LOW MOLECULAR WEIGHT 'LIQUID' POLYMERS IN TIRE TREAD APPLICATIONS

PLASTICIZATION, MODIFICATION
AND INFLUENCE
ON THE SILICA DISPERSION

Marcel Gruendken

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CHAPTER 1

INTRODUCTION

From Chemicals to Innovations in the Tire Industry

The chemical industry is in change: From a simple base chemical provider to a value added approach – that influences technologies in other industries and the tire industry [1]. Figure 1.1 illustrates the different periods with its associated chemical product emergences [2]. From the beginning these changes have been accompanied by the tire industry, starting 180 years ago with the fundamental innovation to vulcanize natural rubber with sulfur. The polymerization itself was discovered during world war II accompanied by the rise of the petrochemical industry. From that on, the most commercial relevant materials have been developed until the 1980s. Since the 1990s, most innovations have been created through incremental improvements of the product design and driven by socio-economic trends. Today, for the chemical industry this can be broken down to three key trends: sustainability, technology (digitalization) and demographic changes [3].

The chemical and the tire industry are both not only connected through their positions in the value chain but also share these three trends. The planet is getting warmer: The sustainability part is therefore in particular focus. For the industry there is the very real challenge to meet existing and potential future regulations to reverse the planet's climate change. These changes can be further broken down from a framework [4] that prevents a 2°C increase by 2050.[3]

The chemical industry contributes significantly to the global CO₂ emissions. Mobility and transportation deliver another large contribution while tires are an essential part of the entire automotive system, developed and ultimately built to link the car with the road [5]. Improving the energy efficiency is where both industries met. One consequence is an electrified energy and more sustainably produced ingredients. Another one is the development of compound formulations that improve the rolling resistances of tires.

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It is presumed that passenger car tires as well as heavy duty truck tires contribute up to 33% to the total global CO₂ emissions [6]. The rolling resistance of tire treads contribute to the total global fuel consumption of cars by 20% [7]. Due to that importance, the rolling resistance is presently the most considered performance indicator, constituting the main field of academic research as well as research in the chemical and tire industry. An example of an already existing regulation, particularly to support CO₂ reductions, is the tire labeling initiative [8] created in 2002 in Europe to achieve more consumer awareness of the tire performance. The current tire label covers the tire's fuel efficiency, rolling resistance and noise. The label concept initiated a further innovation momentum in the tire and related supply industry.

Figure 1.1 Chemicals – turning Innovation in the tire industry [2].

One example of this regulation-initiated market pull was the revolution in the filler technology with the introduction of silica as an alternative active filler in tire tread compounds. This became possible with the “Green tire” technology [9] originally invented by Michelin in 1992. Green refers herein to the sustainability context and should emphasize the lower carbon footprint.

Another example for innovations driven by industry-related regulations was the ban of aromatic oils [10] in 2010, an initiative to safer and more environmental friendly raw materials. In the same period of time, the European Union established REACH (Registration, Evaluation, Authorization of Chemical Substances) [11]. The awareness of hazardous substances was emerged by both the industry and the society. These initiatives –by the government and the industry – continuously transfer chemical products to safer and more sustainable raw materials.

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The European Union is focusing on emissions of greenhouse gases and safeness, other regions concentrate also on other factors, for example on the abrasion resistance. In particular the “maximum mileage” is a common term in North America and associated with the abrasion resistance considered to be a key selling criterion.

Considering other regional differences of the tire industry, different performance scopes and product types can be found. The central and northern part of the EU differentiates between winter and summer tires, associated with seasonal tire changes. Other major industrialized regions like North America or Asia use mainly all-season tires. These tires compromise environmental conditions, cold and moderate temperatures. Moreover, they have to compromise snow and ice traction as well as dry and wet grip and the rolling resistance.

Tire treads are in the immediate contact with the road. They come more and more into focus in science and industry. Most commonly four performance criteria are targeted to be optimized and balanced: rolling resistance, abrasion resistance, wet grip and winter performances (including cold temperature properties as well as snow and ice grip).

A tire tread formulation contains five main ingredient categories: 1. Polymers, 2. Plasticizers, 3. Fillers, 4. Curatives and 5. Additives. Each category has a variety of substances to match and balance the above-mentioned performance targets of the final product.

Together with hydrocarbon resins, liquid polymers are commonly described as “alternative plasticizers”, referring to plasticizers that are not “classical plasticizers” like oils e.g. paraffinic or (Treated) Distillated Aromatic Extracts (DAE, TDAE) oils. Figure 1.2 shows the classical plasticizers and alternative plasticizers as resins and liquid polymers. Differently to the classical plasticizers, the hydrocarbon resins show mainly an anti-plasticizing effect with an increase in T_g . This effect is used to improve e.g. the wet grip performance [12].

To optimize and achieve the performance targets the liquid polymers are considered as a new type of ingredients. They can be categorized in polymers or plasticizers, or as compromise between them. They are used to modify the main polymer as a kind of inter-material plasticizer with the same chemical composition. The liquid polymers are used either to replace or to supplement other plasticizers. From the industry they are marketed as co-vulcanizable plasticizer [13]. However, it is unknown how liquid polymers are incorporated in a compound and how they modify its properties.

Another important variable for the liquid polymers is subjected to the combination to the filler system. Under specific conditions, liquid polymers can improve the filler dispersion [14]. With this, they might help to achieve the performance targets of tires. The probability is given by the liquid state of the liquid polymer and functionalizations to interact with the filler particles. However, only little scientific knowledge has been established.

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PLASTICIZERS	LIQUID POLYMERS	RESINS
<ul style="list-style-type: none"> • Mw < 1,000 g/mol • DAE (Distillate Aromatic Extract) Tg: -37° C • TDAE (Treated Distillate Aromatic Extracts) and MES (Mild Extracted Solvent) Tg: -58 ~ -48° C	<ul style="list-style-type: none"> • Mw < 60,000 g/mol • L-BR / L-IR Tg: -95 - -49° C • L-SBR -6 - -10° C • Functionalization • Mw < 54,000 g/mol • Co-reactivity	<ul style="list-style-type: none"> • Mw < 10,000 g/mol • e.g. Aliphatic or Aromatic Hydrocarbon, Polyterpene, Coumarone-Indene, Phenolic. Tg: -10 ~ +60° C

Figure 1.2 Differentiation of plasticizers, liquid polymers and resins.[2]

As in all industries, the technical requirements in the chemical and the tire industry continuously increase. Liquid polymers gained more attention to meet key performance targets. The present work focusses on liquid polymers, a new category of ingredients in tire tread formulations: From the state-of-the-art and practical use as a plasticizing and reinforcement-supporting material to its structure-property relationship and interactions with silica as a filler. It will cover the incorporation, the crosslinking, the filler-filler and filler-polymer networks.

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CHAPTER 2

PLASTIZATION AND REINFORCEMENT OF TIRE COMPOUNDS

Tire Performance, Polymers, Fillers and Interactions

A Literature Review

Abstract

Today, a significant amount of elastomers consists of reinforcing fillers and plasticizers due to diverse reasons whether technical or commercial. In the industry, a major trend is to plasticize primarily in order to reinforce at the same time. This to minimize the more cost intensive polymer concentration. Today, in an average tread compound the total content of fillers and plasticizers usually exceeds the total content of polymers in the formulation. This chapter discusses fillers and plasticizers and intermixing possibilities. The interaction of the filler with the main polymer is considered to be of key importance: The filler-filler interaction or filler-polymer interaction, respectively. The latter – in the case of silica fillers – is today improved by silane coupling agents. Beside this, new polymer structures are constantly developed to optimize the polymer-filler interactions. For tire treads, a relatively new category of ingredients are low molecular weight polymers commonly called as “liquid” polymers. They are created analogues to common high molecular weight polymers. The materials can co-vulcanize with the main rubber and modify the characteristics further beside a pure plasticizing effect.

2.1. Tire Performance Indicators

The tire tread plays a key role in safe braking because it transmits the braking power to the road and ensures the safety of passenger car users. Besides the tire contribution and the profile, the safety of the drive for end users depends on the interaction between the materials in the tread and the road surface due to the fact that they transfer the required forces for braking, traction and acceleration. When a tire is in motion on the road surface, it undergoes constant deformation which results in hysteresis, i.e. the loss of energy in the form of heat. This loss of energy while the tire is rolling, referred to as the rolling resistance, directly contributes to the fuel consumption of a car.[1]

As a result, alteration of the viscoelastic behavior of the rubber compound is an effective approach to decrease the rolling resistance [2]. The ultimate passenger car tire should show excellent performance capabilities in three specific categories: rolling resistance, wet grip and abrasion resistance. An increase in performance in all three properties proves to be highly unlikely since they are interrelated and these requirements are conflicting. Any improvement in one of these properties is likely to trigger an undesirable change in the other two properties. For low rolling resistance, the rubber has to show a high elastic behavior and low hysteresis. For good wet grip performance, the material should have a higher degree of hysteresis. Compound formulations can be optimized by the selection of the materials and the variations in particular the polymer, filler and plasticizer.

The dynamic mechanical properties – measured with Dynamic Mechanical Analysis (DMA) – in tire tread compounds can be used to estimate the real tire performance on a road surface. An accurate prediction is in particular the dependence of the dynamic mechanical loss factor ($\tan \delta$), the ratio between loss (E'') and the storage modulus (E') as a function of temperature at a low frequency of 10 Hz [3,4]. The visco-elastic behavior of a rubber is represented by the $\tan \delta$ curve as a function of temperature. This curve can be related to functions of an unfilled tire tread rubber shown in Figure 2.1.

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Figure 2.1. Scheme of a DMA curve of a tire tread compounds with the corresponding segments and different performance criteria's according to Nordsiek. [5]

The rolling resistance can be calculated by equation 2.1 [6]. The resulting stress and energy loss can be calculated by equation 2.2 to 2.3 [7,8].

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

U'' (J) is the total mechanical energy loss of rolling over one loop on the road surface. ρ_r (m) is the rolling radius of the tire. The amplitude γ for a rubber subjected under a sinusoidal shear deformation with the amplitude γ_0 and the frequency ω is [6,8]:

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

The strain lags behind the stress by the phase angle δ :

$$\sigma(t) = \sigma_0 \sin (\omega t + \delta) \quad (2.2a)$$

While σ is the stress in N/mm². The stress consists of the sum of in-phase and out-of-phase components and the constants of the storage modulus E' and loss modulus E'' :

$$\sigma(t) = \gamma_0 E' \sin \omega t + \gamma_0 E'' \cos \omega t \quad (2.2b)$$

The ratio of the loss and storage modulus is defined as $\tan \delta$:

$$\tan \delta = E'' / E' \quad (2.2c)$$

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Where:

$$E' = E^* \cos \delta \quad (2.2d)$$

$$E'' = E^* \sin \delta \quad (2.2e)$$

While E^* is the complex modulus:

$$E^* = \sqrt{E'^2 + E''^2} \quad (2.2f)$$

The energy loss Q (J) as heat over a single cycle can be calculated from:

$$Q = \int_0^{2\pi/\omega} \sigma \dot{\gamma} dt = \pi \gamma_0^2 E'' = \pi \gamma_0 \sigma_0 \sin \delta \quad (2.3)$$

A material is purely elastic if δ equals zero. The energy loss is converted to heat that increases the temperature of the tire [6,8].

The range between 30 °C and 70 °C covers the running temperatures of a tire. Thus, $\tan \delta$ in the temperature range between 30 °C and 70 °C at 10 Hz frequency represents a good indication of rolling resistance [9].

From the time-temperature superposition principle [10], the wet traction indication can be determined by the $\tan \delta$ at a temperature range between -10 °C and 30 °C. The concept was empirically developed by Williams, Landel and Ferry in 1955 and is commonly understood as WLF principle [10]. Data obtained from different temperatures and frequencies can be transferred into one mastercurve [11]. The horizontal shift factor a_T can be calculated from equation 2.4. The lower temperature can be indirectly used to compare the lower frequency of wet surfaces.

$$\log a_T = - \frac{C_1(T - T_{ref})}{C_2 + (T - T_{ref})} \quad (2.4)$$

The constants C_1 and C_2 vary with the reference temperature $T_{ref} = T_g$ and the polymer. Diene rubbers have almost universal values ($C_1 = 17.4$ k and $C_2 = 51.6$ k). The WLF equation is limited from T_g to $T_g + 100$ °C. Higher $\tan \delta$ values indicate a higher wet grip. The peak in $\tan \delta$ correlates to the glass transition temperature T_g of the polymer. As a result, the value is one tool to predict a suitable rubber type to achieve a compromise between tire requirements.[12]

It has to take into account that the elasticity is only one component of the tire's wet grip characteristics. Other important influences are the surface characteristic, i.e. hardness and tackiness of the tire.

An important life time characteristic of tires is abrasion. It occurs whenever two surfaces slide against each other. In principle, it describes a mechanical tear and growth process, governed by the tearing energy dissipated in the contact area [13]. Grosch introduced different

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influences on abrasion [14]. The main target was to minimize the energy dissipation and to simulate abrasion under laboratory conditions. The causes of abrasion can mainly be separated into sliding abrasion and abrasion under limited slip. While the abrasion caused by sliding is primarily relevant to all soft rubbers, abrasion under limited slip – the more complex phenomenon – is more applicable to tires. There are six direct and indirect parameters influencing the sliding abrasion: Load and resulting pressure, energy dissipation, temperature and speed, appearance of abraded rubber surfaces and temperature rise in the contact area. The load and friction is associated with the resulting friction coefficient. Rubbers result in different friction coefficients under different loads. However, it appears that the pressure dependence of the sliding abrasion is more important to the friction.[14]

The abrasion is more a mechanical tearing phenomenon. Abrasion loss on smooth surfaces can be moderate, whereas on rough surfaces, the abrasion can be significantly higher.[15]

This is mainly because to the higher force and stress concentration. There is a correlation between non-crystallizing, unfilled gum and the frequency and speed following the WLF transformation [14]. At operational temperatures (i.e. 60 °C), abraded rubber has a rich pattern oriented to the sliding direction. It is called abrasion or Schallamach pattern [16]. During the sliding, small elements (lips) of the rubber are pulled. The limited adhesion allows these lips to slide. However, due to multiple impacts, stress at the bottom of the lips rises and causes crack initiation as well as growth. After numerous passes the lip has become long and weak enough to detach.

Filled rubber usually displays improved mechanical performance. However, gum rubber can show lower abrasion values than filled rubber. The reason for this is the lower extensibility [14,15]. The temperature increase in the contact area of the sliding rubber finally accelerates the abrasion effect. In the contact area, the temperature rises above 300 °C and can reach temperatures up to 700 °C [14]. This temperature is typically above the inflammation point. Nonetheless, the period of time is normally short enough and conductivity is high enough for the particular rubber element to cool down in time, but it is still high enough to influence the decomposition (depolymerization and oxidation). Abrasion under slip requires a more complex description. Slip and slide are always combined and overlapping. Forces and speed are transmitted between the elastic tire and the track. Until forces exceed higher than frictional coefficients, the tire is put back to a neutral position. An abrasion testing equipment, referred to as “LAT 100,” measures abrasion loss over the dissipated energy. The device is suitable for solid rubbers with different slip angles, loads and speeds.[14]

In addition to the abrasion resistance, rolling resistance and wet grip for tires, cold temperature or winter properties furthermore need to be considered. The behavior and material

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mechanisms are more complex and separate definitions are thus to be considered. Under cold and dry conditions, the adhesion from the road and the tire surface as well as the deformation characteristics of the tread are key attributes, as shown in Figure 2.2 (a). The tread requires to behave with high flexibility at low temperatures. As shown in Figure 2.2 (b), on iced roads it is assumed that a liquid aqueous film is present between the tread and the road. This causes a viscous drag of the layer. Another scenario is driving on snowy roads, schematically shown in Figure 2.2 (c). In this case, shearing forces, frictional forces, digging forces and breaking forces are overlapping in parallel. Different models are used for these three conditions and the properties can be generally indicated by the storage modulus, E' . A decrease of the E' in the temperature area of $-25\text{ }^{\circ}\text{C}$ to $-10\text{ }^{\circ}\text{C}$ indicates a softer material behavior that is supportive for the winter properties [17]. However, it is commonly understood that the accuracy is limited as this only describes one parameter among multiple that contribute redundantly. A more precise and common option is to measure the winter properties, in particular the ice grip properties with the use of a friction test stand, i.e. the friction is tested then between a simulated iced road surface and a miniature rubber surface [17].

Figure 2.2. Contact between tire tread and cold dry (left), iced (middle) and snowy road surfaces.[17]

2.2. Polymer and Blends

Polymers are a main ingredient of tires. Styrene Butadiene Rubber (SBR) is the most important synthetic polymer in the tire industry. SBR is divided into emulsion SBR (ESBR) and solution SBR (SSBR). The former was developed in 1937 by radical polymerization [18]. In contrast, SSBR, which was developed in the 1940s, is polymerized by living anionic polymerization. Today, in tire tread formulations, SSBR is one of the more important polymers

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and mostly substituted ESBR with the invention of the Green Tire technology, that comprises silica fillers [19]. It shows a narrower molecular weight distribution and a more adjustable microstructure compared to ESBR. For SSBR, there are three main parameters: 1. styrene content; 2. the resulting glass transition temperature; 3. 1,2-vinyl content. The styrene content is mostly found in the range of 25 % while the spectrum ranges from 12 % (specialty low styrene) to 37 %. The styrene content primarily influences the glass transition temperature, the corresponding abrasion and wet grip balance. 1,2-vinyl of commonly used grades for tire treads varies between 24 % and 70 %. The versatility is obtained from the initiation and propagation reactions that can be controlled by the anionic polymerization technology.[20]

The parameters are used to control the glass transition point and furthermore to set the hysteresis characteristics. SBR is also divided into oil-extended and non-extended grades. It can be highly extended with oil, not merely for a technical purpose but also for commercial reasons. The oil extension is done prior the coagulation after the polymerization. That's why higher molecular weight types can be produced that still can be processed further. It is also easier to incorporate the oil than in the later rubber mixing.[20]

Oil extended grades are available comprising, for instance, 37.5 phr processing oil. Another parameter is the branching of the SBR molecule. Also star polymers – differently to linear polymers – are available. This characteristic controls the hysteresis properties.[21-22]

Figure 2.3 SBR with styrene (I), butadiene 1,4-cis and 1,4-trans (m), 1,2-vinyl (n).

For an increased affinity of filler particles to the polymer, the recently developed SBRs include functional groups. These can be divided into either backbone functionalization – inside the molecular chain – or chain end functionalization, or a combination of both. The polymerization method of living anionic polymerization enables SSBR to add functional groups – both, by chain end or backbone modification. Halasa [23] synthesized SBR with modified styrene monomers, containing amino groups. The presence of these groups result in better filler dispersions in carbon black and silica filled compounds.[23] Another method of functionalization was described by Nagata et al. [24]. SSBR/CB compounds were tested with extra addition of chain end, tin-coupled SSBR. A reduction of the hysteresis was achieved.

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Similar results were also reached by the chain end functionalization of SSBR with 4,4-bis-(diethylamino)benzophenone (EAB).[24]

In silica filled compounds, polar groups on the polymer are more supportive for the polymer-silica interaction. Chain end alkoxy silane functionalized SSBR can be used to reduce the rolling resistance in SSBR/silica mixtures compared to mixtures with unmodified SSBR.[25] Epoxide and dithiol modifications are two more backbone functionalities that can improve the polymer-filler interaction compared to unmodified SSBR [26,27] and enables the reduction of the hysteresis.

Natural rubber (NR) is another important polymer in tire applications. Natural rubber comes from a milky sap or latex. The name for Hevea latex is coming from the tree *Hevea Brasiliensis*. The schematic constitution of natural rubber (NR) is shown in Figure 2.4. The emulsion consists of hydrocarbons (polymer) of 30 to 45 % and non-rubber constituents like proteins, lipids and phospholipids in sum of app. 3 by 5 %, while the rest is water. Natural rubber can be segmented in three categories [28]: 1. Technical Specified Rubber, such as Standard Malaysian Rubber (SMR) or Standard Indonesian Rubber (SIR); 2. Visually Inspected Rubber, e.g. Ribbed Smoked Rubber (RSS); and 3. Specialty Rubber that includes e.g. depolymerized natural rubber or epoxidized natural rubber. The non-rubber constitutions influence the technical properties of a rubber compound, mostly heat build-up and creep [29,30]. The proteins in the natural rubber are responsible for a higher modulus, faster scorch time and higher tear strength [30]. It is assumed that they act as a reinforcing filler at low concentrations [30]. Amnuayporn Sri et al. [31,32] proposed a naturally working network wherein the proteins and phospholipids are building the cross linking sections. This occurring network influences the strain-induced crystallization of natural rubber [33,34].

