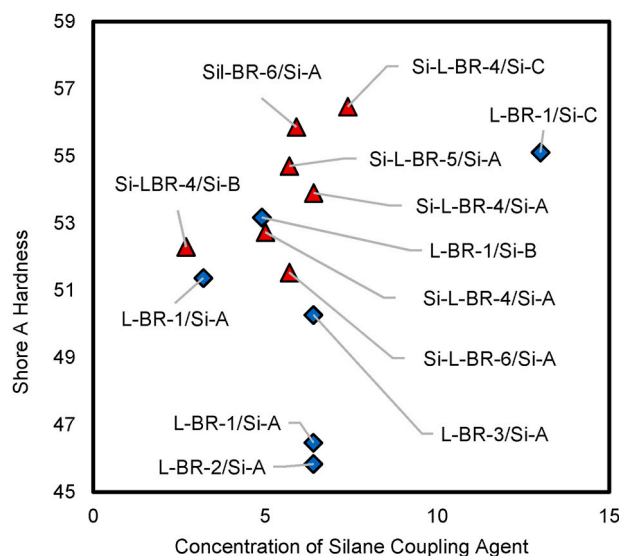

Fig. 10. Relationship of Crosslink Density and Shore A Hardness for the different L-BR and Si-L-BR.

Fig. 11. Shore A Hardness for the different L-BR and Si-LBR in relation to the concentration of the Silane Coupling Agent.

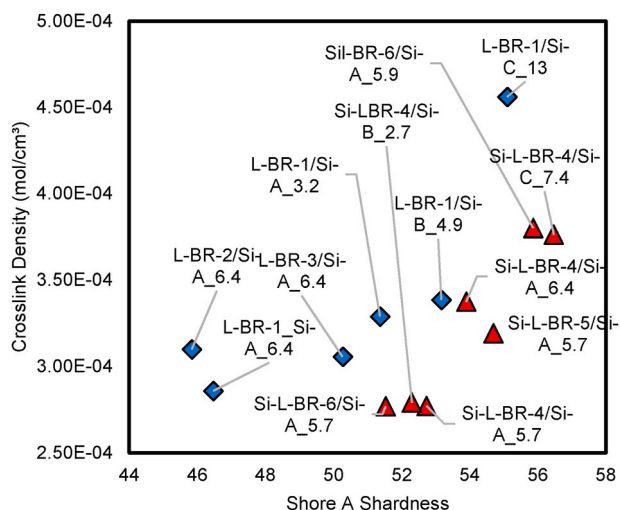combination with the silane-modified liquid polymer, an increase of the silane concentration from a certain concentration (for the Si-L-BR from 2.7 phr to 6.4 phr) shows only slight increased CLD and Payne effects. In general, the viscosity is reduced with an increased concentration of silane. It indicates an increase of the silica-silane-polymer network and lower filler network.

3.2.2. Tensile properties

Fig. 12 shows the Modulus at 300% strain (M300) over the Modulus at 100% strain, (Fig. 10 and c), as well as the elongation at break over tensile strength (Fig. 10b and d). The variation of the moduli of the single measurements is in the range of ± 0.1 MPa. The variation of the tensile strength and elongation at break is in the range of ± 1.5 MPs and ± 80% respectively.

With the on-top addition of the liquid polymers to the compounds, the moduli and tensile strengths are reduced due to the higher content of low molecular weight materials of the total compound. The M300 values are higher for the silane-modified liquid polymers compared to the unmodified types. It is more pronounced than for the M100 values. It indicates generally that the filler-polymer interactions are improved in the presence of the silane-modified liquid polymers.