Sarkawi et al. displayed epoxidized natural rubber in vulcanizates with silica and silane. Compared to the non-functionalized natural rubber, it shows better silica dispersion, increased $\tan \delta$ at 0 °C wet skid resistance, as indicated by $\tan \delta$ at 0 °C, as well as lower rolling resistance as indicated by the $\tan \delta$ at 60 °C.[35] Polar functionalities on the natural rubber show a significant effect on the reinforcement efficiency with silica.[36]

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Figure 2.4 Schematic constitution of natural rubber (NR).[31,32]

Another synthetic polymer used in a tire compound is butadiene rubber (BR). Butadiene rubber can adopt three configurations: cis or trans units with double bonds from 1,4 addition and 1,2-vinyl groups. Technically most interesting is neodymium or lithium anionically polymerized BR. In general, anionically polymerized BR performs in a narrower molecular weight distribution and can offer more tailored solutions in the microstructure i.e. constitution of the three units. On the one hand the higher cis configuration (92 %) shows better abrasion resistance. On the other hand a higher 1,2-vinyl BR typically shows higher hysteresis. This behavior goes along with a glass-rubber transition temperature shift. An increase of the vinyl content from 10 % to 40 % leads to an increase of the glass transition temperature from -90 °C to -50 °C. Correspondingly, the wet grip performance is increased by 20 % while the rolling and abrasion resistances deteriorate (5 %).[35]

From a market point of view, tires are divided into summer, winter and all-season tires as well as for passenger and truck tires. Technically, the differences are influenced by the blending ratios. Depending on the specific characteristic that needs to be optimized, tires in general comprises natural rubber NR and styrene butadiene rubber SBR. Passenger tire treads are usually SBR rich, in particular in case of summer tires. They are mainly defined by the market segment and region, with NR rich tires for optimized abrasion and tire life time – for higher “mileages” - or SBR rich tires for higher wet grip, therefore associated with higher safety. Furthermore tire commonly comprises of butadiene rubber BR that optimizes the loss modulus and abrasion resistance, but mostly compromises wet grip and rolling resistance. A typical summer tire comprises 70 phr SBR and 30 phr BR. Winter and all-season tires offer another compromise: on both the market segmentation and the technical side, these contain contain balanced formulations with SBR, NR and BR.

As described above, tread formulations usually consist of the combination of three polymers: SBR, NR and BR. Each of these polymers provide specific characteristics. In their blends,

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some tire performance indicators can only be optimized by specific blend ratios. BR, for instance, is known for good winter properties. BR shows synergistic properties only when containing a certain amount of NR – a polymer that is not likely for good winter performances.[37]

2.3. Reinforcement

2.3.1. Fillers

From the early 1900s, carbon black was the first filler for tires to improve modulus, tensile strength, abrasion resistance, grip resistance and other physical properties [38,39]. It was used as a commercial filler to reinforce rubbers. In 1992, Michelin introduced the “Green Tire” concept that uses silica as filler [19]. Silica tires provide similar reinforcing effects compared to carbon black but benefit at the same time from lower rolling resistance and better wet grip of tires produced therewith [36,40]. The technical problem of using silica, however, is the polar character of this filler. The surface of silica is acidic and consists of siloxane and silanol groups, as shown in Figure 2.6 (b). This is the main for the difficulty of using silica in blends with non-polar polymers.

Both types of fillers, carbon black and silica, have four main characteristics: 1. surface activity; 2. particle size; 3. specific surface area; and 4. structure. The surface activity differentiates between active and non-active fillers. CB is a functional filler and shows a greater affinity to the rubber, which results in a high physical interaction between the polymer and the filler. Silica furthermore requires a surface modification.[41]

Both, carbon black and silica have a small primary particle size and relatively high specific surface areas, ranging till around 100 m²/g. This range is classified as reinforcing – active – fillers. It includes both precipitated and fumed silica as well as carbon blacks, e.g. N220, N330, N550. When the particle size is higher, i.e. 100 – 1,000 nm – with low surface areas of a few m²/g, the fillers are classified as non-reinforcing fillers (diluent). Further increase in the particle sizes (10,000 nm) are deteriorating rubber properties. Reinforcing fillers illustrate a high specific surface area in order to offer a more active contact area. This also improves the filler-rubber interaction.

The surface area can be measured by nitrogen (N₂) adsorption by nitrogen surface area (NSA) and statistical thickness surface area (STSA) - both measured according the Brunauer–Emmett–Teller (BET) theory or ASTM D6845. Two other common methods are CTAB-adsorption (cetyl-trimethyl-ammoniumbromide) and iodine adsorption (iodine value).

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As shown in Figure 2.6 (left), carbon black is composed of carbon with a lower percentage of other hydrocarbon or oxygen-containing groups on the surface. The polymer mainly interacts with the low amount of amorphous carbon in between the graphitic layers [42]. Figure 2.6 (right) illustrates the surface chemistry of precipitated silica. The silanol groups are very polar and chemically active. In the past, this fact mainly caused problems for the use of silica inside lower polar rubbers [43-45]. It has to be noted that the surface of silica doesn't contain isolated water molecules. With the use of silane coupling agents, the mechanical properties and elasticity were significantly improved [19,40,44-49]. These materials coupling the silica surface with the polymer (*refer to 4.3 Results and Discussion, Improving Filler-Polymer Interaction*).

Figure 2.6 Structure and chemical surface of carbon black (left) and silica (right) [43,50].

2.3.2 The Reinforcing Effect

Active fillers are used to reinforce an elastomeric composition and contribute to the elastic modulus. However, this contribution is strain dependent and differently to the non-strain dependent – as ideally considered – crosslinking network that is formed by the polymer. Payne discovered this strain dependence of filler-reinforced rubbers [51,52]. The features, also called “Payne effect” have been developed into a common understanding for the characterization of the filler-polymer and filler-filler interactions.

The Payne concept [53], shown in Figure 2.7, divides four contributions to the modulus: Filler-filler interaction (Payne effect), filler-polymer interaction, the hydrodynamic effect and the polymer crosslink network. Filler-filler interaction constitutes the strain-dependence of the modulus. The effect is due to the fracture of physical bonds between the filler particles – Van der Waals forces - and hydrogen bonds.

The effect is and originates from a stronger inter-particle strength, which is stronger for silica than for carbon black. It is known that fillers are likely to build agglomerates. In particular at

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high concentrations these agglomerates tend to aggregate or build a secondary network (cluster structure).

The filler-polymer interactions are considered independent of strain. Under ideal situations rubber chains are trapped in voids of filler aggregates and are immobilized from deformation [54,55]. Independently from the filler-filler network it is not strain dependent, strong chemical filler-polymer interactions can be obtained by using silane coupling agents. It provides the possibility for higher filler loading and increases the strain-independent contribution to the modulus.[19,54-57]

Figure 2.7. Reinforcing of rubbers (Payne concept) [53].

Remark: silica without silane.

The two remaining contributions (hydrodynamic effect, polymer-polymer network) to the modulus are assumed to be strain independent – under ideal situation. Hydrodynamic effects are a growth in the modulus of the rubber compound due to the addition of the filler particles. The polymer network is created through the chemical crosslinking and physical entanglements. [19,36]

2.3.3 Improving Filler-Polymer Interaction

Surface modification of silica is the most successful option to optimize the filler-polymer interaction. Luginsland et al. [58] described a model of rubber reinforcement of silica in the presence of a silane coupling agent. Figure 2.8 shows the silica agglomerates forming a network with strong hydrogen bonding and occluded rubber. A layer of bound rubber is attached to the silica surface by a silane coupling agent (silica-polymer coupling). It is

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assumed that some rubber chains reinforce to a minor contribution [58]. Coupling agents are characterized by a dual functionality as X_3SiRY , X representing the hydrolysable alkoxy group, R stands for the alkyl chain group while Y stands for the organofunctional group [19,51]. Using mercaptosilanes in SSSR/Silica vulcanizates, Wagner has demonstrated significant improvements in mixtures with and without coupling agents [45]. For the coupling agent extended versions, 300 % modulus and a 30 % tensile strength increase could be achieved as well as a significant reduction of compression set and heat build-up. This is due to the siloxane linkage which is formed by the reaction between the alkoxy group of the silane and the silanol-group on the silica surface. It reacts either by direct or by indirect condensation after hydrolysis. It is followed by a condensation reaction of neighboring silane molecules through condensation or homocondensation [59,60]. For the silane coupling agent, Figure 2.9 [60] illustrates the reaction of the sulfur with the polymer molecule. It's either a radical or sulfur ion which, however, doesn't impair the principle of the illustrated mechanism.

Figure 2.8 Bound rubber model [58].

Figure 2.9 Silane (TESPT) reaction with rubber [60].

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In Figure 2.10 Blume et al. introduced a proposal [61] of the modification of silica with TESPT in 3D. The reaction starts by the adsorption of silanes at the silica's silanol groups. Mostly with a previous hydrolysis step but also with a direct coupling reaction in case of lower water content. The silane reacts to the isolated and geminal silanol groups. The vicinal silanol groups remain unreacted, they are stabilized by internal hydrogen bonding.[61]

Figure 2.10 Proposal of the silanization reaction in 3D [61].

Polar polymers can also be obtained through modification with maleic anhydride (Figure 2.11). In polypropylene blends, it was found that a compatibilization between nanosilica and polypropylene can be achieved by maleic anhydride grafted polypropylene (PP-g-MAH). The blends displayed reduced agglomerate sizes and finer dispersion [62]. Similar results were observed with maleinized NR by Sahakaro and Beraheng [20].

Figure 2.11 Grafted polymer reaction with silica [62].

2.4. Plasticization of Elastomers

2.4.1. Plasticization Theory

The reasons for the use of plasticizer is to modify the product characteristics – by softening – and improve the processing – by reducing the viscosity. Besides this, they are also used for economic reason in order to use high concentrations of fillers in combination with high concentrations of plasticizers. At the same time, the amount of more expensive polymers can be reduced. In elastomer processing, plasticizers are used to reduce in particular the Mooney viscosity and to improve the flow. The second reason is to modify physical and mechanical properties of the vulcanizates. The reduction of the glass transition temperature, T_g and increase in the softness with lower hardness, modulus and an increase of the elongation [34]. However, the mechanism not always depends on T_g 's between the main polymer and the plasticizer.

The mechanism of a plasticizer is to reduce the intermolecular forces in order to increase the mobilities of the rubber molecules [63,64]. The plasticizing mechanism can be explained by the gel theory. Plasticizers act most efficiently when the interactions between the plasticizer molecules, the interactions between the polymer chains of the rubber as well as the interactions between the plasticizer molecules and the polymer chains are relatively equal. The plasticizer can then be integrated into the polymer chains and increase the mobility.[65]

The selecting of a plasticizer is subjected to the miscibility/compatibility with the main polymer. For the prediction, a general understanding is that similar substances are miscible with each other. Herein, similar can be attributed if a substance is exactly same or if two or more different substances are based on the same class. In both cases, the interactions between the single molecules are similar. These interactions are based on van der Waals forces, dipolar forces and hydrogen bonding. Joel Hildebrandt developed the solubility parameter concept and determines the similarity into one value that can be described and calculated with Equation 2.4.[66]

$$\delta = \sqrt{CED} = \sqrt{\frac{\Delta_v H - R \cdot T}{v_{Mol}}} \quad (2.4)$$

The Hildebrandt solubility parameter δ is defined as the square root of the Cohesion Energy Density (CED). It is derived from the vaporization enthalpy $\Delta_v H$, gas constant R , temperature T and the molar volume v_{Mol} .[66]

In general, if two substances showing a similar solubility parameter δ , a miscibility can be assumed. However, a differentiated observation shows that this is not necessarily the case for all substances. It is mainly caused by the domination of the van der Waals forces whether the

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dipolar forces and hydrogen bonding. The solubility parameter shows therefore a limitation [67]. Hansen further developed the three-dimensional solubility parameter [68]. All interaction are equally taken into consideration (Equation 2.5).

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (2.5)$$

The indices “d”, “p” and “h” are assigned for the three different occurring interaction: d for dispersion interaction (van der Waals forces), p for the dipolar forces and h for the hydrogen bonding forces. The miscibility can be predicted with the single contributions. For the T_g shift in miscible systems, the shift of the glass transition temperature can be predicted by the Fox equation equation 2.6.[11,69]

$$\frac{1}{T_g} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}} \quad (2.6)$$

The T_g is the glass transition temperature of the oil extended polymer. T_{g,1} is the gel point of the plasticizing oil and can be considered to some extend as a glass transition temperature. The T_{g,2} is considered to be the glass transition temperature of the pure polymer. W₁ is the volume of the plasticizing mineral oil and W₂ the volume of the polymer.

Technically, important characteristic items are the viscosity (kinematic viscosity), density, refractive index and viscosity-gravity constant (VGC) [70]. Additionally, the aliphatic or aromatic contents are used to classify the products. The individual elastomers have different preferred VGC ranges [70]. Aromatic oils, for instance, show a relatively high VGC resulting in high and fast absorption in SBR, BR and NR. For tires, high viscous aromatic oils are mostly used [70].

Plasticizers can be generally divided into mineral oils and synthetically and naturally derived liquids. The mineral oils can be paraffinic, naphthenic or aromatic. As a consequence of Health, Safety and Environmental (HSE) concerns, aromatic oils were effectively restricted in 2010 [71]. As a replacement, safer considered MES (Mild Extracted Solvents) and TDAE (Treated Distillated Aromatic Extracts) are commonly used today [65].

Another category of plasticizers are resins. They are typically used to tackify synthetic rubbers. Through the use of tackifiers, better adhesion and sealing can be achieved during the conversion and construction of rubber goods. At the same time, resins reduce the viscosity and improve the processability. In contrast to softeners, they affect the elastic properties less [65]. For NBR and CR, important resins are xylene-formaldehyde resins or phenolic resin. Other resins used for vulcanizates with polar polymers are benzofuran-indene resins. For non-polar diene rubbers like NR, SBR or BR, other hydrocarbon resins are employed: Pine tar based resins, colophony derivatives and coal tar resins. With the introduction of the Directive

2005/69/EC [71] and the respective ban (for highly PNA-containing) on aromatic oils, there is a need for compensation of the deteriorated wet grip of tires which resulted from the lower T_g of the safer oils. Due to the higher T_g of resins compared to TDAE, TDAE-resin mixtures are one option to increase the T_g and therefore improve the wet skid resistance [72]. For this particular purpose, propagated resins are pine tree originated terpene resins and aromatically-modified terpene-phenol resins [73].

2.4.2. Low Molecular Weight 'Liquid' Polymers

Plasticizers are a key ingredient of a rubber compound. As discussed above, they reduce the viscosity by increasing the flow and result in lower hardnesses and moduli on the final product. A disadvantage is the potential bleeding and limited aging resistance. It can be assumed that low molecular weight 'liquid' polymers behave differently. Compared to a mineral plasticizer, the molecular weight is still much higher and the polymer structure is of similar kind with the base polymer. This structural characteristics lower the potential of bleeding and increase the potential to react with the base polymer during vulcanization. They are therefore also commonly called "non-bleeding" or "co-reactive" plasticizer.

Besides the use as plasticizer replacement, liquid polymers are explored for several other purposes. The polymer itself is not a new material class. The first commercial liquid BR ("Plastikator 32") was produced in 1925 [73]. Later, i.e. between the 1950s and 1960s, many major chemical organizations including DuPont "Budium" and Colorado Chemicals "Ricon" explored the production of liquid polymers. However, it was not until the 1970s that more important production volumes could be reached. It was realized throughout the coating and ink industries in western Europe and Japan with their usage of liquid polybutadiene and liquid polyisoprene [74].

The low molecular weight "liquid" polymers are produced similar to common high molecular polymers. The 'liquid' or "L" refers to the liquid character in contrast to high molecular weight base polymers as shown in Figure 2.12 (b): Liquid polyisoprene (Liquid IR: L-IR), liquid polybutadiene (Liquid BR: L-BR) or liquid styrene butadiene-copolymer (Liquid SBR: L-SBR).

During the vulcanization, it is assumed that the liquid polymer co-vulcanizes with the high molecular base rubber [75]. There are two main effects:

1. Plasticization, while changing the mechanical properties only insignificantly, and
2. Co-reaction and non-bleeding due to the fixation of the liquid polymer molecules into the network as shown in Figure 2.12 (a).

Figure 2.12 Mechanism of co-vulcanization (left) of liquid polymers with base rubber and liquid polymer molecular weight range [75].

An important characteristic is the microstructure of the liquid polymer. It includes the molecular weight and distribution, the cis-trans-configuration and the content of 1.2-vinyl as well as 1.4-units. The characteristics can be influenced by the production technology and type of catalyst system. Today, several technologies exist for the production of liquid polymers. The most common one is anionic polymerization.

It provides a controllable range from 90 % or higher 1.2-vinyl to 90 % or higher 1.4-structure. A “living polymer” [75] obtained by living anionic polymerization is considered to provide the widest possible range of microstructural characteristics as well as a low molecular weight distribution that is less than 1.1 [76] as shown in Figure 2.13.

Another technology is the “telopolymerization” [74], a mechanism whose basis is the inclusion in a polymerization recipe of an active chain transfer agent, the “telogen” – in most cases toluene – which possesses a hydrogen atom of sufficient acidity in order to react with a polymeric anion. This technology offers a molecular weight distribution around 1.2, between the living polymers (MWD less than 1.1) and Ziegler-Natta polymerized liquid polydienes (MWD higher than 1.7). There are several other polymerization technologies with lower commercial and technical relevance. They include, e.g., the cationic polymerization or depolymerization of higher molecular weight polydienes. Table 2.1 lists the structural characteristics of three important liquid polydiene classes that are commercially used.

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Figure 2.13. Molecular weight distribution of liquid polybutadienes produced by different production technologies [76].

Table 2.1 Liquid polydienes obtained by “living polymers” [77].

Name	Structure	Mol Weight (M_n)	Melt Viscosity	Glass Transition Temp. ($^{\circ}\text{C}$)
Polyisoprene, liquid Isoprene Rubber (L-IR)	$\left[\text{CH}_2 - \underset{\text{CH}_3}{\text{C}} = \text{CH} - \text{CH}_2 \right]_n$	15,000 to 54,000	15 to 500 Pa*s (38 $^{\circ}\text{C}$)	- 63 $^{\circ}\text{C}$
Polybutadiene, liquid Butadiene Rubber (L-BR)	$\left[\text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2 \right]_m \left[\text{CH}_2 - \underset{\text{CH} = \text{CH}_2}{\text{CH}} \right]_n$	5,000 to 45,000	0.6 to 280 Pa*s (38 $^{\circ}\text{C}$)	- 95 $^{\circ}\text{C}$
1.2-vinyl rich		5,000 to 9,000	0.6 to 280 Pa*s (38 $^{\circ}\text{C}$)	- 85 to - 49 $^{\circ}\text{C}$
Styrene Butadiene Rubber (L-SBR)	$\left[\text{CH}_2 - \underset{\text{C}_6\text{H}_5}{\text{CH}} \right]_I \left[\text{CH}_2 - \text{CH} = \text{CH} - \text{CH}_2 \right]_m \left[\text{CH}_2 - \underset{\text{CH} = \text{CH}_2}{\text{CH}} \right]_n$	8,500 to 10,000	100 Pa*s (60 $^{\circ}\text{C}$) to 350 Pa*s (38 $^{\circ}\text{C}$)	- 14 to - 6 $^{\circ}\text{C}$

Due to the ease of chemical modifications of liquid polymers, these products include a wide range of structural variety and exceed the types listed in Table 2.1. Hydrogenated or partly hydrogenated is, for instance, one common modification type [74]. Hydrogenated liquid polyisoprene can be seen as a mimic to EPM rubber. Other combinations involve copolymers of styrene and isoprene or isoprene and butadiene. All typical modifications that can be done on the high molecular weight polydiene types can also be applied to the liquid polydienes.

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However, in comparison to high molecular weight polymers, the liquid counter types are often easier to modify. The reason for this is based in the higher concentrations of reagents which can be employed in combination with lower amounts of solvents [74]. The most common chemical modification is maleination/carboxylation. The addition of maleic anhydride to polydienes is carried out by free-radical catalysts at high temperatures between 180 and 230 °C in an inert atmosphere. Another benefit is the reactivity, e.g. for crosslinking reactions with polyamines, polyols and epoxy resins. The main advantage, however, is the adhesion promoting performance to several substrates [74]. Another chemical modification is epoxidation. Equivalent to maleic anhydride, epoxide groups can improve the compatibility to polar substances and can be utilized as precursor for several further modifications. Other typical functionalities are hydroxyl-termination and back bone or chain end acrylation.

Considering the production volumes, the tire industry – which is focused in this work – is the most important industry for liquid polymers. As described above, there are three major types in use: L-IR, L-BR and L-SBR, yet for different applications and purposes. Liquid BR is typically used in winter tire treads, thereby improving low temperature properties and abrasion resistances. Liquid SBR is utilized in racing tires to improve wet grip. Liquid IR is mostly employed in high hardness compounds to balance viscosity and hardness.[74]

Apart from the tire segment liquid polymers are mostly used in coatings, sealants and adhesives. It is used to produce semi-finished liquid or pasty products. In these application segment, liquid polymers are used as main components beside fillers, other plasticizers and the crosslinking systems. Functionalized liquid polymers – including carboxylated, epoxidized, hydroxyl terminated or methacrylated – are used to provide extra adhesion to polar surfaces, including metallic or glassy surfaces. Additionally, to the plasticizing function, use is made of liquid polybutadiene as coagents for peroxide curing systems. In EPDM, 1,2-vinyl-rich liquid BR can be employed to replace triallyl cyanurate and other coagents [75]. The liquid polybutadiene shows better curing characteristics and slightly improved mechanical and elastic properties.

Figure 2.14. Maleic anhydride acid functionalized and epoxidized liquid polymers [77].

A new category of a liquid polymer is a polyfarnesene. The monomer, farnesene (C₁₅) is synthesized from a sugar cane extract. It is marketed as a new category of low molecular

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weight diene rubber, liquid farnesene rubber, L-FR. In contrast i.e. to L-BR and L-IR, it is highly branched.[78]

Figure 2.15 Structure of polyfarnesene [79].

2.4.3. Influence of the Molecular Weight and Microstructure

The incorporation of a polymer is influenced by the type, molecular weight and the microstructure of the chosen polymer. This also applies for low molecular weight 'liquid' polymers. The molecular weight is herein of particular concern as it is significantly different to the typical 'solid' polymers with molecular weights usually above 100,000 g/mol. During mixing and vulcanization, the original molecular weight and structure of a polymer is altered [79]. Bartenev et al. have defined a critical molecular weight at 1,000,000 g/mol [80]. A polymer having this or a higher molecular weight starts immediately with the formation of a three-dimensional network. A polymer with a lower molecular weight undergoes first sub-sequential reaction steps prior to the network formation. The added sulfur is used for linking the single polymer chains into a growing and partially crosslinked structure. After achieving the critical molecular weight, the real network formation starts. A study of different molecular weights of different SBR's show deteriorating mechanical characteristics (e.g. tensile strengths, tear) below 50,000 g/mol.[80,81]

The microstructure parameters include styrene content, 1,2-vinyl content, and the percentage of cis or trans configurations. For the styrene content, it is known that tensile strength, tear strength and crack resistance increases with an increase in styrene content until a concentration of approximately 50 % [81]. It is due to the higher stiffness of the bulky styrene groups. A similar tendency based on the same explanation was observed also for an increasing 1,2-vinyl content. Both parameter increases the T_g 's of the polymer and its vulcanizates. The position of the $\tan\delta$ peak shows a linear dependency with the 1,2-vinyl groups [82]. The cis content influences the mechanical properties, too. Increasing cis contents result in higher values of tensile strength, strain at break and tear resistance.[82] It is assumed, that this is caused by a higher reactivity of the cis configuration with sulfur. It was also connected to higher crosslink densities [82]. For silica-filled vulcanizates, Sato further

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confirmed that liquid polybutadiene with high vinyl and high cis content shows a higher reactivity with TESPT and mercaptosilane [83].

The molecular weight has an influence on the dispersion of the filler. Sgodzaj [84] observed a significant effect. In silica-filled compounds, the dispersion is improved with higher molecular weights. The reason is explained by the higher shear forces which goes along with the increasing molecular weights. For silica, the aggregates/ agglomerates are broken down more easily with increasing shear forces which result in a better dispersion. Another interesting finding is that also a broad molecular weight distribution supports the filler dispersion – for both, silica and carbon black. However, there is no explanation given beside the fact that a broad distribution improves the incorporation of the silica into the polymer matrix. The remaining microstructural parameters are the 1,2-vinyl content and the styrene content. The dispersion increases for silica and carbon black with increasing contents of both. It is explained with the stiffer (bulky styrene) polymer chains as well as the higher physical interactions with the fillers.[84]

2.4.3. Aging Properties with Liquid Polymers

Rubber compounds contain certain amounts of lower molecular weight substances, i.e. processing additives, plasticizing oil or residues such as oligomers. These are unvulcanized inside the rubber matrix. During their life time, these substances bleed to the rubber surface, thereby causing losses of the final article performance: Elasticity, strength, softness and appearance. The slow exudation of such oily components leads to an increase in modulus and hardness. Nakazono et al. [85] showed, that this effect is due to the migration and not only to the increase in crosslinking. The migration rate is influenced by molecular weight and differences in polarity between the materials. In styrene-butadiene rubber compounds, the influence of a process oil and some liquid polymers as potential alternatives were studied. Liquid polymers are considered to act as a co-vulcanizable plasticizer with covalent fixation to the rubber matrix.[85,86]

The type of aging itself can be defined as hardening. Softening aging is caused by main chain scission, while hardening aging is caused by an increase in crosslink density due to radical coupling and the exudation. Mechanical properties, extraction (migration) as well as changes in swelling and crosslinking are observed. After an exposure of eight weeks of thermal aging at 100 °C, Nakazono et al. showed a dependence of the processing oil and different liquid polymers (Figure 2.16).[85,86]

The potential of migration can be estimated with extraction tests. It is generally a process where material compounds are separated from specific components, based on their relative

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solubility. It can be used to predict the content of low molecular weight fractions and non-reacted materials. The total extraction – calculated as the sum of acetone, toluene and tetrahydrofuran extraction tests – illustrates lowest migration for the liquid polymers, while it shows yet a strong dependence within the different liquid polymers: Higher molecular polybutadiene (molecular weight $M_w = 26,000$ g/mol) presents the lowest value close to a non-plasticized SBR compound.[85,86]

A similar tendency can be seen in the mechanical properties (hardness, tensile strength and modulus at 100 % elongation). While substituting oil with the different liquid polymers, the three values remain more constant over time. This leads to the conclusion that the liquid polymer is integrated into the rubber network.[85,86]

Figure 2.16 Change in mechanical properties (a) and total extraction (b) in SBR vulcanizates (I: without plasticizer, II: Processing Oil, III: Liquid SBR (molecular weight M_n 8,000 g/mol), IV: Liquid BR (molecular weight M_n 8,000 g/mol), V: Liquid BR (molecular weight M_n 26,000 g/mol) [88] (Acetone Extraction (AE) and Chloroform Extraction (CE))

The results manifest that the polymer network is changed during heating, including scission of the main chain and crosslinking reactions. Crosslinking can be calculated from the volume of the dry polymer as well as the volume of the swollen polymer by the Flory-Rehner equation [89]. The results show higher post crosslinking of non- and oil-plasticized vulcanizates than in the liquid polymer extended counter formulations [86]. A lower migration and better aging resistance can be therefore expected.

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2.5. Low Molecular Weight ‘Liquid’ Polymers in Tire Tread Compounds

Choi et al. tested different low molecular weight liquid polybutadienes in an ESBR formulation with Silica. The molecular weight was varied between 3.900 and 8.000 g/mol, whereas the 1.2-vinyl content was varied between 28 % and 85 %. The main invention was the plasticizing effect: the addition of 4 phr of liquid polymer results by approximately 10 % of drop in the Mooney viscosity. This leads to improved processability. The crosslinking density is reduced and the 100 % modulus reduces very slightly of about 2-4 %, while the 300 % modulus – indicating the polymer-filler interaction – decreases as well and somehow more significantly (depending on the liquid BR between app. 5-20 %).[88]

In the tire industry, the initial and most common use of liquid polymers is the application as a co-vulcanizable plasticizer: Plasticizing but maintaining a good balance of mechanical and elastic properties at the same time. Table 2.2 shows a comparison of a liquid polyisoprene (LIR-50, Mn 48,000 g/mol) as a partial replacement of natural rubber. The results illustrates that the addition of 4 phr. reduces the Mooney viscosity from 78 to 72 (-9 %). The Shore hardness remains unchanged and the tensile strength was only slightly reduced. A similar formulation showed improved processability (extrudate surface measured according ASTM D2230) and also a slightly improvement of the carbon black dispersion. The results lead to the conclusion that a co-reaction of the liquid polymer with the base rubber has taken place.[78]

Table 2.2 Properties of a liquid polyisoprene modified vulcanizate [79].

Formulation	Reference	Liquid Rubber Extended
NR (RSS#3)	70	66
SBR (1502)	30	30
Liquid IR (LIR-50)	0	4
Carbon black (FEF)	50	50
Curatives and Antioxidant	ZnO (5), Stearic Acid (2), Sulfur (2.2) CBS (1.2), IPPD (1)	
Mooney Viscosity ML 1+4 (100°C)	79	72
Shore A Hardness	71	71
Tackiness (N) (Sigma Tack) at 25°C 90.5% RH	7,5	13

2.6. Improved Filler Dispersion with Functionalized Liquid Polymers

As discussed above, the filler dispersion can be related to the filler-filler and filler-polymer interactions. It is influenced by material properties and the processing, the final mixing performance. In rubber-filler mixing it is a trade-off viscosity and shearing. The viscosity reduction can possibly improve the dispersion. However, it's also reducing the necessary shear forces inside the compounds during mixing. Tire producer and some researches claim improvements in the distribution (*Chapter 2.7*). However, it is not yet well understood how the two parameters contribute and compete.

Saramolee et al. studied the use of different epoxidized low molecular weight natural rubber, obtained by depolymerization of higher molecular weight natural rubber [89]. The molecular weight M_w was in the range of 49.000 to 65.000 g/mol, while the epoxide content was between 0 and 51 mol%. The introduction was done in NR/Silica compounds as a substitution for the silane coupling agent and in NR/CB compounds. The authors differentiate the pure plasticizing effect and a property improvement. The plasticizing effect can be seen in both compound types. The Mooney and complex viscosities are reduced. In the case of the CB filled vulcanizates, the plasticizing effect is independent from the epoxidization rate. Nonetheless, in the silica-filled compounds, due to the reaction between the epoxide group and the hydroxyl group of the silica surface, the epoxide concentration has an effect. The 51 mol% epoxide containing polymer shows the highest viscosity reduction. In case of the silica vulcanizates, the higher concentrations of epoxide containing polymers (10 to 15 phr) display an upward trend for the viscosity, curing torques and Payne effect. This can be explained by the self-association and self-crosslinking of the epoxide groups. In contrast to the CB vulcanizates, in the silica vulcanizates, the Payne effect can be significantly reduced, compared to non-silanized vulcanizates and 0 mol% epoxide containing polymers, yet it is still slightly higher in comparison to the vulcanizate comprising a silane coupling agent. Compared to the compound properties such as viscosities, curing kinetics, Payne effects and mechanical properties, the two vulcanizates with silane coupling agent and 10 phr of the 28 mol% epoxide containing NR display relatively good property characteristics. The DMA analysis provides a different result. The T_g of the blank vulcanizate is at $-50\text{ }^{\circ}\text{C}$. When the TESPT coupling agent is used, the T_g is slightly shifted to $-48\text{ }^{\circ}\text{C}$. This change is associated with the reduced mobility of the polymers and the increased crosslinking network due to the silica-polymer interaction. In contrast, the T_g 's of the vulcanizates containing the epoxidized polymers remain at $-50\text{ }^{\circ}\text{C}$. It is assumed that the crosslinking density is not increased. A more important observation, however, is the reduced $\tan\delta$ maximum. The higher the epoxide content, the lower is the $\tan\delta$ maximum. This can be explained by higher self-association of the epoxide groups and reduced chain mobility due to the epoxide modification versus the pure NR. Consequently, the DMA performance

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indications are not favorable for tires, since lower temperatures display lower hysteresis values and the service temperature area shows potentially higher service temperatures.[89]

Braum and Jacobi [90] investigated an epoxidized and silica grafted liquid polybutadiene in silica filled SSBR/BR blends. The mechanical properties and dynamic properties were evaluated over different epoxidation degrees, molecular weight of the low molecular weight liquid polybutadiene and its structure. The silane coupling agent was partially or fully replaced. Previously, the use of epoxidized NR was also approached by Kaewsakul et. al [91] and Saramolee et al. [94]. Compounds can achieve similar properties – viscosities and Payne effects – to compounds using TESPT, yet with some drawbacks on the mechanical properties. The investigation of Braum and Jacobi [90], is using a silica grafted liquid BR achieved from an epoxidized liquid BR as precursor. The vulcanizates are SSBR/BR/Silica (phr ratio of 25/95/62) based. The reference uses 5 phr of TESPT. The silica grafted liquid BR were added between 75 and 100 phr as replacement for a partial replacement of the silica, BR and TESPT.

Both hydroxyl terminated and homopolymer precursors illustrate a lower strain dependence than the blank vulcanizate without using a silane coupling agent. 13 mol% epoxidization displays the best results. 8 mol% provides a slightly higher Payne effect, whereas 17 and 28 mol% demonstrate the highest strain dependence. At the homopolymers, the molecular weight with 8,000 g/mol shows the lowest Payne effect while both the 26,000 g/mol and 44,000 g/mol based grades are comparably high. For the epoxidized liquid BR grafted silica filled vulcanizates, the hysteresis and maximum $\tan\delta$ at low temperatures decline as the degree of epoxidation rate increases. The homopolymer backbones show more diverse results. Similar to the non-epoxidized countertypes, a clear reduction of the E' was measured for the 8,000 g/mol type. This version also illustrates a similar maximum $\tan\delta$ to the reference vulcanizate, the higher molecular types showing similar characteristics and reduced hysteresis at low temperature.[90]

Based on these results, a model was proposed to explain the findings (Figure 2.18) [90]. The liquid polymer builds an immobilized layer. The chemical and physical bonds are marked with A and B. As the molecular weight increases, the amount of entanglements and co-vulcanization rises. A higher epoxidization degree increases the chemical bonding to the silica. Both parameters, however, are assumed to end up in similar property tendencies.

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Figure 2.18 Schematic mechanism of the reaction between the silica and epoxidized liquid polybutadiene [90].

Fang et al. investigated liquid polymers in combination with rubber/clay nanocomposites in ESBR (ESBR/Liquid Polymer). One approach to mix is to use a solvent assistant dispersion method wherein the polymer is solved. However, the difficulty of this approach is to release the solvent after the mixing. The approach of using the liquid polymers is therefore to replace the solvent assistant method. The liquid polymer utilized is a liquid BR with 3,200 g/mol. molecular weight and backbone functionalized with maleic anhydride. The clay and liquid polymer were prepared as a masterbatch (Liquid Polymer/Clay = 10 phr/5 phr, 10 phr/10 phr, 10 phr/15 phr, 10 phr/20 phr) by high speed centrifugal mixing. Compared to the reference mixtures without the liquid functionalized polymer, the use of the liquid polymer/clay masterbatch indicated a better dispersion measured by X-ray diffraction as well as higher tensile properties and elongations.[92]

Castellano et al. synthesized and evaluated two new coupling agents based on polybutadiene oligomers, designated as 3-mercapto-propyltrimethoxysilane grafted polybutadiene, as illustrated in Figure 2.19. Herein, two different polybutadienes were compared: One with Mn 900 g/mol and approx. 40 % content of 1,2-vinyl units and another one with Mn 5,000 g/mol with approx. 20 % content of 1,2-vinyl units. Their performances were compared in a relatively low-filled formulation comprising ESBR/CB/Silica (=100 phr/30 phr/ 30 phr) against TESPT and without a coupling agent. The investigation was divided into an in-situ and a pre-graft method. In the former approach, the new coupling agents were added directly to the ingredients prior to the mixing and vulcanization – similar to the common method of adding a conventional silane coupling agent. The latter approach includes a separate step, where the new coupling agent was grafted onto the surface of the silica; in this respect, it is a similar approach to the epoxidized liquid polymers grafted silica introduced by Braum and Jacobi [90]. The grafting degree was between 3.8 and 17 %.[93]

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Figure 2.19 Scheme of the 3-mercaptopropyltrimethoxysilane grafted polybutadiene and its bonding to the silica surface.[93]

The morphology and filler dispersion was evaluated by TEM, as is shown in Figure 2.20. The vulcanizates without coupling agents (Figure 2.20 (a)) provide a low dispersed morphology including agglomerates, in the picture about approx. 15 μm . It can be observed that the dispersion becomes finer with reduced agglomeration when TESPT is used as a coupling agent (Figure 2.20 (b)). This is also the case for the new polybutadiene-based coupling agents, particularly when comparing Figures 2.20 (c), (e) and (f) (with similar grafting degrees of around 10 %). It was not possible to draw a clear conclusion for the dispersion quality of the situ and pre-grafted morphologies. The authors assessed, however, that a higher grafting degree (17 %) tended to give a finer dispersion (Figure 2.20 (d)). The qualitative evaluation of the morphology is confirmed by the results of the Payne effect. Compared to the blank formulation without a coupling agent, a clear reduction of the Payne effect was obtained. Furthermore, the new coupling agents with around 10 % grafting degree showed similar results compared to the vulcanizates comprising TESPT, and even lower values with the version of 17 % grafting degree. For the two approaches, i.e. in-situ and pre-grafting silica, a clear conclusion could not be drawn. The same counts for the dependence of the influence from the molecular weight and 1,2-vinyl content. Only mixed results without a clear tendency were observed.[93]

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Figure 2.20 TEM results of ESRB/CB/Silica vulcanizates: no coupling agent (a), TESPT (b), 3-mercaptopropyltrimethoxysilane grafted polybutadiene (c, e, f), higher grafting degree of 3-mercaptopropyltrimethoxysilane grafted polybutadiene (d) [93].

Salort and Henning reported that a silane-terminated liquid polybutadiene can work synergistically with silane coupling agents: the silane coupling agent reacts with the silica surface and the liquid polymer with the silane coupling agent. It shows an improved microdispersion according to the Payne effect result and changes in the viscoelastic properties, leading to a potentially improved balance of tire performances. The authors suggest that a both-end silane-terminated liquid polybutadiene chain can condensate with another chain via one functional group as well as interact with the silane coupling agent. By this, it forms a higher molecular weight and creates an interpenetrating network.[94]

2.7. Improvement of Tires – A Patent Review

In recent years, many patents about the improvement of tire performances with liquid polymers have been published from different tire producers (i.e. Continental Reifen, Pirelli Tyre, Sumitomo Rubber and Bridgestone). Improvements are claimed for the abrasion resistance and better balance for low temperature properties in winter and all season tire properties [95-102,107]. The second big applications field is in racing tires. Herein the wet and dry grip properties are claimed to be improved [103,104]. From the characteristics, the patents

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concluding the advantages of the used of liquid polymers in particular as a contribution to improved filler dispersions [105-111].

Continental Reifen claims a series of patents of highly filled silica SSBR/BR vulcanizates. In WO2012084360 [95], the addition of 17.5 phr liquid BR (Mn 2,500 g/mol) improves the abrasion resistance index up to 10 % with only a slight effect on the breaking performance and rolling resistance (both are only 2-3 % worse). Another 22.5 phr (40 phr in total) improves the abrasion by 14 % and do not show disadvantages for the other considered properties, i.e. dry and wet breaking as well as rolling resistance. Based on the total solid polydiene concentration, Continental claims the use of liquid BR (Mn 500 to 9,000 g/mol) for up to 50 phr. The use of liquid BR could also be confirmed for winter tires in an earlier filed patent [96]. In a composition of NR/BR/SSBR/Silica, 40 phr of liquid BR (Mn 1,100 and 2,500 g/mol) improves the snowy traction compared to a comparative example with TDAE. Similar to these patents, a significant improvement of the abrasion resistance (30 % higher) could be achieved without affecting dry handling, dry and wet breaking as well as rolling resistance in EP2518106A1.[99] EP2345696A1 [97], specifically employing liquid BR (Mn 7,000 g/mol) and emphasizing the molecular range as main claim for excellent winter tire properties.[95-97]

Similar ice grip tendencies were discovered earlier by Yokohama Rubber. In a special tire composition comprising NR, BR and CB, the introduction of 15 phr of a liquid polybutadiene with Mw 16,000 enhanced the friction on ice – especially more significantly after heat aging.[98]

Yokohama Rubber investigated and patented the use of liquid polymers as a plasticizer in all-season tire applications. The results display a good balance of low temperature properties, wear resistance and dry/wet grip. The investigation includes a design of experiment with varying contents and a combination of three ingredients: aromatic oil, liquid polymer and an ester plasticizer (benzyl butyl phthalate, diisononyl phthalate or bis (2-ethylhexyl phthalate). Further, the effect of filler contents and microstructure of the plasticizers were evaluated. An excerpt of the results is summarized in Table 2.7. The combination of liquid polybutadiene (Mn 2,500 g/mol, 28 % 1.2-vinyl) and an ester plasticizer showed improved balanced performances in contrast to the reference comprising an aromatic plasticizer. Replacing 50 % or 100 % of the aromatic oil by the liquid polymer and the ester plasticizer in the ratio 2:1, the wet grip, wear resistance and low temperature properties are enhanced, yet at the costs of the rolling resistance. Increasing the filler contents and matching ratios compensate the overall properties. Another improvement of the overall performance can be achieved by exchanging the carbon black (CB) type. The change from N234 (113 m²/g STSA) to the finer N110 (117 m²/g STSA) illustrates improved overall properties and thus compensates for the drawback of the rolling resistance, with slightly reduced low temperature properties. A change

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to the less finer carbon black N550 (39 m²/g STSA) pronounces the improvement with the liquid polymer. This formulation shows three best low temperature properties among all tested formulations. The type of liquid polybutadiene shows an effect too: the exchange of the above polybutadiene with a higher 1.2-vinyl content (M_n 2.9k, 80 % 1.2-vinyl) demonstrates improved overall performance versus the reference. A similar tendency was observed when increasing the molecular weight (M_n 4.5k).[99]

Table 2.7. Tire properties (relative improvements) for different phr ratios of carbon black (CB), silica and oil, liquid polymer (LP) and ester plasticizer [99].