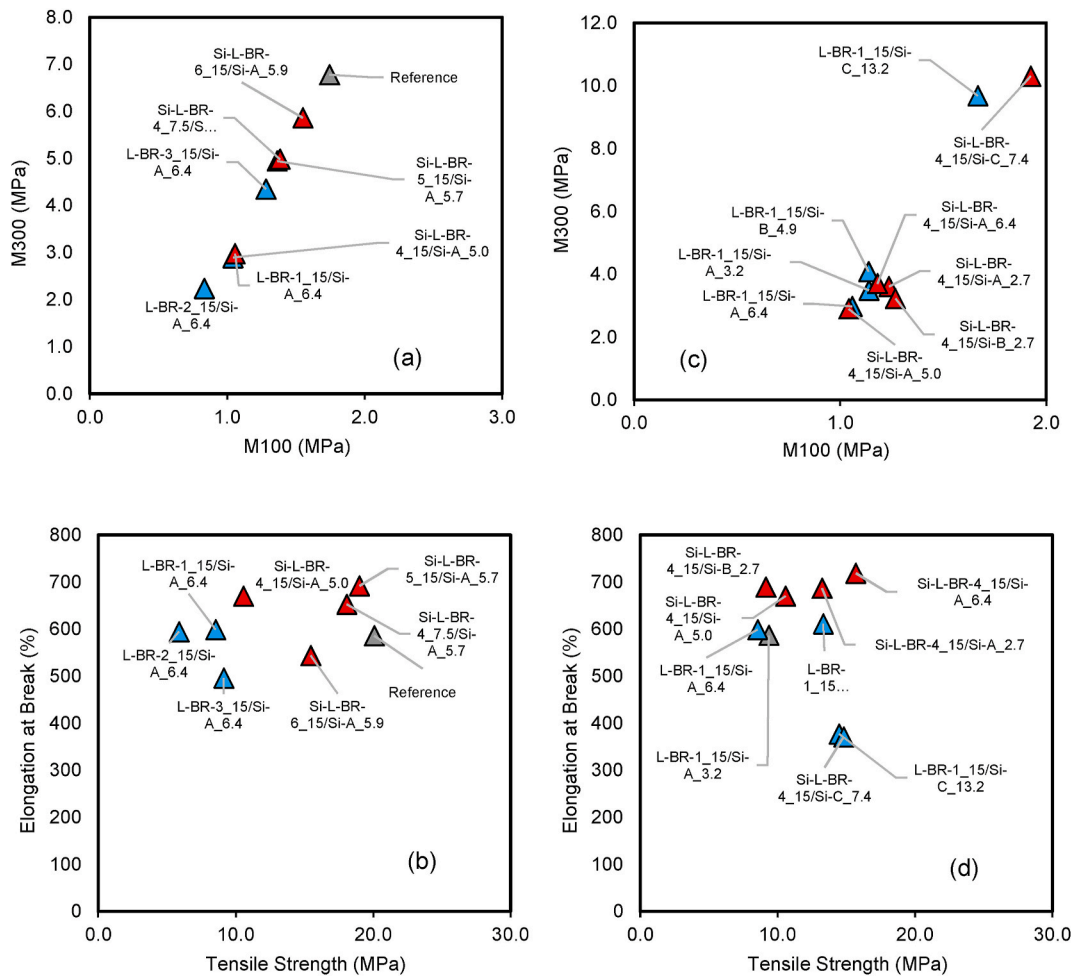Compared to the non-functionalized L-BR's, the silane modified

Fig. 12. Influence of different L-BR and Si-LBR (a, b) in combination with different Silanes (c, d) on the Mechanical Properties.

types results in higher moduli (more significant for the M300 values), higher tensile strength and higher elongation at break. The order for increasing M300 is as follows: Si-L-BR-4 (1), Si-L-BR-5 (2) and Si-L-BR-6 (3). This is in line with previous discussed result.

For the mercaptosilanes (Fig. 12b), the high molecular version Si–C shows the highest M300 but also the highest M100. It is in-line with the results from the Payne effect of the uncured compounds – which showed the lowest values. It can be assumed that an effective coupling reactions

are obtained. Taken additionally the CLD into consideration, the medium-range tensile strength and elongation is also plausible. It is due that the mechanical properties are defined by the CLD. However, generally if an optimum CLD is exceeded, the crosslink network becomes less elastic – associated to higher contents of monosulfidic versus polysulfidic connections.
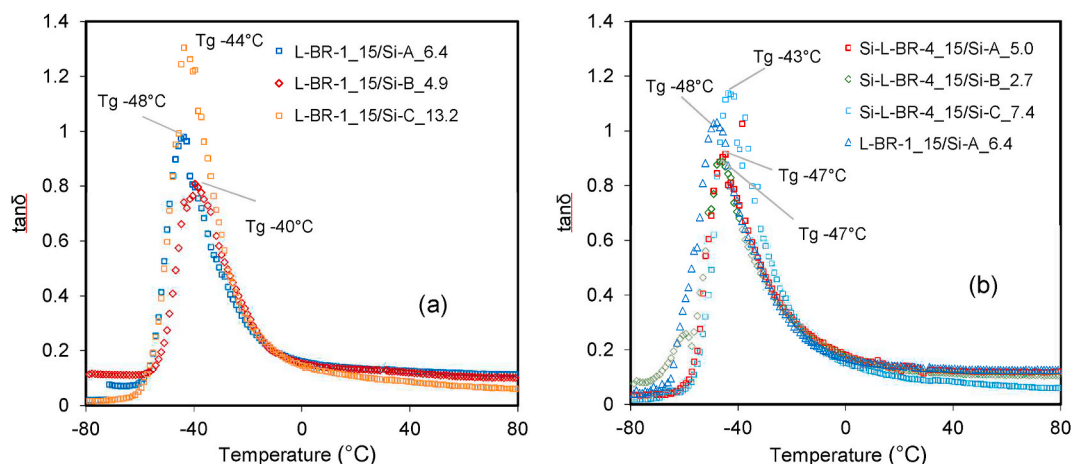

Fig. 13. Influence of different L-BR (a) and Si-LBR (b) in combination with different Silanes on the Dynamic Mechanical Properties.

3.2.3. Dynamic Mechanical Properties

The dynamic properties were characterized to – restive – predict the tire performance. Fig. 13 shows the tanδ temperature sweep for the non-functionalized liquid polymers (Fig. 13a) and for the functionalized liquid polymers (Fig. 13b). Between repeated measurements the maximum variation is in the range of ± 5% for the single values of the tanδ and E'.

The compounds containing the bifunctional Si-A show the lowest T_g's at −48 °C for both types of the liquid polymers (the non-functionalized in Fig. 13a and functionalized in Fig. 13b). The exchange with the mercaptosilanes Si–B or Si–C leads to an increase in the T_g's and lower tanδ values in the range of 0 °C–80 °C. It is known that the T_g decreases almost linearly with the increase of the CLD [32,33]. It is because of reduced chain mobility and denser network. In case of Si–B this is a result of an increased E' as shown in Fig. 14d. The result is in accordance with the increased CLD and confirms for the mercaptosilanes the assumed network (D) according to Fig. 8. The T_g dependence also changes with the type of the liquid polymer. In particular the 1,2-vinyl groups of the liquid polymer are reacting with the mercaptosilan's thiol groups. For the L-BR-1/Si–B the T_g is −40 °C for Si-L-BR-4/Si–B the T_g is −47 °C. For Si–C, the reduction of the tanδ is due to a decrease of the E', for the non-functionalized L-BR and an increase of the E' for the functionalized L-BR. As explained above, the 1,2-vinyl-rich L-BR is reacting with the thiol group. Additionally, the silane-functionalized Si-L-BR is reacting with the silica surface (Fig. 5). The consequence is a reduced filler network – which is confirmed by the E' value.

Fig. 14 shows the tanδ at 70 °C versus tanδ at 0 °C and E' at 70 °C versus E' at 0 °C for the different liquid polymer and silane pairings. These values can be used for a prediction of the in-rubber properties, in particular the rolling resistance (at 70 °C) and wet grip (at 0 °C). The accuracy of the rolling resistance predictor is relatively good. However, it has to be taken into account that wet grip is a more complicated phenomena and not reliable to predict from the DMA value.

Independently of the microstructure, the silane-function of the liquid polymers reduces the tanδ at 70 °C (Fig. 14a). For the low molecular weight types, the tanδ at 70 °C stays relatively constant compared to the non-functionalized types. For the grafted silane-functionalized low molecular Si-L-BR-4, it goes along with a reduction of E' (Fig. 14b). It is due to the higher CLD and hardness of Si-L-BR-6. However, the ratio of the tanδ at 70 °C and tanδ at 0 °C is lower and could be interpreted as a more favorable balance - compared to Si-L-BR-6 version. From this results it can be assumed that Si-L-BR-4 is stronger interacting with the silica and Si-L-BR-6 is contributing to a higher extend to the polymer network. It is in accordance to Fig. 8: a hydrophobization and modification of the networks can be assumed for Si-L-BR-6 (A) and (B), an additional network can be proposed for Si-L-BR-4.