	Reference	1	2	3	4	5
CB / Silica	10 / 70	20 / 80	20 / 80	10 / 70	10 / 70	10 / 70
Oil / LP / Ester	30 / 0 / 0	15 / 10 / 5	0 / 20 / 10	20 / 10 / 0	15 / 10 / 5	0 / 10 / 20
300% Modulus (%)	100	103	102	94	104	98
Wet Grip (%)	100	109	108	97	105	101
Wear Resistance (%)	100	105	110	101	98	101
Rolling Resistance (%)	100	94	90	99	101	93
Low Temp. Properties (%)	100	103	107	103	96	107

In order to enhance the wet grip of a tire tread, SBR with a high glass transition temperature or high amount of CB with low particle size is typically applied. Sumitomo Rubber claimed a tire tread composition with well-balanced performance of wet grip and resistance for embrittlement at low temperature. In this invention, a rubber composition comprises SBR, BR and NR, and a higher amount of silica. The formulation provides well-balanced performance on wear resistance, wet grip and resistance against embrittlement at low temperature. In this formulation of SBR, NR, BR and Silica, hydroxyl terminated L-BR (M_n 1,500 g/mol) is one key ingredient and can be added up to 20 wt.%.[100]

In another patent, Sumitomo Rubber published a composition with epoxidized liquid polyisoprene (L-IR). It mentioned improved abrasion resistance and decreased hardness at low temperatures without affecting other properties. Beside the epoxidized L-IR, the composition contains silica as well as CB, NR and BR.[101]

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In 2017, a Pirelli tire patent [102] published a combination of three alternative plasticizers: Terpene/styrene resin, liquid polybutadiene and TDAE. Two vulcanizates were investigated: One for the intention of winter tires and another for the intention for all-seasons tires. In both cases the vulcanizates are considered as highly silica filled (95 phr). The winter tire formulation consists of modified SBR (40 phr), BR (32 phr) and NR (28 phr), the all-season tire formulation merely consists of SBR (74.5 phr) and BR (25.5 phr). In the case of the winter tire formulation, the main part of the TDAE (55 phr) was replaced either 1) by the liquid polybutadiene, or 2) by the terpene/styrene copolymer, or 3) by a combination of liquid polybutadiene and terpene resin. In case of the DMA results, the patent doesn't show a clear tendency. Furthermore, the Modulus at 300 % did not give an indication of an increase that may lead to a conclusion of increased filler-polymer interaction. By the use of the liquid polybutadiene and the combination with the terpene/styrene resin, however, the Modulus at 100 % drops more significantly compared to the modulus at 300 %, which, in turn, indicates a lower filler-filler interaction. The Shore hardness is slightly dropped compared to the pure TDAE. The adjustment can be compensated by an increased crosslinking density. In addition to the conventional mixing and dispersion, the investigated vulcanizates were produced by a separate mixing step of continuous blending under vacuum. The performance indicators measured by DMA displayed, that the Shore hardness and the Modulus are slightly improved but the tendencies between the different formulations are insignificant. However, Pirelli showed data of actual tire performance tests. The formulation with the liquid polybutadiene illustrates improved snow grip while the combination of liquid polybutadiene and terpene/styrene shows clearly improved overall performances. Compared to the TDAE: Driving and breaking on snow (3% improvement), Behavior on wet (10 % improvement), behavior on dry (13 % improvement), breaking on wet (2 % improvement) and breaking on dry (2 % improvement).[102]

Racing tires need high grip and high wear resistance, therefore SBR with high glass transition temperature is generally applied. For racing tires, Sumitomo Rubber published a patent for a rubber composition which specifically improves the grip performance under high and low temperature for long duration as well as wear resistance. Normally, Zinc Oxide (ZnO), with a specific average particle diameter of less than 200nm, makes it difficult to be well dispersed in rubber composition and deteriorates grip performance. A rubber composition comprising SBR, ZnO with low particle size and additionally liquid SBR shows improved grip performance at both low and high temperatures, measured by tire tests. This is possibly attributed to a better ZnO dispersion. It might also enhance the grip performance and wear resistance for a longer duration.[103]

Bridgestone investigated different microstructural influences of liquid SBR, solid SBR and different resins (Figure 2.21.). The formulations are combinations of solid SBR (100 phr),

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hydrogenated liquid SBR (80 phr), CB (80 phr) and resins (40 phr). The targeted property was defined as “dry gripping characteristics” tested by real tire tests. This value is proportional to the average lap time required for a defined car and driving condition. From the polymer microstructures, excellent results were achieved from solid SBR with 33 % styrene content, molecular weight M_w 700,000 g/mol, and 40 % 1.2-vinyl content together in a combination with liquid SBR with 50 % styrene, molecular weight M_w 15,000 g/mol and 85 % hydrogenation rate. In both cases, for the liquid and solid type SBR, the reduction of the styrene content deteriorates the grip values, possibly correlating with the change of the glass transition temperature. Another parameter is the molecular weight. In case of the liquid SBR, this characteristic appears to have a lower dependence within the analyzed range: Lowering the molecular weight from M_w 15,000 to M_w 3,000 did not show any significant influence. However, changing the molecular weight of the solid SBR displays a clear influence, yet without a clear tendency or conclusion about the direction. A higher 1.2-vinyl content typically results in higher hysteresis values, thereby potentially increasing the heat build-up and dry grip. Nonetheless, in the solid SBR case, 40 % 1.2-vinyl content of the liquid SBR appears to be the optimum range, a further increase deteriorates the dry grip performance. Another parameter investigated in the liquid SBR is the hydrogenation rate, varied from 0 to 85 %. The results indicate that a higher hydrogenation increases the dry grip performance. In another separate test plan, the effect of different resins was investigated as shown in Figure 2.22. For the specific properties wet grip, dry grip and hysteresis, resins and liquid SBR show a good synergy with common resins like coumarone-indene resins, aromatic or aliphatic C9 resins, C5/C9 resins, and phenolic resins. The highest grip performance was achieved with terpene-resins. Enhancements were achieved by alkylphenol resins and dicyclopentadiene (DCPD), yet merely to a lower extent.[104]

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Figure 2.21 Relative performance of dry grip of SSBR/L-SBR/Resin compounds with different L-SBR's (a) and high molecular weight SSBR (b). Variation of the styrene content (St.), molecular weight (with "k" for 1,000 in g/mol and degree of hydrogenation (hydr.) [104].

Figure 2.22 Relative performance of dry and wet grip and the $\tan\delta$ at 50 °C of SBR/L-SBR/Resin compounds with different resins [104].

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Liquid rubber is employed to enhance dry and wet grip of tires. However, it can adhere to the internal mixer walls and contribute less to the distribution. Sumitomo Rubber describes this phenomena as a result of the viscosity drop due to the use of liquid polymers. The main claim of their invention is therefore a production method of a rubber composition with well-dispersed carbon black and silica that avoids such scattering or adhesion of the rubber to the kneader. The considered formulation is an oil extended SBR (150 phr) with CB and silica, 70 phr/0 phr and 10 phr/60 phr, respectively. A liquid SBR in the range of Mw 1,000 to 10,000 was prepared as a masterbatch with silica or carbon black, each including two different types. The results provide 5 to 8 % better filler dispersions and much lower rubber residues inside the mixer. The main claims of this invention include the incorporation of the liquid SBR and the use of the masterbatch.[105]

Toyo Tire invented a rubber composition for improved tire heat build-up. This formulation contained a silica surface treated with sulfur that contains a silane coupling agent and modified liquid polymer - or a sulfur containing silica, amino silane coupling agent and modified liquid rubber. It is commented that the silica dispersion in the rubber composition is improved compared to the reference compound. In this invention, the modified liquid rubber is, for instance, a two end functionalized diene polymer which possesses amino-, carboxy-, acid anhydride-, epoxide-, or hydroxy-group at the polymer chain end.[106]

Yokohama Rubber published a combination of a low molecular weight liquid polymer and a carboxylated liquid polymer for good dispersion, in particular for high specific surface areas of silica (nitrogen adsorption specific surface area, (N₂SA), of 194 to 225 m²/g and (CTAB) of 170 to 210 m²/g). The formulation comprises SBR, BR, silica and aromatic oil (80 phr / 20 phr / 80 phr to 130 phr / 10 phr to 15 phr). Two different liquid polyisoprenes were applied: A homopolymer with Mn 54,000 and a carboxyl grafted polyisoprene with Mn 34,000 g/mol and an average of 10 functional groups per polymer chain. The liquid types were added as a partial replacement of the oil. The carboxylated liquid polymer displays significantly reduced rolling resistance compared to the control compound indicated by lower tan δ at 60 °C values. At the same time, the samples show only slight changes in hardness and tear resistance. The comparison of the non-functionalized homopolymer with the aromatic oil does not illustrate any significance and merely a slight change in terms of the rolling resistance.[107]

A production method for a polymer composition with an L-SBR and an amino-, carboxyl-, epoxide- or hydroxyl-modified liquid polymer, as well as a silica were investigated by Asahi Kasei. This invention specifies a production method by adjusting each component and mixing conditions. The patent claims good silica dispersion, vulcanization characteristics, tensile properties and excellent balance of rolling resistance, wet grip and wear resistance. The tested amino-, carboxyl- and hydroxyl-terminated liquid polymers were in the range of Mw 2,800 to

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3,500 g/mol. The compared non-functionalized liquid polymer had a molecular weight of Mn 7,000 g/mol. Compared to the non-functionalized liquid polymer, all three modification types increased the viscosities and displayed higher wet grip (approx. 20 %), but also higher rolling resistance (approx. 15 %). As indicated by the DMA measurement, different vulcanizate properties can also be reached by changing the introduction of the liquid polymer. When the modified liquid polymers are added into the first mixing step together with the solid SBR, higher wet grip and lower rolling resistance can be achieved, compared to the results realized by the addition of the liquid polymers in the second mixing step - together with curatives and fillers.[108]

Toyo claimed alkoxysilyl modified liquid polymers for improved CB dispersion. The rubber composition comprise a combination of NR/BR and CB as well as the modified liquid polymers. The investigation include a test plan with different liquid polymers: Liquid IR (Mn 28,000 g/mol), liquid BR (Mn 7,000 g/mol), liquid SBR (Mn 3,200 g/mol), hydroxyl terminated IR (Mn 2,500 g/mol), BR (Mn 2,800 g/mol), alkoxysilyl modified IR (Mn 2,500 g/mol of precursor IR) and BR (Mn 2,800 of precursor BR). Even for the non-modified versions, the 100% moduli were decreased between 7 % and 9 %. The heat build-up was reduced by 2 % (L-IR) and 6 % (L-BR). Only the liquid SBR showed an increased in heat build-up. The two hydroxyl-terminated polymers displayed a slight decrease of the moduli at 100 %, between 10 % and 12 % decreases whereas the heat build-up is maintained. For the alkoxysilyl modified types, an increased drop of up to 18 % heat build-up was observed. However, the modulus at 100 % rises.[109]

Kuraray investigated the use of different liquid IR and BR, modified with maleic anhydride and maleic acid monomethyl ester. For a tire formulation comprising SSBR, TDAE, silica, curatives and additives, they assumed a better dispersability and better abrasion resistance of the vulcanisate while simultaneously keeping a well-balanced rolling resistance, steering stability and ice grip evaluated and estimated by DMA of the tire made thereof. The used liquid IR and BR types vary between Mn 30,000 g/mol to 100,000 g/mol molecular weight and an average of 5 to 70 functional groups per polymer chain. In case of the maleic anhydride, an improvement could be seen in abrasion resistance (2 to 5 % improvement), wet traction (5 %) and rolling resistance (5 %). The ice grip was also slightly enhanced. However, no clear conclusion could be drawn for the dependence on the molecular weight as well as on the degree of functionalization. The rolling resistance shows s a slightly higher reduction for the liquid BR types. The IR modified with maleic acid monomethyl ester displays the highest potential to improve the steering stability with improvements up to 15 %.[110,111]

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CHAPTER 3

STRUCTURE-PROPERTY RELATIONSHIP OF LOW MOLECULAR WEIGHT ‘LIQUID’ POLYMERS

In Blends of Sulfur Cured SSBR-rich Compounds

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Abstract

In recent years, many patents have been published that are claiming the use of low molecular weight ‘liquid’ polymers in tire tread applications. Herein, tire producers generally introduce improved balances of the tire performances such as wet grip, abrasion resistance and rolling resistance. To understand the influence of the low molecular weight ‘liquid’ polymers in detail, an investigation was carried out to create more clarity about the influence of the structure of these polymers on in-rubber properties and about their interaction with the base polymers and fillers. One basic formulation was selected: A silica filled compound with styrene butadiene copolymer (SSBR), polybutadiene (BR) and natural rubber (NR) that is representing a winter tire tread formulation. Different structures of the low molecular weight ‘liquid’ polymer were added to this compound and compared. Results are discussed for the curing torques and crosslink densities to evaluate the influence on the crosslinking. Payne effect and bound rubber content was measured to evaluate the filler-filler interactions and filler-polymer interactions, respectively. The mechanical properties and dynamic mechanical analysis results deliver finally indications for the expected tire performance.

3.1. Introduction

This investigation focuses on the usage of low molecular weight polymers in passenger car tire applications, particularly compounds used in winter tire treads. The molecular weight typically ranges from 1,000 to 50,000 g/mol [1]. Liquid Butadiene Rubber (L-BR), Liquid Isoprene Rubber (L-IR) and Liquid Styrene-Butadiene Rubber (L-SBR), commonly called “Liquid Polymers”, are special materials that modify the softness and elastic properties.

Industrially manufactured “Liquid Polymers” are widely used as a co-vulcanizable plasticizer in tires, mechanical rubber compounds, plastic products, printing inks, paints and coatings or sealants. “Liquid” refers to the physical state as a result from the low molecular weight. However, they are produced in a similar way than solid diene polymers and copolymers [2]. The first L-BR, “Plastikator 32”, was produced in 1925 in Germany [3]. Later, in the fifties, many major chemical corporations including DuPont, Budium, and Colorado Chemicals, Ricon, explored the production of liquid polymers [2]. However, it was not before the 1970s, that more significant production volumes were achieved. It was realized by introducing these new materials to the coating and ink industry in Western Europe and Japan [3]. Besides this, nowadays the main use is in tires.

In recent years, many patents about the improvement of tire performances with liquid polymers have been filed from different tire producers [4-7]. Improvements are claimed for the abrasion resistance and for a better balance for low temperature properties in winter tires [4,5]. The second big application field are racing tires. Herein the wet and dry grip properties are claimed to be improved [6,7]. From the mixture characteristics, the patents concluding the advantages of the use of Liquid Polymers as a contribution to improved filler distributions. Choi et al. [8] also showed similar conclusions in their research of L-BR in a silica-filled ESBR compound. Reduced Mooney viscosities, reduced crosslinking densities and reduced Modulus - implying the more destructive filler-filler interactions – were also observed.

The patents describe the effects and performances of the tire formulations that comprises the liquid polymers. However, there are no publications that describes the reasons for the observed effects. A better understanding of it would lead to more effective developments and usages in tire tread compounds. Therefore, the goal of the present investigation is to provide more clarity about the effects of liquid polymers in tire formulations: i) influence of the polymer structure of liquid polymers on crosslinking and mechanical properties; ii) the impact on the filler interactions and the dynamic mechanical properties of the liquid polymers in-rubber performances.

For the study, a passenger car tire tread formulation was defined according to the references [4-7]. This formulation contains silica as a filler and SSBR, BR and NR as the polymer

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composition and TDAE as a standard plasticizer. The compound filled only with TDAE was used as reference. The liquid polymer was used to replace the TDAE and study the properties as an alternative plasticizer.

3.2. Experimental

3.2.1. Raw Materials

The raw materials used are commonly known in the tire industry and commercially available. The following raw materials were used: Solution polymerized styrene-butadiene copolymer (SSBR), SPRINTAN™ 4601 supplied by Trinseo, high cis-polybutadiene (BR), BUNA CB24 supplied by Arlanxco and ribbed smoked natural rubber sheets (RSS3), supplied from Saksham Gati were used as polymers. Carbon black (N330) and highly dispersible silica, ULTRASIL® 7000 with organosilane, bis(triethoxysilylpropyl)disulfide (TESPD), Si266 were used as filler system, all supplied from Evonik. 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. Rubber accelerators used throughout the formulations were n-cyclohexyl-2-benzothiazolesulfenamide (CBS), supplied from Flexsys and diphenyl guanidine (DPG), supplied from Sigma Aldrich. As a commonly used plasticizer, an aromatic oil, Treated Distillate Aromatic Extract (TDAE), VIVATEC 500, supplied from Hansen & Rosenthal was used for the comparison with the different liquid polymers.

The low molecular weight polydienes were selected from Kuraray to cover a wide range of types (butadiene, isoprene and styrene-butadiene), molecular weights and 1,2-vinyl contents. The main properties of these grades are shown in Table 3.1. The "L" refers to liquid or low molecular weight polymer; "BR", "IR", "SBR" refer to the type of polymer: butadiene, isoprene or styrene-butadiene rubber, respectively. The number refers to the molecular weight (M_N) of the polymer.

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Table 3.1 Main properties of the liquid polybutadiene, polyisoprene and styrene-butadiene copolymer [1].

Polymer	Product Name	Monomer	Molecular Weight (<i>M_n</i> , g/mol)	1,2-vinyl (mol%)	T _g (°C)	Viscosity (Pa·s at 38 °C)
L-BR-8.0	L-BR-307	Butadiene	8,000	Low ¹	-95	1.5
L-BR-9.0	L-BR-352	Butadiene	9,000	High ¹	-60	6
L-BR-45.0	L-BR-300	Butadiene	45,000	Low	-95	280
L-IR-10.0	L-IR-10	Isoprene	10,000	Low	-63	3
L-SBR-8.5²	L-SBR-820	Styrene, Butadiene	8,500	Low	-14	350

¹) L-BR-8.0 with low cis content, L-BR-9.0 with high cis content according to the supplier

²) L-SBR-8.5 with low styrene content (15 - 30 %) according to the supplier

3.2.2. Preparation of Blends and Sample Plates

Table 3.2 shows the SSBR-rich/Silica based winter tire tread formulation. The liquid polymer is used as replacement of the plasticizer TDAE.

The compounds were mixed in three stages. The first two steps were 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, carbon black, 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 7:20 (minute:second). The starting temperature of the 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. The second mixing step was applied to homogenize the compound, 16 hours 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} of the specific compounds, obtained from Figure 3.1a. The cured specimens

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measured 100 mm in length and width and 2.0 mm in thickness. The liquid polymer was used to replace the TDAE and study the influence on the properties as an alternative plasticizer.

Table 3.2 Reference compound for the winter tire tread study.

Formulation	Concentration
SSBR	65
BR	25
NR	10
Silica	80
Carbon Black	20
TESPD	6
TDAE or Liquid Polymer	25
Zinc Oxide	3
Additives	1.5 (6PPD) 1.7 (Stearic Acid) 1.5 (Wax)
Sulfur	1.4
Accelerator	1.7 (CBS) 2.0 (DPG)

3.2.3. 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 minutes. The frequencies applied were 1.667 and 10 Hz. The optimal vulcanization time (t_{90}) of the compounds was determined.

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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 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 ($\tan \delta$ at -50 °C), wet grip performance ($\tan \delta$ at 0 °C) and rolling resistance ($\tan \delta$ at 70 °C) can be determined from the data.

3.2.4. Filler-Filler and Filler-Polymer Interactions

The Payne effect and the Bound Rubber Content (BRC) was measured to study the filler-filler and filler-polymer interactions. Both measurements provide an indication of the microdispersion of the filler.

Payne Effect

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.

Bound Rubber Content

Approximately, 0.25 to 0.3 g of the uncured compound obtained after the second mixing without sulfur and accelerators were introduced into a glass container and mixed/dissolved in 20 ml toluene. The samples were removed after 7 days at room temperature from the solvent and dried for 24 hours at 85 °C. The bound rubber measurements were carried out with and without ammonia treatment. The total bound rubber is determined without ammonia treatment. The chemical bound rubber is with ammonia treatment and cleaves the physical linkages between the polymer chains and the silica [9]. The bound rubber content was calculated according to Equation 3.1 [9]:

$$\text{Bound Rubber Content (\%)} = \frac{W_{fg} - W_f}{W_p} * 100 \quad (3.1)$$

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Where W_{ig} (g) is the weight of the filler and the bound rubber. It is determined from the sample weight after exposure in solvent. W_p (g) is the polymer amount in the sample and W_f (g) is the filler amount in the sample. W_p and W_f are calculated from the formulation.

3.2.5. Crosslinking 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 [10] (Equation 3.2):

$$\nu = - \frac{\ln(1-V_r) + V_r + \chi V_r^2}{V_0 \left(V_r^{\frac{1}{3}} - \frac{2V_r}{f} \right)} \quad (3.2)$$

ν is the CLD per unit volume (mol/cm³), 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 cm³/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. [11]. 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 [12]. However, in the present investigation the filler content and the filler system are the same for all compositions. For this reason, the crosslink densities were calculated without the Kraus correction.

3.3. Results and Discussion

3.3.1. Curing Characteristics and Crosslinking Density (CLD)

Curing Characteristics

The cure characteristics of the sulfur vulcanized mixtures with different liquid polymers are depicted in Figure 3.1a. All compounds comprising the liquid polymers showing clear differences in the curing kinetics depending on their molecular weight, viscosity and polymer

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structure. In general, the L-IR and L-BR containing compounds vulcanizes initially faster than the compound with TDAE. However, they reach lower maximum torque levels, indicating a decrease in the CLD (crosslinking density), introduced in the next section. The maximum torque decreases in the order L-SBR-8.5 > L-BR-45.0 > L-IR-10.0 > L-BR-9.0 > L-BR-8.0.

The liquid styrene-butadiene copolymer (L-SBR-8.5) and high molecular weight polybutadiene (L-BR-45.0) show similar curing profiles. High initial torques and high maximum torques compared to the other polymers were obtained. Both polymers show by far the highest static viscosities as shown in Table 3.1: 280 Pa*s (L-BR-45.0) and 350 Pa*s (L-SBR-8.5). However, the molecular weights are significantly different: 45,000 g/mol (L-BR-45.0) and 8,500 (L-SBR-8.5).

From these results, it could be interpreted that the styrene butadiene structure reaches a higher CLD at low molecular weights compared to the polyisoprene or polybutadiene. The reason could be related to the similarity of the structure with the SSBR as the main polymer. It has to be taken into account that the L-SBR-8.5 exhibits the highest static viscosity. This may also contribute to the maximum torque and not only the high CLD.

Figure 3.1 Rheograms of the investigated compounds at 160 °C: a) silica/SSBR compounds at frequencies of 1,667 Hz, b) three selected silica/SSBR compounds at frequencies of 10 Hz.

Similar results were obtained between the polyisoprene (L-IR-10.0) and high vinyl polybutadiene (L-BR-9.0). Both polymers have relatively similar static viscosities, 3 Pa*s (L-IR-10.0) and 6 Pa*s (L-BR-9.0) and similar molecular weights of 10,000 g/mol (L-IR-10.0) and

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9,000 g/mol (L-BR-9.0), as shown in Table 3.1. The initial level of torque of the high vinyl L-BR-9.0 compound is lower than the value of the L-IR-10.0 compound. This is because of the higher reactivity of the double bond of the isoprene structure [13]. This means that similar maximum torques were obtained at the end of the analysis.

The replacement of the TDAE by different liquid polymers results in lower torque end values. It is not obvious. The viscosity of the liquid polymers is higher than the TDAE and the total content of polymers – conventional polymers plus the liquid polymer versus conventional polymers plus TDAE – in the mixture is higher. It has to be taken into consideration that the frequency range influences the viscoelastic behavior of the polymer and the filler interaction differently. Figure 3.1b shows additionally the curing measurement at a higher frequency (10 Hz). It can be assumed that a higher frequency minimizes the filler contribution to the torque and increases the contribution of the polymer – relatively to the total torque value. The filler network is reduced and cannot regenerate fast enough. A similar observation and explanation was reported by Lion et al. [14]. For this reason the liquid polymer's structure dependency and interaction can be clearer observed. As a result, the comparison can be attributed to the interaction between the liquid polymer and the main polymer.

Assuming that TDAE is not contributing to the crosslinking network, the total reactive polymer composition decreases in the conventional / liquid polymer blends which results in an average lower molecular weight. The assumption is therefore that the overall CLD is reduced in the presence of liquid polymers, except for the L-SBR-8.5 which shows a higher crosslink density as shown below in the section “*Crosslink Density*”. The liquid polymer is co-reacting with the base polymer. However, it occurs most likely with a lower statistical probability compared to the base polymers reacting with each other. As an example, considering that only one double bond is reactive out of 100, statistically speaking, it can be assumed that with a small amount of liquid low molecular weight polymer, not every molecule has co-reacted with the base polymer.

An explanation can be related to the different network formation between the liquid polymers compared to TDAE. From the vulcanization, a three-dimensional network is formed from separate polymer chain molecules that are chemically linked to each other [15,16]. However, several limitations have to be considered to the model of the ideal network. One is the influence of entanglements – also considered as physical crosslink units – and another one is the building of dangling ends, chains that are only connected with one crosslinking unit. In both cases, the contribution of the crosslinking units to the modulus, compared to the ideal network formation, is reduced. The modulus is reduced proportionally to the amount of dangling ends [15,16].

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The molecular weight per volume unit is reduced with the usage of the low molecular weight polymers. The formation of an ideal network is therefore reduced what consequently results in a higher amount of dangling ends. These chains are reacting with the network but do not contribute to the total modulus. According to the ideal network theory, at least two crosslinking units are required to connect a chain. Figure 3.2 shows the possible incorporation of liquid polymer into the vulcanized network. It is possible that the liquid polymer is connected with one or two or more crosslinking units per chain with the base polymer.

Figure 3.2 Crosslinking network built with liquid polymer assuming the combination with one or two polymer chains.

The differences are also affected by the filler-filler interactions – which are higher for all compounds with liquid polymers, as discussed in the section “*Filler-Filler and Filler-Polymer Interactions*”. It can be assumed that a higher polymeric content, with a higher initial torque (higher compound viscosity) versus the TDAE causes an increase in the Payne effect.

The network theory is limited to the explanation of molecular weight per unit and the crosslinking units. It cannot fully explain the results. Indeed, it is possible that the L-SBR occupies a larger volume compared to the L-BR-45.0 which might reduce the free available volume between the individual polymer chains. A similar effect can be found in different polymers extended with TDAE oil. The bulky aromatic groups of the TDAE reduces the segmental motion of linear BR chains and results in an anti-plasticizing effect [17]. Different to SBR, where the bulky aromatics pushing the chains apart and increasing the free volume and segmental motion [17]. This finally results in similar torque values because the L-BR-45.0 has on the other hand more crosslinking connections: Two opposite effects might lead in the end to similar characteristics. This can also be one basis of the discrepancy for the values of the

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torque (lower for the liquid polymers) and hardness (higher for the liquid polymers) as shown in Table 3.3.

Crosslinking Density

The CLD was determined by swelling test and calculated according to the Flory-Rehner equation [10]. It is shown in Figure 3.3 as a function of the molecular weight, separately for two ranges of 1,2-vinyl contents (<30 % and >50 %) and different polymer types. Comparing the 1,2-vinyl contents: L-BR-8.0 and L-BR-9.0 show close CLD values. As the molecular weight is close, it can be assumed that the vinyl content is of less significance for the CLD. However, as the maximum torque for L-BR-9.0 is higher than L-BR-8.0, as shown in Figure 3.1, it can be regarded to a slightly stronger pronounced filler network.

The increase of the molecular weight of the L-BR shows a clear increase in the CLD. The same is true for the change of the polymer type, isoprene and styrene-butadiene polymers, both leads to a clear increase in CLD. This is coherent with the maximum torque values as shown in Figure 3.4. The same picture was already observed in the rheometer curves. The L-SBR shows the highest CLD, higher than the control formulation that contains TDAE. The torque curve measured with the high frequency shown in Figure 3.1b, measuring a lower filler-filler network contribution shows closer correlation to the CLD. The L-BR's and L-IR having a lower CLD than TDAE in correlation with the results shown previously in Figure 3.1b.

Figure 3.3 CLD of the compounds measured by equilibrium swelling according to Flory-Rehner.

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Figure 3.4 Maximum torque and CLD of the compounds measured by equilibrium swelling according to Flory-Rehner.

3.3.2. Filler-Filler and Filler-Polymer Interactions

Payne Effect

The Payne effect provides information of the strain dependence on the modulus of filled rubber [18]. It is used for the characterization of the filler-filler and filler-polymer interactions. Figure 3.5 shows the storage modulus G' as a function of the dynamic strain at 100 °C for the unvulcanized compounds after the second mixing step. The frequency was set at 0.5 Hz. The Payne effect is calculated as the difference of the modulus between the strain at 0.56 % and 100 % (Figure 3.6).

Figure 3.5 Strain dependence of G' for the different polymer types and microstructures measured at 100°C for 0.5 Hz.

In general, all compounds with liquid polymers show higher Payne effects than the compound with TDAE. The modulus at 0.56 % strain is significantly higher for the different liquid polymer filled compounds. This would lead to the assumption that the filler-filler interactions are more increased than the filler-polymer interactions.

It has to be taken into account that the exchange of TDAE with the different liquid polymers increases the compound's initial viscosities that can be obtained from the minimum of the curing curves in Figure 3.1. A good filler dispersion requires sufficient shearing and a high viscosity.

However, if the viscosity is too high, an effective mixing may be impaired and consequently the dispersion can be worse. The change in the viscosity can result in a worse dispersion, which means a higher filler-filler network, resulting in a higher modulus G' at lower strain and a higher Payne effect. Comparing the different liquid polymers, the moduli at 0.56 % strain show the same trend with the maximum torques measured in the curing kinetics in Figure 3.7.

The strongest filler-filler interactions are measured for the L-SBR and high molecular weight L-BR. The resulting Payne effects show also the highest values.

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Figure 3.6 Payne effect values of the compounds.

Figure 3.7 Maximum torque and Payne effect values of the compounds.

Bound Rubber Content

Figure 3.8 shows the results of the bound rubber measurement for TDAE as the reference and the compounds containing the liquid polymers. The total bound rubber and the chemical bound rubber versus the molecular weight, vinyl content and type is displayed.

A higher total bound rubber content than that of the reference is achieved in the presence of all liquid polymers. The tendencies are comparable for the total and chemical bound rubber. An interesting result is that both bound rubber contents for the L-SBR show a closer similarity

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to those of the two low molecular weight L-BR's. The high 1,2-vinyl content L-BR-9.0 shows a higher total and chemical bound rubber. This can be attributed to the higher cis content of the L-BR-9.0 that has a higher possibility to react with the silane and the silica. Sato confirmed that liquid polybutadiene with high vinyl and high cis content show a higher reactivity with TESPT and a mercaptosilane [19]. The finding is in contrast to the curing kinetics and Payne effect in which the L-SBR shows a relative similarity to the high molecular weight version of the L-BR.

From thermodynamic processes, it can be expected that the attachment to the polymer active side of the silane coupling agent is more likely in the case of the liquid polymer. The total polymer content per volume fraction is higher in case of the TDAE. Additionally, the average molecular weight is reduced. The mobility of the shorter polymer chains has a higher possibility to fill the voids of the silica surface and finally bound the polymer more effective. This can be the reason for the significant higher chemical bound rubber of the high vinyl and high molecular weight L-BR's compared to the TDAE and low molecular weight L-BR.

High Payne effects for each sample shows a high bound rubber value for the same sample too. It can be assumed that both, higher filler-filler interactions and higher filler-polymer interactions are obtained in parallel.

Figure 3.8 Bound rubber content for the different compounds with TDAE and liquid polymers.

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3.3.3 Mechanical Properties

The mechanical properties are shown in Table 3.3. The tensile properties are comparatively summarized together with the Shore hardness, maximum torques and CLD. Most liquid polymer types show lower tensile strength at break and lower maximum elongation compared to TDAE. The compounds are slightly more brittle and show a lower elasticity than the reference. The tensile properties vary strongly based on the specific liquid polymer that is incorporated. Three types of liquid polymers, the polyisoprene L-IR-10.0, the styrene-butadiene copolymer L-SBR-8.5 and the high molecular weight polybutadiene, L-BR-45.0 show the highest reduction of the tensile strength and elongation compared to the reference. Except for L-BR-8.0 and L-IR-10.0, an increase of the M100 is shown for all liquid polymers compared to the TDAE. For the tensile strength, the L-BR-9.0 shows even a higher value than the reference compound. The compound with low molecular weight L-BR-8.0 shows lower tensile strength, higher elongation and similar M100 in comparison with the TDAE. The high 1,2-vinyl L-BR-9.0 shows a contradictive tendency: higher tensile strengths, lower elongation and higher modulus than the reference. Although the values are relatively close to the TDAE, differences for the vinyl contents are well pronounced. The higher tensile strength and modulus with the high 1,2-vinyl type are also coherent with the higher vulcanization torque and CLD as discussed above. The explanation for this can be attributed to the higher filler network for the high vinyl types.

Table 3.3 Comparison of crosslinking and mechanical properties.

	CLD (10 ⁴ mol/cm ³)	Max. Torque (dNm)	Shore A Hardness	M100 (MPa)	M300 (MPa)	Tensile Strength (MPa)	Elongation at break (%)
TDAE	3.60E-04	18,9	54	1,8	7,7	13,2	427
L-BR-8.0	2.88E-04	15,2	57	1,9	5,0	10,7	525
L-IR-10.0	3.56E-04	16,4	62	1,9	-	4,4	271
L-SBR-8.5	4.68E-04	18,0	68	3,5	-	11	271
L-BR-45.0	3.58E-04	17,9	66	2,5	-	5,7	200
L-BR-9.0	2.90E-04	15,9	60	3,8	12,5	14,9	359

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In summary, the different mechanical properties can be interpreted with a change in the filler-filler network and in the CLD. E.g. comparing L-BR-45.0 with L-BR-8.0, the increase of the liquid polymers' molecular weight increases the CLD. The higher modulus of L-BR-45.0 in combination with the higher Payne effect can be further explained with a worse filler dispersion that also affects the tensile strengths and elongation at break. A further possibility is that the tensile strength and elongation at break is caused by exceeding an optimum crosslinking structure and density for a liquid polymer based compound with the creation of shorter polysulfidic connections [12].

Not fully in line is the property profile of the high 1,2-vinyl content L-BR-9.0. This polymer causes a comparable low Payne effect but a significant increase in the M100. The torque values are lower and show a more pronounced formation of dangling ends which are not contributing to the reinforcement. However, in the other cases – in the hardness and M100 measurement – the contribution of the filler network is measured more pronounced.

For all liquid polymer containing mixtures, an explanation for the loss in the maximum torque compared to TDAE can be attributed to the free volume. The free volume is the volume that is not filled with atoms and molecules. It is defined as the difference between a total specific volume of sample and an occupied volume [20,21]. It is related to the space between molecular chains. This space provides to the chains a certain mobility and therefore the possibility of a free movement. In uncured polymeric materials, the highest free volume is in the temperature range between the glass transition temperature and the crystalline melting temperature. The free volume decreases with increasing crosslinking density [22]. Comparing the compounds with different liquid polymers to the reference with TDAE, it can be considered that the free volume has changed. The longer and more complex molecules compared to the TDAE molecules of the low molecular weight polymers can act as spacers between the molecular chains of the solid rubber as shown in Figure 3.9. The remaining free volume could be lower. In this case, the liquid polymers would fill and utilize free volume. This, however, needs to be investigated in a separate study (*Chapter 6*).

Figure 3.9 Utilization of the free volume with liquid polymer (L-IR) and TDAE.

3.3.3. Dynamic Mechanical Properties

The dynamic mechanical properties were measured for two purposes: 1. to characterize the material blends and predict the miscibility, in particular by the T_g shift and pronouncement of the T_g , which is influenced by the filler and 2. to discuss the potential tire performance based on the storage modulus and hysteresis according to the different performance indicators of a tire. However, it has to be taken into account that only the rolling resistance is understood as a reliable prediction obtained from the DMA.

The properties of a viscoelastic material vary in response to the frequency, the applied force and temperature. At low frequency, the deformation occurs slowly and the material appears to be elastic, the hysteresis is low. An increase in frequency causes a resistance in the material and the viscoelastic behavior becomes more important. At low temperature, the modulus of the rubber is high and at high temperature, the modulus is low. Around the glass transition temperature (T_g) of the material, the rubber shows more viscous behavior, the chain segments can sufficiently be deformed between the sulfur bridges. Furthermore, the T_g increases with the stress frequency for a rubber compound.

The DMA further provides information about the material characteristics such as compound compatibility and homogeneity. By incorporation of the different liquid polymers into the mixtures, a clear shift of the $\tan\delta$ curves compared to the reference compound can be observed as shown in Figure 3.10. This can be related to the liquid polymer's type and structure – miscibility with the other compound ingredients, especially the different base polymers – as well as the glass transition temperature that determines the extent of these shifts. The reference compound and the compounds containing L-BR-8.0 and L-SBR-8.5 show

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similar compatibilities, visibly by the sharper pronounced $\tan\delta$ peaks. The $\tan\delta$ shift compared to the reference sample with TDAE can be explained by the glass transition temperatures of the individual liquid polymer types: L-BR-8.0 ($T_g = -95\text{ }^\circ\text{C}$), L-IR-10.0 ($T_g = -63\text{ }^\circ\text{C}$), L-SBR ($T_g = -14\text{ }^\circ\text{C}$) compared to TDAE ($T_g = -55\text{ }^\circ\text{C}$). The resulting $\tan\delta$ peaks of the compounds are for L-BR-8.0 ($-44\text{ }^\circ\text{C}$), L-IR-10.0 ($-42\text{ }^\circ\text{C}$), L-SBR-8.5 ($-32\text{ }^\circ\text{C}$) and TDAE ($-40\text{ }^\circ\text{C}$) (Table 3.4). Tendencies of these changes can be indicatively explained using the Flory-Fox equation [20,22].

$$\frac{1}{T_g} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}} \quad (3.3)$$

Where w_1 and w_2 are the weight fractions and $T_{g,1}$ and $T_{g,2}$ the glass transition temperatures of the different polymers. In general, the tendencies of the results are in line with results that can be calculated and predicted according this equation, shown in Table 3.4. The T_g for the compound comprising L-SBR is higher compared to the reference compound with TDAE due to the increased contribution of the bulky styrene groups. These groups inhibit the free movement of the polymer chains and more energy is required for the polymer chains to flow.

Equation 3.3 is simplified for a homogeneously mixed polymer blend. It has to be taken into consideration that the different liquid polymers do not distribute weight-proportionally according to their affinity and compatibility to one of the base polymers. This can be one reason for the relatively high differences between calculated and experimental results of the two low 1,2-vinyl L-BR's (L-BR-8.0 and L-BR-45.).

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Table 3.4 Comparison of glass transition temperatures of the compound: calculated values according to Equation 3.3 (compound $T_{g,1}$ without plasticizer assumed and defined at -36 °C), and evaluated values from the $\tan\delta$ curve.

	T_g (calculated) (°C)	T_g (DMA) (°C)
TDAE	-40 °C	-40 °C
L-BR-8.0	-51 °C	-44 °C
L-IR-10.0	-42 °C	-42 °C
L-SBR-8.5	-32 °C	-32 °C
L-BR-45.0	-51 °C	-39 °C
L-BR-9.0	-41 °C	-40 °C

An interesting result is the pronouncement of the different L-BR structures as shown in Figure 3.10b. The high 1,2-vinyl L-BR-9.0 (T_g -60 °C) shows the same compound T_g as for the TDAE, both at -40 °C. As these both material show more similar T_g values, the result is plausible and in line with the Flory Fox equation. However, the compound that comprises the high molecular weight L-BR-45.0 shows a T_g of -39 °C. Even though its individual T_g is -95 °C. The compound's $\tan\delta$ curve shows a broad and low pronounced peak that indicates a lower miscibility compared to the lower molecular weight types. As shown in the previous sections *Curing and CLD* and *Tensile Properties* the high molecular weight type shows a higher CLD with higher hardness and modulus, too, compared to the reference. The high CLD in this particular case contributes to the torque modulus.

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Figure 3.10: Dynamic mechanical properties of the silica/SSBR-rich mixtures with different polymer types (a) and structures (b).

The DMA is used to predict the performance of tires [24-26]. For the wet grip, the frequency temperature equivalence can be determined with the WLF equation (Williams-Landel-Ferry). [25] In this model, time and temperature can be mathematically interchanged. Wet grip is a high frequency phenomenon (MHz) and requires low test temperatures (-20 °C to 0 °C) in the DMA at a stress frequency of 10 Hz. The rolling resistance correlates as a direct parameter from the DMA temperature area between 60 °C to 70 °C at 10 Hz. Figure 3.11 shows the tanδ values and storage moduli for the compounds with different liquid polymers and the TDAE at 0 °C (a) (b) and 70 °C (c) (d). All compounds with liquid polymers show higher Tanδ values at 0 °C and 70 °C (Figure 3.11a and 11c).

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Figure 3.11 Dynamic mechanical properties of the mixtures at 0 °C (a) (b) and 70 °C (c) (d)

The low molecular weight L-BR-8.0 and L-SBR-8.5 show a good balance compared to the TDAE and the other liquid polymers: At 0 °C – as the indicator or the wet grip – the LBR-8.0 and the L-SBR-8.5 show a higher value for tanδ implying a higher hysteresis. For the L-SBR-8.5, this is associated with an increase of the storage modulus. For the L-BR-8.0 the same storage modulus and higher loss modulus than the reference was measured. At 70 °C – as the indication for the rolling resistance – both types show a higher hysteresis compared to the TDAE based reference compound, in both cases due the decrease in the storage moduli – and increase of the loss moduli too. The L-IR and high 1,2-vinyl L-BR show similarities, similar

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$\tan\delta$ values at 0 °C and 70 °C. It can be explained by overlapping effects, the reduced overall T_g and the increased filler-filler network. Generally, the hysteresis in the temperature range from -10°C to 80°C is increased. For the cases of the different L-BR types and the L-IR, this can be attributed to the lower CLD and reduced elasticity.

3.4. Conclusion

Different low molecular weight 'liquid' polymers have been added to a typical winter tire tread formulation of a sulfur curable mixture of SSBR/BR/NR with silica as a filler. The structure of the liquid polymers such as type (isoprene, butadiene and styrene butadiene), molecular weight and 1,2-vinyl content was varied to understand the influence on the compound's characteristics and prediction of in-rubber properties. It includes mainly the study on the curing characteristics and final CLD, the mechanical and dynamical properties and filler interactions.

In general, higher molecular weight types result in higher CLD. Compared to TDAE, all liquid polymers show lower levels of CLD. As a lower molecular weight-based material is introduced, the average molecular weight in the total compound is reduced. The potential to create a less ideal network – in particular through dangling ends – seems to be increased. This is not an obvious conclusion in the first moment as the total polymer content is higher. However, as TDAE is in principle not competing with the network formation, the liquid polymer reduces the average molecular weight and changes the molecular weight distribution of the total polymer composition. The reduction of the CLD could be compensated by adding additional sulfur to increase the number of crosslinking units per chain.