The mercaptosilane Si–B shows a different balance comparing the functionalized and non-functionalized L-BR, shown in Fig. 14c. With the silane-functionalization, the tanδ at 0 °C is strongly and at 70 °C very slightly increased – in both cases with a reduction of the E'. It is different to the other mercaptosilane, Si–C, possibly due its strong dominance. It shows no changes of the tanδ if the silane-modified liquid polymer is used, however, the E' is responding clearly to it and increases for both temperatures strongly. From these results, a strong interaction between
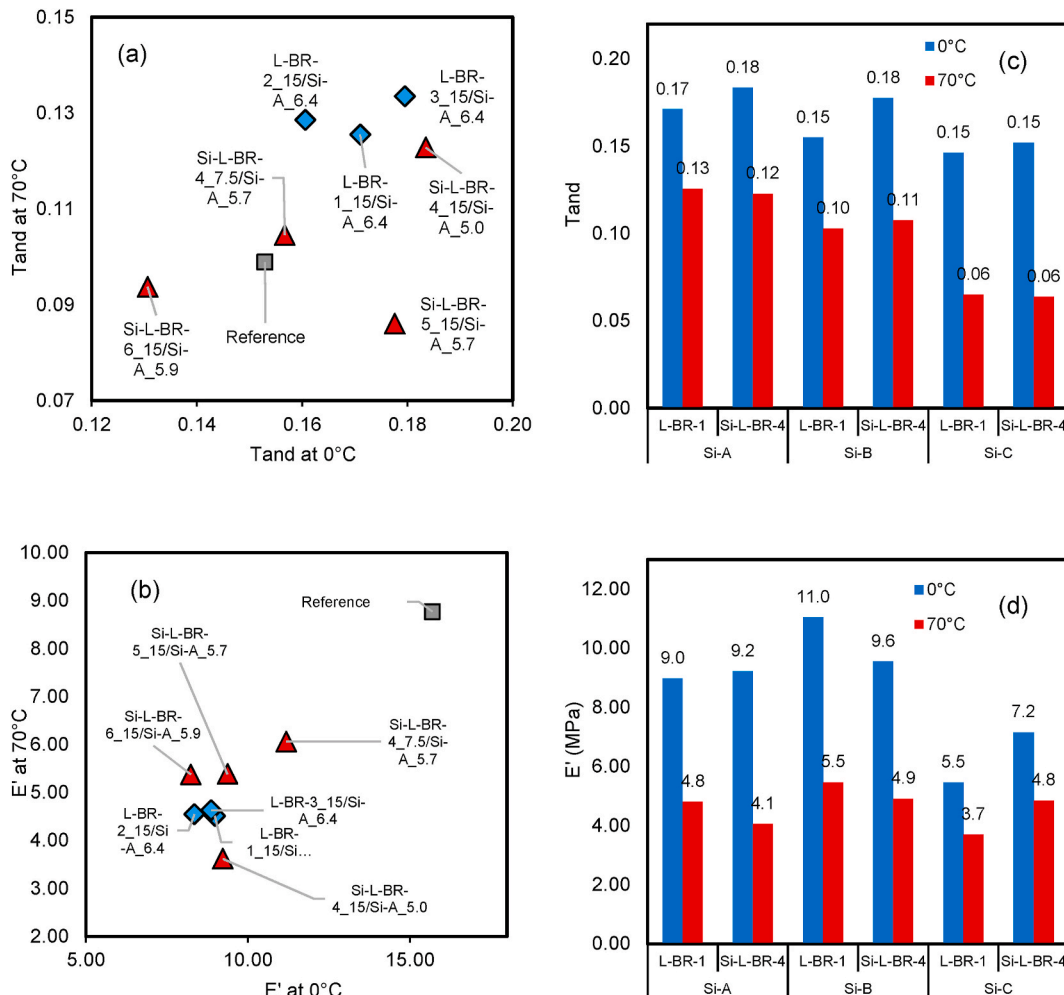
Fig. 14. Influence of different L-BR and Si-LBR (a, b) in combination with different Silanes (c, d) on the Dynamic Mechanical Properties.