The measurements of the filler-filler interactions and filler-polymer interactions show contrary results. The use of liquid polymers and higher molecular weights increases the filler-filler interactions while increasing the filler-polymer interactions at the same time. It is likely, that a too viscous compound (due to the higher molecular weight) supports the agglomeration and the building of a more pronounced filler-filler network caused by a lower dispersion efficiency. However, this molecular weight causes also a higher interaction with the polymer (a higher molecular weight polymer is more probable to attach to the polymer active side of silane coupling agent as a TDAE).

The mechanical properties show differentiated results with the liquid polymers. While the molecular weight and CLD increases, the modulus (M100 and M300) increases as well. The tensile strength and elongation at break decrease. The properties can be explained by the crosslinking density, filler dispersion and compatibility. It further subjected to the free volume which should be investigated in a separate study.

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The DMA shows T_g shifts according the liquid polymer's T_g . Generally, for all types, the hysteresis, $\tan\delta$ is increased compared to TDAE in the temperature range from 0 °C to 80 °C. By adjusting the curing and crosslinking, hardness level and compound's T_g , the performance can be comparatively evaluated.

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CHAPTER 4

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A Supplementary Study:

Adjusted Blends of Sulfur Cured SSBR-rich/Silica and ESR/CB

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Abstract

This study focuses on the influence of liquid polymers and its types, molecular weight and microstructure on rheological, mechanical, crosslinking network and in-rubber properties. Compared to the previous chapter, this study uses varying parameters in a winter tire tread formulations based on SSBR-rich/Silica and a racing tire tread formulation based on ESR/Carbon Black. Liquid polybutadiene rubber (L-BR) and different liquid styrene butadiene rubber (L-SBR) were added to these compounds and compared. Results are discussed for the curing torques and crosslink densities to evaluate the influences on the crosslinking. The mechanical properties and dynamic mechanical analysis results deliver finally indications for the expected tire performance. The comparison to a partially hydrogenated L-SBR shows comparable results to TDAE, which verifies the type of incorporation of liquid polymers.

4.1. Introduction

In recent years, many patents about the improvement of tire performances with liquid polymers have been filed from different tire producers [1-4]. Improvements are claimed for the abrasion resistance and for a better balance for low temperature properties in winter tires [1,2]. The second application field of liquid polymer are racing tires. Herein the wet and dry grip properties are claimed to be improved [3,4].

In *chapter 3* the structure-property relationship of liquid polymers in a winter tire tread formulation was investigated. The structure of the liquid polymers such as type (isoprene, butadiene and styrene butadiene), molecular weight and 1,2-vinyl content was varied to understand the influence on the compounds' characteristics and prediction of in-rubber properties by keeping the curing system constant. Compared to Treated Distillate Aromatic Extracts (TDAE), all liquid polymers lead to lower levels of Crosslink Densities (CLD). Higher molecular weight types result in comparably higher CLD. When a lower molecular weight-based material is introduced as replacement for TDAE, the average molecular weight in the total compound is reduced, which is one explanation for this tendency.

However, only with an adjustment of the curing and crosslinking, of the hardness level and compound's T_g , the performance can be comparatively evaluated. The reduction of the CLD can be e.g. compensated by adding additional sulfur to increase the number of crosslinking units per chain (*Chapter 3*). The present study provides further analysis about adjusting the influences by changing the formulation.

A standard passenger car tire tread formulation was defined according to the previous study (*Chapter 3*). This formulation contains silica as a filler and SSB, BR and NR as the polymer composition and TDAE as a standard plasticizer. The compound filled only with TDAE was used as reference. The liquid polymer was used to replace the TDAE and study the properties as an alternative plasticizer. Different to the previous work, the formulation was varied to adjust and compensate the liquid polymer containing compound: It includes two different sulfur contents, two different SSB/BR ratios and the addition of a polyterpene resin. With higher SSB contents and the addition of resin, the in-rubber properties, i.e. the balance of wet grip and rolling resistance can be adjusted and potentially optimized.

For a second model formulation, a racing tire tread formulation was used. This formulation contains carbon black as a filler and ESB as a polymer. A combination of TDAE and polyterpene resin was used as standard plasticizer. Different L-SBRs were used to partially replace TDAE. In this sub-study, also the curing, CLD and in-rubber properties were targeted to be optimized.

4.2. Experimental

4.2.1. Raw Materials

The same raw materials were used as listed in chapter 3.2.1. Further raw materials for the present study include ESBR, Buna 1502 supplied by Arlanxeo, and polyterpene resin, Sylvagum TR90 supplied by Kraton.

The low molecular weight polydienes were selected from Kuraray to cover two chemical types (butadiene and styrene-butadiene), different 1,2-vinyl contents and different degrees of hydrogenation. The main properties of these grades are shown in Table 4.1. The “L” refers to liquid or low molecular weight polymer; “BR”, “SBR” refer to the type of polymer: butadiene or styrene-butadiene rubber, respectively. The number refers to the molecular weight (M_N) of the polymer.

Table 4.1 Tested liquid polymers [7].

Polymer	Product Name	Monomer	Molecular Weight (M_N , g/mol)	1,2-vinyl (mol%)	T _g (°C)	Viscosity (Pa·s at 38 °C)
L-BR-8.0	LBR-307	Butadiene	8,000	Low	-95	1.5
L-SBR-8.5	L-SBR-820	Styrene, Butadiene	8,500	Low	-14	350
L-SBR-10.0	L-SBR-841	Styrene, Butadiene	10,000	Medium	-6	100 (at 60 °C)
L-SBR-8.5H	Experimental	Styrene, Butadiene ^A	8,500	Medium	-14	884

Partially hydrogenated (H) polymer

4.2.2. Preparation of Blends and Sample Plates

The SSBR-rich/Silica reference, representing a winter tire tread formulation is shown in chapter 3.2.2. The ESBR/CB based formulation (Table 4.2) is representing a racing tire tread formulation. Deviated contents are indicated in the name and legends of the following figures and table: L-BR-8.0_Su-1.7, means 1.7 phr sulfur content, L-BR-8.0_SSBR-75, means 75 phr of SSBR with a corresponding reduction of BR to 15 phr. L-BR-8.0_PT-10, means 10 phr polyterpene resin with a corresponding reduction of the L-BR-8.0 to 15 phr.

The compounds were mixed and cured according to the procedure described in chapter 3.2.2..

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Table 4.2 Formulation of ESBR and carbon black.

Formulation	Concentration
ESBR	100
Carbon Black	80
TDAE	5
Resin	5
TDAE or Liquid Polymer	20
Zinc Oxide	3
Stearic Acid	2
Sulfur	2
Accelerator	1.5 (CBS) 1.7 (DPG)

4.2.3. Evaluation

The compounds' curing kinetics, tensile properties, Shore A hardness values, dynamic measurements and crosslink densities were determined according to chapter 3.2.

4.3. Results and Discussion

4.3.1. Results for L-BR in adjusted SSBR-rich/Silica Compounds

Figure 4.1 shows the CLD and maximum torques of the L-BR-8.0 and the different adjustments of the SSBR-rich/Silica compounds. As presented in the previous study (chapter 3), the replacement of the TDAE by a liquid polymer results in lower values of both properties. Assuming that TDAE is not contributing to the crosslinking network, the total reactive polymer composition increases in the liquid polymer blends. This is associated to the fact that the liquid polymer contributes to the rubber network. It results in a reduction of the average molecular weight of the total compound. The overall CLD is therefore reduced in the presence of liquid polymers. The liquid polymer is co-reacting with the base polymer. This occurs most likely with a lower statistical probability compared to the base polymers reacting with each other.

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With the increase of sulfur content to 1.7 phr in L-BR-8.0-SU-1.7, it can be seen that the maximum torque and CLD is closer to the reference compound, using TDAE. It is one option to compensate the formulation containing a liquid polymer. The change to a different polymer ratio (increase of 10 phr SSBR compared to the reference) to SSBR/BR/NR (=75/15/10) with L-BR.8.0_SSBR-75 is another concept. It shows also an increase in the CLD. It is plausible because of the higher reactivity of the SSBR compared to the BR. However, the maximum torque is reduced. This may be attributed to the phase morphology: L-BR has a stronger compatibility with BR. If the BR content of the base blend is reduced, the connection of the L-BR with the base polymer is assumed to be reduced. Compared to the blend-ratio of SSBR/BR, the combination of L-BR/polyterpene resin shows a slightly higher CLD and a more pronounced increase in maximum torque. At least partially, this tendency can be derived from the non-reactivity of the resin, meaning that the base rubber is curing more effectively.

Figure 4.1 CLD versus maximum torque of the Silica/SSBR compounds.

In all liquid polymer containing blends, the potential to create a less ideal network – in particular through dangling ends – seems to be increased [5,6]. In such case, the liquid polymer is assumed to be connected with the main polymer but will not fully contribute to the mechanical properties. To contribute i.e. to the modulus, according to the ideal network theory, at least two crosslinking units are required to connect a chain. Figure 3.2 shows the possible incorporation of liquid polymer into the vulcanized network. It is possible that the liquid polymer is connected with one or two or more crosslinking units per chain with the base polymer.

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The mechanical properties are shown in Table 4.3. The tensile properties are comparatively summarized together with the Shore hardness, maximum torques and CLD. The L-BR-8.0 shows a slight increase in hardness, M100 and elongation at break. The adjusted formulations generally further increase the hardness, moduli and lower the elongations at break. The results can be interpreted with a possible change in the filler-filler network (higher in the presence of liquid polymers) and in the CLD (lower in the presence of liquid polymers). A further possibility is that the reduction of tensile strength and elongation at break is caused by exceeding an optimum crosslinking structure and density for a liquid polymer based compound – with the creation of shorter polysulfidic connections [8].

Table 4.3 Comparison of crosslinking and mechanical properties of the silica/SSBR compounds.

	CLD (10 ⁴ mol/cm ³)	Torque (dNm)	Shore A Hardness	M100 (MPa)	M300 (MPa)	Tensile Strength (MPa)	Elongation at break (%)
TDAE	3.60E-04	18.9	54	1.8	7.7	13.2	427
L-BR-8.0	2.88E-04	15.2	57	1.9	5.0	10.7	525
_Su-1.7	3.34E-04	17.8	62	1.7	-	5.3	285
_SSBR-75	3.49E-04	11.6	62	2.7	11.2	11.6	310
_PT-10	2.92E-04	18.7	59	2.7	11.9	12.5	310

4.3.2. Result for L-SBR in ESB/Carbon Black Compounds

The comparison of the CLD and torque of the different L-SBRs in the carbon black/ESBR compounds is shown in Figure 4.3. Similar to the results above, the torque and CLD are reduced for the liquid polymer containing compounds compared to the reference compound using TDAE. An interesting effect is visible by the introduction of the hydrogenated type L-SBR-8.5H. With the fewer amounts of double bonds, the reactivity of the L-SBR is reduced. The curing becomes more similar to the reference, with a higher maximum torque and CLD. However, with the remaining non-hydrogenated backbone, it can be assumed that at least some polymer chains are connected to the base network.

Figure 4.3 CLD versus maximum torque of the CB/ESBR compounds

The mechanical properties (Table 4.4) are coherent for the vulcanization and crosslink density. Compared to the TDAE, all liquid polymer types show slightly lower tensile strengths, lower moduli and slightly higher ultimate elongation values.

The partial hydrogenated L-SBR-8.5H combines the characteristics of both, the TDAE and the liquid polymers. It manifests the theory of the network formation discussed above. With the L-SBR-8.5H the curing and CLD is comparable with the TDAE. At the same time the advantages of the liquid polymer can be utilized in such a way that a certain connection and compatibility to the base polymer is created.

Table 4.4 Comparison of crosslinking and mechanical properties.

	CLD (10 ⁴ mol/cm ³)	Torque (dNm)	Shore A Hardness	M100 (MPa)	M300 (MPa)	Tensile Strength (MPa)	Elongation at break (%)
TDAE	2.71E-04	9.6	55	1.8	8.3	14.4	496
L-SBR-8.5	2.15E-04	7.2	54	1.4	5.3	9.4	493
L-SBR-8.5HG	2.36E-04	9.2	49	1.7	7.5	13.1	500
L-SBR-10.0	1.84E-04	7.4	49	1.1	4.8	9.2	450

The DMA shows T_g shifts according the liquid polymers' T_g . Figure 4.4 shows the $\tan\delta$ values versus T_g for 0 °C (a) and 70 °C (b). Generally, for all types, the hysteresis, $\tan\delta$ is increased

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compared to TDAE for the temperatures 0 °C and 70 °C. Compared to the non-hydrogenated L-SBRs, the T_g for the L-SBR-8.5H is increased due to the higher resulting CLD. This further corresponds to the increase of the $\tan\delta$ values.

This is an indication for better performance balance, knowing that the expected real tire values subject on many other factors as well. The wet grip is indicated to be improved. The significant increase of the $\tan\delta$ at 70 °C – for passenger car tires normally a drawback, indicating a higher rolling resistance – is for the special case of racing tires an improvement and relates to the heat build-up and dry grip.

Figure 4.4 Dynamic Mechanical Properties of the CB/ESBR at 0 °C (a) and 70 °C (b)

4.4. Conclusion

Low molecular weight 'liquid' polymers have been added to two different formulations for a winter tire and racing tire tread. Two different model formulations were used, an SSBR/BR/NR blend filled with silica (representing a winter tire tread formulation) and ESBR filled with carbon black (representing a racing tire tread formulation). The formulation of the winter tire was adjusted with varying concentrations of sulfur and different SSBR/BR ratios and liquid polymer/polyterpene ratios. The racing tire formulation was varied by three different liquid polymers such as molecular weight and 1,2-vinyl content and hydrogenation. The target is to gain a better understanding on how liquid polymers can be used in these applications. For this purpose, the characteristics were studied with an adjustment of the main formulation.

As already shown in previous study, the overall CLD is reduced in the presence of liquid polymers. This can be partially derived from the liquid polymer's co-reaction with the base polymer. With the increase of sulfur content and change in the SSBR/BR-ratio, the maximum

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torque and CLD can be shifted closer to that of the reference compound with TDAE. Therefore, these are two options to adjust the CLD. The combination with a polyterpene resin is another option to increase the CLD - derived from the non-reactivity of the resin - and more particular the T_g to improve the performance balance of the in-rubber properties. The adjusted formulations increase the hardness, moduli and lower the elongations at break.

An interesting result is also given by the different L-SBR's in ESB/CB. With the hydrogenated type, the curing torque and CLD becomes clearly closer to the reference version with TDAE. The material is less reactive due to the fewer available double bonds. However, the L-SBR-8.5H is still be partially connected with the base polymer network and combines the advantages of a liquid polymer with the curing of a TDAE. The increased CLD results in a higher T_g and finally higher $\tan\delta$ values.

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CHAPTER 5

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 filler-polymer interactions and to lower the filler-filler interactions. In addition, silane functionalized polymers can be used. Special types of polymers are low molecular weight 'liquid' polymers. The goal of this chapter 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 influences on the glass transition temperatures, loss moduli and $\tan \delta$ values.

5.1. 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 CO₂ 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.

Next to 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].

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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 X_3SiRY , X representing the hydrolysable alkoxy group, R stands for the alkyl chain group while Y stands for the organofunctional group [2]. 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 chapter 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 contain

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ethoxysilane groups along the chain (Figure 5.1) – the other three are not functionalized. 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. They were chosen to initiate different interactions with the different liquid polymers.

Figure 5.1 Structure (schematic) of silane grafted low molecular weight ‘liquid’ polymer.

5.2. Experimental

5.2.1. Raw Materials

The same raw materials were used as listed in chapter 3.2.1. A different solution polymerized styrene-butadiene copolymer (SSBR), containing 15 % bound styrene, was used: SPRINTAN™ SLR 3402 supplied by Trinseo. Further raw materials for the present study include tetrabenzylthiuram disulfide (accelerator) (TBzTD), supplied from Flexsys. Three different organosilanes were chosen to trigger different interactions with the other components. They are shown in Table 5.1. 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 low molecular weight polybutadienes were provided from Kuraray and are listed in Table 5.2. 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 5.2) 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 a triethoxysilyl-group is along the polymer chain. The “terminated type” means the triethoxysilyl-group is at the chain end.

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Table 5.1 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	$\begin{array}{c} \text{CH}_3\text{CH}_2\text{O} \\ \\ \text{CH}_3\text{CH}_2\text{O}-\text{Si}-(\text{CH}_2)_3-\text{S}_2-(\text{CH}_2)_3-\text{Si}-\text{OCH}_2\text{CH}_3 \\ \qquad \qquad \qquad \\ \text{CH}_3\text{CH}_2\text{O} \qquad \qquad \text{with } x \approx 3,70 \qquad \qquad \text{OCH}_2\text{CH}_3 \\ \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \text{OCH}_2\text{CH}_3 \end{array}$	480
Si-B	NXT[19] 3-Octanoylthio-1- propyltriethoxysilane	$\begin{array}{c} \text{CH}_3\text{CH}_2\text{O} \\ \\ \text{CH}_3\text{CH}_2\text{O}-\text{Si}-(\text{CH}_2)_3-\text{S}-\text{C}(=\text{O})-(\text{CH}_2)_6\text{CH}_3 \\ \\ \text{CH}_3\text{CH}_2\text{O} \end{array}$	365
Si-C	Si 363[18] 3-Mercaptopropyl-di(tridecan- 1-oxy-13-penta (ethyleneoxide))ethoxysilane	$\begin{array}{c} \text{CH}_3(\text{CH}_2)_{12}(\text{OC}_2\text{H}_4)_5\text{O} \\ \\ \text{CH}_3\text{CH}_2\text{O}-\text{Si}-(\text{CH}_2)_3-\text{SH} \\ \\ \text{CH}_3(\text{CH}_2)_{12}(\text{OC}_2\text{H}_4)_5\text{O} \end{array}$	987.5

Table 5.2 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	-	5,500	High	-60	3.5
L-BR-2	L-BR-302	-	5,500	Low	-85	0.6
L-BR-3	LBR-305	-	30,000	Low	-95	40
Si-L-BR-4	-	2.0 (Grafted)	6,000	High	-50	5.3
Si-L-BR-5	-	0.9 (Terminated)	5,500	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 %

5.2.2. Preparation of Rubber Compounds

Table 5.3 shows the SSBR/Silica based model formulation. The liquid polymer is added additionally to the formulation.

The compounds were mixed in three stages according to the procedure described in chapter 3.2.2. The used procedure in this chapter differs from that in chapter 3.2.2. in the following way: no carbon black was used, the discharging time was set to 7:00 (minute:second).

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The compounds were cured on a Wickert press according to the procedure described in chapter 3.2.2.

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 Figure 5.2 to Figure 5.12. 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).

Table 5.3 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 0.2 TBzTD	2.0 CBS 0.2 TBzTD
Antidegradants	1.5 6PPD 1.5 Wax	1.5 6PPD 1.5 Wax

^ADifferent silanes: Si-A, Si-B, Si-C, content in phr adjusted according to the total ethoxysilane concentration of the reference formulation (isomolar)

5.2.3. Rheological and Mechanical Properties

The tensile properties, hardness and dynamic measurements were performed according to the description in chapter 3.2.3. The compound's curing kinetics was also performed according to the description in chapter 3.2.3. with the exception that only one frequency (at 1.667 Hz) was used.

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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 performed according to the description in chapter 3.2.4.

5.2.4. Solubility and Swelling

The Crosslink Density (CLD) was performed according to the description in chapter 3.2.5.

5.3. Results and Discussion

5.3.1. Curing Characteristics, Crosslinking Density and Payne Effect

Curing Characteristics

Figure 5.2a 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). Figure 5.2b 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 sulfenamide 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 [21,22]. 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.

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In both graphs of Figure 5.2 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 through 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-BRs, shown in Figure 5.2a, are showing slightly 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 5.3. 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 as shown in *chapter 3*. 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 in case of a higher 1,2-vinyl content as well as 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 Figure 5.2b. Even though they consist retarding groups, the curing speed is faster than that

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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 mercaptosilanes reduces the initial curing speed - due to a delayed acceleration - but results in higher maximum torques. The end torque value of the compound with Si-C is more significant increased as with Si-B. An interesting result is that the Si-A and Si-B lead to 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-BRs 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 particularly true and more significant for the mercaptosilanes as their reactivity is faster for the compound containing the non-functionalized materials.

Figure 5.2 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).

Crosslinking Density

Together with the curing kinetics, the CLD provides a more complete discussion about the liquid polymers and silanes' influences. Figure 5.3a shows the CLD of the different L-BRs and Si-L-BRs containing compounds with bis(triethoxysilylpropyl)disulfide (Si-A). The deviation of the result is in the range of $\pm 1.96 \cdot 10^{-5} \text{ mol/cm}^3$.

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 high 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 Figure 5.2, 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 as shown in *chapter 3*.

The CLD of the reference compound with SSBR is $\nu = 4.1 \cdot 10^{-4} \text{ mol/cm}^3$. It is a plausible value and comparable to ranges obtained in other investigations of SSBR and BR [23,24]. 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 5.2 [25].

$$\nu = \frac{\rho}{2} \left(\frac{1}{M_{CS}} - \frac{1}{M_N} \right) \quad (5.2)$$

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 $M_{CS} = 1220 \text{ g/mol}$. Approximately every 30th double bond has reacted. Adding the unmodified liquid polymers, this value increases to app. $M_{CS} = 1610 \text{ g/mol}$. In this case

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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 5,500 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 (5,000 g/mol to 6,000 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.

Figure 5.3b 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-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 [8,26]. This is also confirmed by the strong CLD increase of the non-functionalized L-BRs with both mercaptosilanes. The 1,2-vinyl content of the main polymer is 63 % and contributes therefore significantly to the interaction.

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Figure 5.3 CLD of the SSBR/Silica compounds with different liquid polymers (a) and different silanes (b).

Mooney Viscosity

Figure 5.4 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 Figure 5.2. The Si-L-BRs show higher values than the non-functionalized L-BRs.

Figure 5.4 Influence of different L-BR and Si-LBR (a) in combination with different silanes (b) on the Mooney Viscosity.

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]. Figure 5.5 and 5.6 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 [5,27] and enables a further estimation of the compounds performance. Between repeated measurements the maximum variation is +/-2.8 kPa.

Figure 5.6a shows the Payne effects for the different uncured compounds that contain the varying L-BRs and Si-L-BRs 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 show 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, 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.

Figure 5.5 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 silane-functionalized liquid polymer is acting effectively and can partially replace the silane coupling agent.

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Figure 5.5 Payne effect for the different L-BR and Si-LBR in relation to the concentration of the silane coupling agent.

In combination with Si-B (Figure 5.6b), 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 network) but a greater 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 show a predominated effect in the reaction with the 1,2-vinyl-rich polybutadiene [26,27]. The L-BR-1 and Si-L-BR-4 can react together according to Figure 5.7 (B). It is particularly plausible, since the CLD (Figure 5.3) is significantly higher for these types.

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Figure 5.6 Payne effect for the different L-BR and Si-L-BR (a) in combination with different silanes (b) on the Payne effect.

Figure 5.7 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 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 content shows a higher probability to react with the thiol-groups resulting in a faster curing maximum torque.

Figure 5.7 Reaction of the liquid polymer with the main polymer, with sulfur (A) and with the mercaptosilane (B).

Figure 5.8 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 create 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) do not form own networks but may modify the existing networks between silane, 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 difference 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 couples 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 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 above in the section *Crosslink Density*. It is therefore a plausible assumption that in this case more connections of (A) and

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(B) are created. While, in case of the low 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 reacts with the 1,2-vinyl groups of the liquid polymer.

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Figure 5.8 Possible reactions between the low molecular 'liquid' polymer, silane coupling agent and silica.

5.3.2. Mechanical Properties

Hardness

Figure 5.9 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 Figure 5.2. The Si-L-BRs show higher values than the non-functionalized L-BRs. This is associated with the creation of an additional network, supported by the silane group as discussed in the previous chapter 3.

Figure 5.9 Shore A hardness of the different L-BR and Si-L-BR (a, b).

Generally, higher CLD values show higher Shore A hardness values as shown in Figure 5.10. 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.

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Figure 5.10 Relationship of crosslink density and Shore A hardness for the different L-BR and Si-L-BR.

The silane coupling agent concentrations show no clear tendency as shown in Figure 5.9 and Figure 5.11. As shown in the previous segments, in 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 slightly increased CLD and Payne effect. 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.

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Figure 5.11 Shore A hardness for the different L-BR and Si-L-BR in relation to the concentration of the silane coupling agent.

Tensile Properties

Figure 5.12 shows the Modulus at 300 % strain (M300) over the Modulus at 100 % strain, (Figure 5.10a and Figure 5.10c), as well as the elongation at break over tensile strength (Figure 5.10b and Figure 5.10d). 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 MPa 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-BRs, the silane modified types result 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 (Figure 5.12b), 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

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

Figure 5.12 Influence of different L-BR and Si-LBR (a, b) in combination with different silanes (c, d) on the mechanical properties.

Dynamic Mechanical Properties

The dynamic properties were characterized predict the tire performance. Figure 5.13 shows the $\tan\delta$ temperature sweep for the non-functionalized liquid polymers (Figure 5.13a) and for

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the functionalized liquid polymers (Figure 5.13b). Between repeated measurements the maximum variation is in the range of $\pm 5\%$ for the single values of the $\tan\delta$ and E' .

The compounds containing the bifunctional Si-A show the lowest T_g s at $-48\text{ }^\circ\text{C}$ for both types of the liquid polymers (the non-functionalized in Figure 5.13a and functionalized in Figure 5.13b). The exchange with the mercaptosilanes Si-B or Si-C leads to an increase in the T_g s and lower $\tan\delta$ values in the range of $0\text{ }^\circ\text{C}$ to $80\text{ }^\circ\text{C}$. It is known that the T_g decreases almost linearly with the increase of the CLD [28,29]. 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 Figure 5.14d. The result is in accordance with the increased CLD and confirms for the mercaptosilanes the assumed network (D) according to Figure 5.8. 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 $-40\text{ }^\circ\text{C}$ for Si-L-BR-4/Si-B the T_g is $-47\text{ }^\circ\text{C}$. For Si-C, the reduction of the $\tan\delta$ goes along with a comparably low E' for the non-functionalized L-BR and a comparably high 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 (Figure 5.5). The consequence is a reduced filler network which is confirmed by the E' value.

Figure 5.13 Influence of different L-BR (a) and Si-LBR (b) in combination with different silanes on the dynamic mechanical properties.

Figure 5.14 shows the $\tan\delta$ at $70\text{ }^\circ\text{C}$ versus $\tan\delta$ at $0\text{ }^\circ\text{C}$ and E' at $70\text{ }^\circ\text{C}$ versus E' at $0\text{ }^\circ\text{C}$ 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 $70\text{ }^\circ\text{C}$) and wet grip (at $0\text{ }^\circ\text{C}$).

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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 phenomenon and not reliably to predicted from the DMA value.

Independently of the microstructure, the silane-functionalization of the liquid polymers reduces the $\tan\delta$ at 70 °C (Figure 5.14a). For the low molecular weight types, the $\tan\delta$ 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' (Figure 5.14b). It is due to the higher CLD and hardness of Si-L-BR-6. However, the ratio of the $\tan\delta$ at 70 °C and $\tan\delta$ 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 Figure 5.8: a hydrophobation 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 Figure 5.14c. With the silane-functionalization, the $\tan\delta$ 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, due to its predominant effect. It does not show changes of the $\tan\delta$ when 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 Si-C with the silane-functionalized liquid polymer can be further confirmed.

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Figure 5.14 Influence of different L-BR and Si-LBR (a, c) in combination with different silanes (d, d) on the dynamic mechanical properties.

5.4. Conclusion

This chapter 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 were 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-

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rubber performance in passenger car tires. The tendencies of the influence are summarized in Table 5.4.

Table 5.4 Influences of the liquid polymers' microstructure and combination with different silanes on the final compound 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	0	+	++	++	-	0
High 1.2-vinyl	(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/-)".

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 (5,000 to 6,000 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 reduces the filler-filler interactions by a strong hydrophobation of the silica surface.

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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 result in a hydrophobation 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 $\tan\delta$ 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.

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CHAPTER 6

LOW MOLECULAR WEIGHT ‘LIQUID’ POLYMER EXTENDED COMPOUNDS

Impact on Free Volume and Crosslink Density studied by Positron
Lifetime Spectroscopy and Stress-Strain Analysis according to Mooney-
Rivlin

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Abstract

Liquid polymers are used in elastomeric compounds to modify their processing and final characteristics. The material is considered as a polymeric plasticizer and is used to substitute or supplement conventional plasticizer like paraffinic or aromatic oils, or hydrocarbon resins. Their plasticizing effect and contribution to the crosslinking in sulfur cured SSBR mixtures is studied. Aromatic oil, aliphatic resin and different liquid polymers, varied in type, molecular weight and microstructure are discussed. Different plasticizing effects are shown with corresponding curing torques and Shore hardness values. The free volume – measured by positron annihilation lifetime spectroscopy - increases or decreases according to the liquid polymer's incorporation in the main polymer.

6.1. Introduction

In polymeric mixtures, plasticizers are mainly used to improve processing and influence material characteristics by reducing the hardness and viscosity. Additionally, they are used for economic reasons, e.g. to use high concentrations of fillers in combination with high concentrations of plasticizers - at the same time, the amount of expensive polymers can be reduced.

For elastomeric oil-extended compounds, physical and mechanical properties – e.g. Shore hardness values, moduli and elongations – are mainly associated to the glass transition temperature, T_g . Plasticizers usually show a lower T_g than the main polymer. Correspondingly, the T_g of their mixtures are lower. However, this is not always the case and subject on the individual T_g s of the polymer and plasticizer. The compound's T_g can therefore increase or decrease [1]. The decrease of the compound's T_g can be described as a plasticizing effect, the increase as an anti-plasticizing effect [2,3].

Plasticizers reduce the intermolecular forces between the polymer chains [4,5]. An explanation can be provided by the gel theory: Plasticizers act most efficiently when the interactions between the plasticizer molecules, the interactions between the polymer chains, as well as the interactions between the plasticizer molecules and the polymer chains are relatively equal. If this is the case, the plasticizer can easily be incorporated between the three-dimensional gel structure of the polymer chains and increase its mobility [6].

The plasticizing is associated to the free volume [7,8], defined as the total volume minus the volume occupied by the molecules. It can further be explained as the empty internal volume, free for the movement of the polymer chains. Above T_g , the polymer motion starts, resulting in an increase of the free volume. The shift and the change of the molecular free volume can be explained by the Fox equation [9].

In the present study, Positron Annihilation Lifetime Spectroscopy (PALS) was used to evaluate the free volume in elastomeric compounds. The lifetime of the ortho-positronium (o-Ps) is measured, which is an unstable pairing of an electron and its anti-particle, the positron, that is formed in low electron density sites. These sites are considered as the free volume of the compound. The o-Ps lifetime in this case depends on the free volume size. A direct relationship between this lifetime in the pick-off process and its radius is well established [10,11]. It can further be linked to the fractional free volume [12]. This is proportional to the average size of the free volumes and their number.

Alongside the above-mentioned plasticization, the crosslinking reaction – the curing or vulcanization – has an important effect on elastomeric compounds. The sulfur, activator, and accelerator package initiate the crosslinking reaction between the polymer chains. Processing

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oils and resins do not actively contribute to these reactions and the final crosslinking network. Liquid polymers contribute to it depending on their type, structure and molecular weight. A previous study has shown that the replacement of TDAE with different liquid polymers results in a lower Crosslink Density (CLD) as shown in *chapter 3*. This is due to the consumption of sulfur by the co-reactive liquid polymer. However, this previous study was also influenced by a mix of different main polymers and fillers. The current study focuses only on an unfilled and basic Solution polymerized Styrene Butadiene Rubber (SSBR) formulation in the presence or absence of liquid polymers. The target is to gain a clearer understanding of the plasticizing effect and contribution to the crosslinking of the different materials of the liquid polymer and the comparative materials.

In the present study, Treated Distillate Aromatic Extract (TDAE), aliphatic hydrocarbon resin and different liquid polymers were comparatively introduced in SSBR blends. PALS was used to determine the free volume in relation to the T_g s, measured by Differential Scanning Calorimetry (DSC). The Mooney-Rivlin method [13,14] was used as a measure for the CLD. It is compared to the rheometer curing characteristics as well as Shore hardness values.

6.2. Experimental

6.2.1. Raw Materials

The same raw materials were used as listed in chapter 3.2.1. Cyclo-aliphatic C5 resin (Al-C5), IMPERA R1507 ($T_g = 47\text{ }^{\circ}\text{C}$) supplied by Eastman, was used additionally in this study. The low molecular weight 'liquid' polymers were selected from Kuraray and are listed in Table 6.1. The range covers different types having different molecular weights and 1,2-vinyl contents. The "L" refers to liquid or low molecular weight polymer; "BR", "SBR" and "IR" refer to the type of polymer, butadiene, styrene-butadiene and isoprene rubber.

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Table 6.1 Main properties of the liquid polymers [15].

Synonym	Product Name	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-307	8,000	Low	-95	1.5
L-BR-2	L-BR-361	5,500	High	-49	0.6
L-BR-3	L-BR-305	26,000	Low	-95	40
L-IR	Experimental	10,000	Low	-63	3
L-SBR	L-SBR-820	8,500	High	-14	350

^A Vinyl Content: Low 10 – 40 %, High 40 – 70 %

6.2.2. Preparation of Blends and Sample Plates

Table 6.2 shows a basic rubber formulation. No fillers were added to allow a focused discussion on the effects of the extending materials. The reference formulation is only with SSBR as main polymer and without any extending materials. Different liquid polymers, TDAE and Al-C5 resin were added on top to this basic formulation.

The compounds were mixed in three stages according to the procedure described in chapter 3.2.2. The used procedure in this chapter differs from that in chapter 3.2.2. in the following way: no fillers were used, the discharging time was set to 7:00 (minute:second).

The compounds were cured on a Wickert press according to the procedure described in chapter 3.2.2.

In Figure 6.4, 6.5 and 6.7, each compound version will be labeled according to the introduced liquid polymer as described in the previous chapter and Table 6.2. The concentration will be included in the designation, e.g. 30 phr L-BR-1 will be labeled with L-BR-1_30.

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Table 6.2 Formulation of the model compounds.

Formulation	Reference	Extended
SSBR	100	100
TDAE, Resin or Liquid Polymer	0	15 - 30
Zinc Oxide	3	
Additives	1.5 (6PPD) 2 (Stearic Acid) 1.5 (Wax)	
Sulfur	1.5	
Accelerator	2 (CBS) 0.2 (DPG)	

6.2.3. Measurement and Analysis

Hardness and Rheology

The hardness and curing kinetics were performed according to the description in chapter 3.2.3 with the exception that only one frequency (at 1.667 Hz) was used to evaluate the curing torques.

Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry (DSC) was performed with DSC Polyma 214 from Netzsch-Gerätebau. Approximately 10 mg of the sample was placed in an aluminium pan with lids. The measurements were carried out under nitrogen atmosphere. The heating rate was set to 10 °C/min from -100 °C to +80 °C. The data was taken from the inflection points of the heat capacity change during the heating steps and defined as the glass transition temperature.

Positron Annihilation Lifetime Spectroscopy (PALS)

A positron is the antiparticle of the electron, which will be annihilated after encountering the electron. In the present study the positron is obtained from β^+ decays of the isotope ^{22}Na as shown in Figure 6.1. Their mass is transformed into photons, mainly into two photons emitted in opposite directions. Each has an energy equal to the mass of a resting electron m_0c^2 of 511 keV. Photons can change their energy according to the Doppler effect. The direction of

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the emission is therefore slightly changed and broadened to the opposite 180° angle. Another effect that accompanies the appearance of the positron is the fact that it does not annihilate immediately. The lifetime of the positron depends on the annihilation from the moment the positron appears.

Figure 6.1 Scheme of generation and annihilation of a positron in the Positronium state.

A typical lifetime of a positron differs between 100 and 500 ps. In low electron density areas the positron and electron create first an unstable positron-electron bound state. Such a hydrogen-like atom is called the Positronium (Ps). Ps can appear in regions with very low electron density, mainly pores, or regions of local free volume between molecules.

The positron lifetime spectrum measurements were conducted with a spectrometer whose assignment is shown in Figure 6.2. It consists of two scintillation detectors in which the scintillator is a barium fluoride (BaF_2) crystal and the photomultiplier is an XP2020Q by Philips. The detectors register the photons emitted from the positron source, isotope ^{22}Na , enclosed in the Kapton film, and two identical samples that surround the source. Two differential discriminators (ORETC CFD 573) allow the amplitude spectrum to receive pulses that correspond to the annihilation photon produced during the positron annihilation. The energy is 511 keV. The second discriminator at the output gives pulses corresponding to 1274 keV energy photon, which occurs when the positron is generated. These two pulses are converted into voltage signals and transferred to the time-amplitude converter (ORTEC TAC 566) whose height is proportional to the time interval between them. The amplitude spectrum of these pulses is recorded in a multi-channel analyzer (Hetaman 8002 based on the Camberra ADC 8701 system) and corresponds to the positron lifetime spectrum.

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Figure 6.2 Assignment (schematic) of the spectrometer for the measurements of the positron lifetime spectrum. MCA represents the multichannel analyzer and HV means high voltage.

The time resolution capability, the Full Width at Half Maximum (FWHM) of this system, is 0.28 ns and the background to peak ratio is 1.3 %. The presented spectrometer works in a fast-fast system. The term relates to the time and energy selection measurement which is carried out in a fast differential discriminator.

The measured spectrum is a convolution of Equation 6.1 and timing resolution of the spectrometer applied. In the process of deconvolutions of the spectrum, and thus the determination of intensity and corresponding positron lifetime components, other parameters are also taken into account, i.e. the contribution of the positron source [10].

The positron lifetime spectrum is an important measured characteristic, providing counts per time by detecting the time between generation and annihilation of positrons. Assuming that at time $t = 0$ the positrons (obtained from β^+ decays of isotope ^{22}Na entering the sample), the number dn of annihilating positrons in the time interval dt varies with the passage of time according to Equation 6.1):

$$-\frac{1}{n_0} \frac{dn}{dt} = \frac{I_1}{\tau_1} \exp\left(-\frac{t}{\tau_1}\right) + \frac{I_2}{\tau_2} \exp\left(-\frac{t}{\tau_2}\right) + \frac{I_3}{\tau_3} \exp\left(-\frac{t}{\tau_3}\right) \quad (6.1)$$

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where I_i is the component intensity which corresponds to the counts of generation or annihilation of a positron, τ_i is the positron's lifetime, $i = 1, 2, \dots$ numerates the number of state from which the positrons annihilate. In practice, this equation is convoluted with the timing resolution of the spectrometer and added with a background. Due to the arrangement of the spins of both particles, the electron and the positron, Ps can exist in two states, the para-Ps (p-Ps) when the spins are set antiparallel and the ortho-Ps (o-Ps) when the spins are parallel. This fact is essential for the self-annihilation of Ps. p-Ps annihilates after 125 ps converting into two gamma quanta, and o-Ps after 142 ns. The o-Ps state is formed in the ratio of 3:1 in relation to p-Ps.

In vacuum, p-Ps and o-Ps decay with an average time of 125 ps into two annihilated photons and three photons with the average time of 142 ns, respectively. The o-Ps state is formed in the ratio of 3:1 in relation to p-Ps. However, these numbers can be changed significantly due to different types of interactions. For example, the o-Ps can be quenched in several processes [16]. The decay time of the o-Ps is therefore significantly shortened. Additionally, this time is influenced by the environment, in particular the radius of the free volume. For the spherical free volume, its radius R is related to the average lifetime τ_3 of the o-Ps decay during the pick-off process [11,12]:

$$\tau_3[ns] = 0.5 \left[1 - \frac{R}{R+\Delta} + \frac{1}{2\pi} \sin 2\pi \frac{R}{R+\Delta} \right]^{-1} \quad (6.2)$$

where $\Delta = 0.1656$ nm. This is an empirical parameter describing the depth of penetration of the positional wave function into the area where the electrons are located. The increase in the value of the radius R of the free volume causes a non-linear increase in the value of the life time, component τ_3 .

Another important parameter characterizing the properties of the material is the fraction of free volumes f_v . It is connected with the intensity of I_3 of o-Ps in the spectrum of life times in the following relation [17].

$$f_v = a V_v I_3 \quad (6.3)$$

where $V_v = 4\pi R^3/3$ is expressed in $\text{\AA}^3$, and coefficient a of 0.0018 [12]. The relation is only valid if no other effects lead to changes of the measured positron lifetimes, e.g. the presence of dangling bonds.

f_v provides an indication of the number of the total free volume sites. R provides an indication for the average size of the free volume.

Mooney-Rivlin Stress Strain Analysis

The stress strain measurement is performed on a Zwick Z020 tensile device. It is conducted without pre-strain due to the absence of fillers. The determination is taken from a gradually increased extension ratio, which is defined as λ . The reduced stress is taken from the equilibrium stress of the sample [18,19]. For the calculation of the CLD, the reduced stress, σ_{red} is plotted over the reciprocal extension and can be defined by the semi-empirical equation 6.4 [13,14]:

$$\sigma_{red} = \frac{F}{A_0(\lambda - \lambda^{-2})} = 2C_1 + \frac{2}{\lambda}C_2 \quad (6.4)$$

F is the force in N, A_0 is the cross-sectional area measured in mm². C_1 and C_2 are material constants, while C_1 is assumed to be the contribution of the crosslinking units. C_2 is the Mooney-Rivlin elastic constant and considered as the contribution of trapped entanglements.

The graph obtained from equation 6.4 for the different stress-strain values consists of a linear region. The slope is C_2 and the interception is C_1 . The material constant C_1 can be calculated to the crosslink density, v_e in mol/m³ by Equation 6.5.[13,14]

$$2C_1 = RTv_e \quad (6.5)$$

R is the gas constant in J*K⁻¹*mol⁻¹ and T is the temperature in K. In the further discussion, the crosslink density will be expressed as C_1 in mol/m³ and the entanglements will be expressed as C_2 , corresponding to its elastic contribution in MPa.

6.3. Results and Discussion

Curing and Hardness

The cure characteristics and hardness values of the sulfur cured mixtures with different plasticizers and liquid polymers are depicted in Table 6.3. Corresponding to the unextended reference, all samples show clear plasticizing effects indicated by the decreased torque and hardness values. The TDAE and aliphatic resin Al-C5 show higher maximum torques and hardness values compared to the liquid polymers. An exception is true for the high molecular weight L-BR-3, it indicates a higher CLD for the liquid polymers. In this case, the polymer chains of L-BR-3 react more effectively with the polymer chains of the main polymer due to the higher chain length.