Si–C with the silane-functionalized liquid polymer can be further confirmed.

4. Conclusion

This paper discusses the use of low molecular weight 'liquid' polymers in SSBR/silica compounds. One of the main questions is if this material hydrophobizes the silica surface, and if it is incorporated into the main rubber network. Three different silane coupling agents and six different low molecular weight 'liquid' polymers were selected, evaluated and comparatively introduced in mixtures of a curable SSBR/silica compound. The curing kinetic, crosslinking density and Payne effect was measured to evaluate the strain dependence of the mixtures and to estimate the filler-polymer and filler-filler interactions. Mechanical properties were evaluated to describe the materials comprehensively and to predict their in-rubber performance in passenger car tires. The tendencies of the influence are summarized in Table 4.

From the statistical standpoint it is highly probable that the liquid polymer is integrated or at least partially connected with the main polymer network. The molecular weight still allows a minimum of connections per chain. In case of the low molecular weight types (5000 to 6000 g/mol), two to three crosslink units per chain are created. In case of the high molecular weight type (30,000 g/mol) around fourteen crosslink units per chain are created.

The curing curves and CLD shows a clear indication for the building of an additional network that is generated by the silane-functionalized liquid polymer. The additional network is based on a coupling between the 'main polymer' – 'liquid polymer' – silica. Also reactions between the liquid polymer and the silane or liquid polymer with silane and silica are taken place. This reduce the filler-filler interactions by a strong hydrophobization of the silica surface.

It is assumed that the generation of the networks occurs in parallel and with different probabilities according to the microstructures of the liquid polymers, the types of silane and the concentrations. They are also occurring and competing with the generations of the known networks, built between the silica, silane and main polymer. The silica-silica, polymer-polymer networks as well as the silica-silane-polymer network. For the high molecular weight type, Si-L-BR-6, it is a plausible assumption that primarily connections of 'main polymer'–'liquid polymer'–silane (A) and 'main polymer'–'liquid polymer'–silane–silica (B) are created. It is due its stronger contribution to the polymer network. This will results in a hydrophobization of the silica. Compared to this, for the low molecular weight type, Si-L-BR-4, the polymer chains can move more freely with a higher possibility to connect both, the silica and the main polymer. More connections of 'main polymer'–'liquid polymer'–silica (C) will be created, consequently resulting in an additional network. In case of the mercaptosilanes, silica– ('main-polymer') –'liquid polymer'–silane–silica (D) can be assumed as the most probable connection. The silane groups of both materials react with the silica. The thiol group of the silane react with the 1,2-vinyl groups of the liquid polymer. This results in a long and flexible additional network.

The micro dispersion and mechanical properties correspond to the intensity of the networks. From the DMA evaluation, the E' shows the highest values of the high molecular mercaptosilane and high molecular weight silane-functionalized liquid polymer. However, the tanδ values show more favorable indication of the performance balance (wet grip and rolling resistance) with the low molecular types. For these types, compared to non-functionalized types, the balance could be clearly improved, knowing well that this is only an indication of the real performance.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

Table 4

Influences of the liquid polymer's microstructure and combination with different silanes on the final compound's properties.

Parameter	Torque	CLD	Mooney Viscosity	Hardness	Payne Effect	T_g
Low 1.2-vinyl, low Mw L-BR	0	0	0	0	0	
high Mw High 1.2-vinyl	0 (0/+)	+ (0/+)	++ (0/+)	++ (0/+)	– (0/-)	0
High 1.2-vinyl with Si–B	0	+	+	+	+	++
High 1.2-vinyl with Si–C	+	++	++	+	0	+
High 1.2-vinyl Si-L-BR	(0/-)	–	+	+	–	(0/+)
High 1.2-vinyl, high Mw Si-LBR	++	++	++	++	+	
High 1.2-vinyl Si-L-BR with Si–B	–	–	+	0	–	+
High 1.2-vinyl Si-L-BR with Si–C	++	–	–	0	0	(0/+)

Reference or same as reference ("0"), small increase or decrease ("+" or "-"), high increase or decrease ("++" or "–", very slight tendencies are indicated "(0/+)" and "(0/-)".

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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