Comparing the minimum torque values of L-BR-3 with the value for the TDAE-filled compound, the tendencies are converse to the CLD: the liquid polymers show a higher value. It can at least partially be derived from the higher initial viscosities of the compounds containing the

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liquid polymers – indicated by the higher minimum torque value. The reason for this higher viscosity is due to the higher molecular weight compared to the TDAE. Similar tendencies, higher minimum torques and lower maximum torques with liquid polymer have also been demonstrated in silica-filled compounds as shown in *chapter 3*. In the presently study, no fillers are used and the discussion can focus on the main polymer and the extending material. The differences of Shore hardness values and minimum torques are still present, yet of higher significance.

Comparing the microstructures of three different L-BR's, only small differences can be observed in dependence of the 1,2-vinyl contents. It is anyhow noteworthy and different to the previous investigation shown in *chapter 3*, wherein the difference between the torques and CLD were clearly pronounced. However, this was achieved by a higher reactivity between the 1,2-vinyl-rich structure and the silane coupling agent [20]. It is a different case as for the present investigation with an unfilled compound, where only elemental sulfur and not a sulfur-containing silane is used. The small difference shown in Table 6.3 can therefore be attributed mainly to the slightly higher molecular weight.

Table 6.3 Comparison of curing torques and Shore A hardness of the different mixtures.

	Min. Torque (dNm)	Max. Torque (dNm)	Shore A Hardness
Reference	0.38	7.50	42
TDAE	0.12 (0.20 ¹⁾)	5.01 (5.81 ¹⁾)	38 (41 ¹⁾)
Al-C5	0.18 (0.24 ¹⁾)	4.55 (5.60 ¹⁾)	40 (39 ¹⁾)
L-BR-1 (<i>low MW, low 1.2-vinyl</i>)	0.11 (0.18 ¹⁾)	3.91 (5.28 ¹⁾)	38 (40 ¹⁾)
L-BR-2 (<i>very low MW, high 1.2-vinyl</i>)	0.12	4.02	39
L-BR-3 (<i>high Mw, low 1.2-vinyl</i>)	0.14	5.49	42
L-IR	0.12	4.02	33
L-SBR	0.16 (0.23 ¹⁾)	4.38 (5.37 ¹⁾)	36 (39 ¹⁾)

¹⁾ Contains 15 phr of the extending plasticizers and liquid polymers, all other extended mixtures contain 30 phr.

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This influence of the different molecular weights can clearly be observed by comparing L-BR-1 and L-BR-3. The high molecular version shows a high torque and high hardness value. Compared to the other liquid polymers, it can be assumed that a higher CLD is achieved. This is associated with the higher statistical possibility – i.e. higher molecular weight – to achieve two or more crosslinking units per molecule of the liquid polymer and the higher contribution to the final mechanical strength or modulus [21].

The polymer type of the liquid polymers shows the following dependences: The polyisoprene L-IR shows a comparable torque value with the low 1.2-vinyl content L-BR-1. Normally, a higher torque would be assumed because of the higher reactivity of the double bond of the isoprene structure [22]. However, the reason herein is associated with the lower compatibility of the L-IR together with the SSBR base polymer compared to all L-BRs and the L-SBR. It is also plausible regarding to the strong decrease of the Shore hardness compared to the other versions. Within the molecular weight range, the L-SBR shows the highest maximum torque value, which indicates the highest CLD. This is also attributed to the compatibility which is logically higher in the case of the L-SBR.

Glass Transition and Positron Lifetime

The free volume is the total volume minus the volume occupied by the molecules. Above the T_g , the polymer motion starts, resulting in a higher increase of the free volume. For the evaluation of the free volume, the T_g should therefore be taken into consideration.

For the different plasticizer and liquid polymer extended SSBR blends, Table 6.4 shows the individual material T_g s, the calculated compound T_g s and measured T_g s by DSC. All T_g values were compared to the positron lifetimes obtained from the PALS measurement. The difference between measured and calculated T_g provide a further information of the compatibility of the materials. The calculated T_g s were obtained from the Fox equation as below [9].

$$\frac{1}{T_g} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}} \quad (6.6)$$

Where w_1 and w_2 are the weight fractions and $T_{g,1}$ and $T_{g,2}$ the glass transition temperatures of the different polymers.

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Table 6.4 Glass transition temperatures and Positron Lifetime of materials and compounds.

	T_g^1 of the polymer (°C)	T_g of the compound, calculated (°C)	T_g of the compound, DSC (°C)	τ_3 (ns)
Reference ¹	-25	-25	-23	2.59
TDAE	-49	-31 (-28 ²)	-28 (-24 ²)	2.69 (2.63 ²)
Al-C5	47	-11 (-18 ²)	-18 (-19 ²)	2.49 (2.52 ²)
L-BR-1 (low MW, low 1.2-vinyl)	-95	-46 (-37 ²)	-40 (-35 ²)	2.78 (2.73 ²)
L-BR-2 (very low MW, high 1.2-vinyl)	-49	-31	-39	2.70
L-BR-3 (high Mw, low 1.2-vinyl)	-95	-46	-40	2.75
L-IR	-63	-35	-25	2.63
L-SBR	-14	-23 (-24 ²)	-23 (-27 ²)	2.53 (2.58 ²)

¹) T_g of pure polymer, SSBR (Remaining values are for the TDAE, Al-C5 and liquid polymers). All data obtained from the suppliers.

²) Values in () contain 15 phr of the extending plasticizers and liquid polymers, all other extended mixtures contain 30 phr

³) The variation of the single measurements of τ_3 is in the range of +/- 0.02 ns.

Clear differences are shown for the difference in 1,2-vinyl contents of the L-BRs, comparing the L-BR-1 and L-BR-2: The measured T_g of the compounds are almost identical with -40 °C for L-BR-1 and -39 °C for L-BR-2. However, the calculated T_g s showing a difference of 15 °C between the two versions. It is related to the main polymer, which is based on a 1,2-vinyl-rich SSBR. From the solubility parameter concept, developed by Joel Hildebrandt [23], it is an obvious assumption that the butadiene segment of the main polymer interacts preferable with the 1,2-vinyl rich L-BR-2 – and less with L-BR-1.

This is based on the general understanding that similar substances are miscible with each other. Herein, similar can be attributed if the chemical substances are identical or if two or more different substances are based on the same chemical basis. In both cases, the interactions between the single molecules are similar. These interactions are based on van der Waals forces, dipolar forces and hydrogen bondings. The solubility parameter concept determines similarities with a value that can be described and calculated with equation 6.7 [26].

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$$\delta = \sqrt{CED} = \sqrt{\frac{\Delta_v H - R \cdot T}{v_{Mol}}} \quad (6.7)$$

The Hildebrandt solubility parameter δ is defined as the square root of the Cohesion Energy Density (CED). It is derived from the vaporization enthalpy $\Delta_v H$, while R is the gas constant and T the temperature, v_{Mol} is the mol volume. In general, the closer the solubility parameters δ between two substances the better are their miscibility with each other.[23]

The δ value - obtained from the literature - of the different plasticizers and liquid polymers are displayed in Table 6.5.

Table 6.5 Solubility parameters of the pure materials, the SSBR, different plasticizers and liquid polymers.

	Solubility parameter, δ (J ^{1/2} /cm ^{3/2})	$\delta_{SSBR} - \delta_{Plasticizer}$ (J ^{1/2} /cm ^{3/2})
SSBR ¹	18.6 [24]	-
TDAE	17.2 [25]	1.4
Al-C5	17.9 [26]	0.7
L-BR-1 (low MW, low 1.2-vinyl)	16.1 [27]	2.5
L-BR-2 (very low MW, high 1.2-vinyl)	17.4 [28]	1.2
L-BR-3 (high Mw, low 1.2-vinyl)	16.1 [27]	2.5
L-IR	16.7 [29]	0.9
L-SBR	18.6 [25]	0

¹) δ of pure polymer, SSBR (other values are for the TDAE, Al-C5 and different liquid polymers).

From the calculated differences it can be presumed that the compatibility of the extending materials with the SSBR is in the following order): L-SBR (1), Al-C5 (2), L-IR (3), L-BR-2 and TDAE (both 4), L-BR-1 and L-BR-3 (both 5). While 1 indicates the highest and 5 the lowest compatibility. Comparing the structures, this order is plausible. Some of the indicated

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compatibilities correspond to the measured T_g s. The L-SBR – rated with 1 – shows for example the same values for the calculated and measured T_g s.

Figure 6.3 shows the possible incorporation and interactions of the different liquid polymers and plasticizers into the main polymer network. L-BR-2 can be assumed to be integrated. This can occur by a covalent connection through the co-reaction with the main polymer or by physical interactions between the 1,2-vinyl groups.

Figure 6.3 Co-crosslinking of liquid polymers with the main polymer network, Schematically visualized for the different liquid polymer types.

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The free volume, associated with the τ_3 value, is the lowest for L-BR-2 among the three L-BRs. It is a further indication of the higher interaction of its 1,2-vinyl groups with the main polymer, resulting in a more compact morphology. The difference of the molecular weight is less significant as the difference between L-BR-1 and L-BR-3. An effective plasticization is generally created throughout spacers in-between the polymer chains, according to the plasticizing theory with an increased free volume [4,5].

The L-SBR – with a higher T_g as the main polymer – shows an anti-plasticization effect with an increase of the compound T_g . It shows the lowest τ_3 value of all considered liquid polymers.

A lower impact on the T_g of the extending material is visible with regard to the L-IR and the Al-C5 resin. It is also a plausible assumption that the compatibility is lower. The L-SBR shows the opposite and a stronger impact on the measured T_g . The T_g corresponds also to the crosslink density and the compatibility. This fact explains the differences among the three materials. Based on Figure 6.3, it can be presumed that L-SBR is incorporated more effectively (through the interactions of the aromatic groups), followed by L-IR (mainly through the co-crosslinking) and Al-C5 (through the cycloaliphatic and aromatic groups interaction).

Free Volume Radius

Table 6.6 shows the calculated free volume radius according to equation 6.2. For the purpose of verification, three versions are repeated and compared to the original results. The reproduction was carried out on a different mixer with a mixing size of 100 ml. The raw materials, mixing and curing condition were applied according the procedure, aligned with the original tests. Table 6.6 shows the original Free Volume Radius R compared to the repeated results, the Control- R . The deviation between the original and repeated versions correlates well. The control value of L-BR-1 shows a slightly lower value than the original mixture. It can be attributed to the variation of the mixing procedure. However, the tendencies shown above still remain. From these results, a high liability of the comparative results in the previous figures can be estimated. The deviation is small and within the range ± 0.002 nm.

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Table 6.6 Verification of PALS Results, original Free Volume Radius R and repeated Control- R .

	R (nm)	Control- R (nm)	Deviation between R Control- R (%)
TDAE	0.334	0.332	0.6%
L-BR-1 (<i>low MW, low 1.2-vinyl</i>)	0.348	0.336	3.5%
L-SBR	0.329	0.329	0.0%

¹⁾ All extended mixtures contain 30 phr of TDAE, L-BR-1 and L-SBR

²⁾ The variation of the single measurements is in the range ± 0.002 nm.

The effect becomes more visible in Figure 6.4, showing the calculated free volume radius according to equation 6.2 versus the glass transition temperature. With the introduction of the different extending materials, the free volume changes in accordance with the material type in two directions:

1. In the presence of liquid butadiene (L-BR) and liquid isoprene (L-IR), the free volume is increased.
2. In the presence of the aromatic (TDAE, L-SBR) and cycloaliphatic (AI-C5) materials, the free volume is maintained or reduced.

In case of the different L-BRs and the L-IR (1.), the material acts - as explained above – more as a spacer according to the plasticizing theory [4,5]. As shown in Figure 6.3 it is likely to be connected with the main polymer throughout a co-reaction. The lower interactions between the 1,2-vinyl segments with the main polymer lead to a higher mobility and more space. This leads to the effect of pushing apart the polymer chains of the main polymer. Consequently, the free volume radius is increased. The effect is particular true for the L-BR-1. Compared to L-BR-1, the higher molecular weight L-BR-3 shows slightly lower free volumes. However, still higher compared to the reference. It is possibly due to a higher CLD (for L-BR-3).

The high 1.2-vinyl containing L-BR-2 shows the lowest increase of the free volume radius among the three L-BRs. It is associated to the interactions of the 1,2-vinyl segments between the main polymer and L-BR-2.

In case of the aromatic and cyclic containing materials (2.), alongside the constant or decreased free volume, an anti-plasticizing effect - visible through the increased T_g - can be

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seen when referring to the Al-C5 resin. Generally, with the introduction and increased content of Al-C5 and L-SBR, the free volume decreases constantly. It is different in the case of the TDAE: a 15 phr addition increases the free volume while a further addition to 30 phr reduces it. This tendency is in accordance with a previous study with TDAE extended SSBR and BR compounds. 10 phr TDAE showed an increase of the free volume, while a further increase to 20 phr did not show any or, if at all, merely a small effect. It is assumed that this is attributed to the crystallization: a rivaling progress of the spherulite formation (with lower contents) and spherulite hindrance (with higher contents).[7]

Both the L-SBR and Al-C5 resin show very similar tendencies. According to their T_g s and aromatic or cyclic groups, they display a decrease in terms of the free volume. The chain mobilities are reduced, thus corresponding to the reduced T_g values. Compared to the reference, the Al-C5 and the 30 phr L-SBR containing compounds show an anti-plasticizing effect with higher T_g s.

Figure 6.4 Free volume radius versus glass transition temperatures of compounds containing TDAE, resin and liquid polymer.

A previous study concluded that the bulky aromatic groups of TDAE are pushing the SSBR chains apart, which is in accordance with the plasticizing theory [7]. This leads to an increase of the free volume and segmental mobility. With the increased Free Volume Radius and reduced T_g , it is true and visible for the 15 phr TDAE extended SSBR. However, the L-SBR shows another tendency: The free volume is reduced even though it contains aromatic groups.

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The explanation for this is based on the high compatibility between the L-SBR and SSBR. According to a previous study in *chapter 3* L-SBR/SSBR combinations result in high crosslink densities and modified dynamic properties corresponding to relatively high compatibilities and incorporation into the polymer network. Instead of pushing the chains apart, it is therefore a plausible explanation that the bulky aromatic groups of the L-SBR fill voids between SSBR chains. The aromatic groups contain a conjugated system with delocalized electrons that are not clearly associated to individual atoms, the π electron system. Herein, different π electron systems can interact together by the non-covalent π - π interactions. It results to π - π stacking and therefore a strong concentration of the different aromatic π systems.

It is still in accordance with the plasticizing theory [4,5]: the result implies that a certain compatibility is necessary, while at the same time, a certain incompatibility is equally necessary in order to not fully dissolve the plasticizing material into the base material. The effect is similar with regard to the aromatic TDAE and cyclic Al-C5 resin.

The V_h value is connected to the intensity, I_3 , which is associated with the number of free volume sites. This provides a statistical average in percent of the total free volume, the fractional free volume, F_v , calculated according to Equation 6.3. Figure 6.5 shows F_v versus the T_g . The two main tendencies, as described above for the free volume radius, can be confirmed: 1. Increased free volume for the L-BR, 2. Reduced free volume for the aromatic and cyclic materials. However, there is no correlation in this case, a regression curve leads to a r_2 of only 0.2.

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Figure 6.5 Fraction of free volume calculated using Equation 6.3 of compounds containing TDAE, resin and liquid polymer as a function of glass transition

Figure 6.6 schematically shows the effect on the free volume by incorporating the different materials. The less compatible L-BR is acting as a spacer and pushes the polymer chains apart. It avoids a concentration and meshing of the styrene groups. The free volume radius is consequently increased. In case of the L-SBR, the aromatic groups concentrate together with the SSBR's styrene groups and reduce the free volume by filling the voids. Similar effect will happen with the AI-C5 resin and the TDAE. However, this is one explanation, it has to be taken into account that the liquid polymer becomes part of the polymer network, which will be discussed herein after.

Figure 6.6 Free volume radius of L-BR and L-SBR extended SSBR (scheme) and the possible area where Positronium is formed.

Crosslink Density

The free volume depends on the crosslinking network and compatibility. It is known that increased crosslink densities result in increased T_g s [29,30]. A higher thermal energy is required to enable the mobility of the polymer segments [31]. Bandzierz et al showed that the free volume is reduced almost linearly with an increased crosslink density [32]. For the interpretation of the results, the crosslink densities have to be considered besides the compatibility considerations discussed above.

The CLD was determined by the Mooney-Rivlin approach. It is demonstrated that this method correlates well with other methods [33], e.g. to the equilibrium swelling methods according to Flory-Rehner. However, the latter subjects more on a swollen ideal network. For the present evaluation, the Mooney-Rivlin method was chosen to provide a broader information and the contribution of the entanglements C_2 to the reduced stress, according to Equation 6.4.

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Figure 6.7 shows the CLD versus the elastic contribution of the entanglements C_2 . There is no correlation, a regression curve leads to a r_2 of only 0.2. The range of the CLD is between 70 mol/m³ and 100 mol/m³ or 0.7E-4 mol/cm³ and 1.0 E-4 mol/cm³, respectively. The range is lower but comparable to the studies in *chapter 3 and chapter 5*. Therein, additionally sulfur-containing coupling agents and silica as a filler were used. In these studies the CLD was determined by the Flory-Rehner method. Comparing the reference with the two non-reactive plasticizers (TDAE and AI-C5), the reference compound without plasticizer shows the lowest CLD and a significant higher C_2 , implying a high contribution of trapped entanglements. The TDAE shows a higher CLD and lower C_2 . The AI-C5 shows the highest CLD and lowest C_2 .

The results imply that both, plasticizer and curatives are necessary for an efficient crosslinking. In the non-plasticized compound, the curatives and the connected high molecular weight chains are limited in their mobility. Consequently they react and form connections associated to a less-ideal network [21]. It is particularly with more intermolecular connections and trapped entanglements due to the lower flowability between the chains. It is a different case for the plasticized compounds wherein the mobility is increased, supported by a lubrication effect that allows re-entanglement of the polymer chains – due to a lower restriction of the polymer chains. Another reason for the effective crosslinking may be associated to a better distribution of the curatives inside the compound due to the liquefaction.

Several studies mention that the presence and type of the plasticizers in general not only support the crosslinking reaction but also actively influence the crosslinking reaction [34,35]. The same is true for the two non-reactive plasticizers, the TDAE and AI-C5.

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Figure 6.7 CLD and entanglements of compounds containing TDAE, resin and liquid polymer as a function of glass transition.

The high CLD for Al-C5 can be associated to the concentration of the cycloaliphatic and aromatic groups. In between, the butadiene segments move freely and efficiently form crosslink sections. It further increased the lubrication between the polymer chains and therefore shows a low amount of trapped entanglements. The same explanation is true for the TDAE. However, the lower polarity and lower solubility parameter δ – and lower individual and compound T_g – result in a slight increase in the free volume as shown above in Figure 6.4 and Figure 6.5.

Compared to the non-reactive plasticizer (TDAE and Al-C5), most liquid polymer extended compounds show lower crosslink densities. This is a result of the co-reaction with the main polymer as shown in *chapter 3, 4 and 5*. More polymers consuming the same concentration of curatives. The liquid polymer will form a less ideal network with a lower amount of crosslink sections per chain - due to its significant lower molecular weight. Compared to the TDAE and Al-C5, particularly noteworthy but plausible is the concentration dependency. In both cases, for L-BR-1 and L-SBR, the increase from 15 phr to 30 phr result in reduced CLD and increased amount of entanglements. The higher concentration of liquid polymer increases the reactive polymeric content while the content of curatives is constant. In case of the TDAE and Al-C5, the change from 15 phr to 30 phr shows no effect on the CLD and entanglements.

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The L-BR-1 – with its highest free volume as previously shown in Figure 6.4 and Figure 6.5 – shows a relative low CLD, along with the highest amount of entanglements within the liquid polymers. The tendency is inverse to Al-C5 that shows the lowest free volume, lowest entanglements and a highest CLD. It is in correspondence with the entanglements, where L-BR-1 shows the highest value of C_2 and Al-C5 the lowest. Different to this shows the L-BR-1 a spacer function according to the plasticizing effect with a clearly higher free volume. Additionally - due the co-reaction with the main polymer – it creates a less ideal network according to the network theory.

The L-SBR shows a relatively high CLD and a lower C_2 compared to the L-BR-1. It is therefore plausible that the aromatic styrene groups of the L-SBR concentrate with the styrene groups of the main polymer as shown in Figure 6.5 by the π - π interactions as described above. It results in a lower free volume, a higher reactivity of the butadiene segments and finally a higher CLD.

The 1,2-vinyl-rich LBR-2 shows the lowest CLD with a low concentration of entanglements. It is different to all previous discussed results that always showed an inverse tendency between CLD and entanglements: a high CLD along with a low C_2 or vice versa, a low CLD along with a high C_2 . It can be assumed that L-BR-2 is highly incorporated into the main polymer network with the 1,2-vinyl-rich based SSBR, as discussed in the sections *Glass Transition and Free Volume*. The free volume is lower than for the L-BR-1, implying an increased compatibility and a lower spacer function. As a combined result, a higher participation of L-BR-2 to the total crosslinking reaction can be assumed. However, it generates a lower CLD compared to the L-BR-1 containing compound. The reason is that L-BR-1 is less participating in the crosslinking reaction. Consequently, the SSBR main polymer builds a slightly more effective network. It is through more crosslinks that are connecting the main chains and with a lower deterioration the total network.

Compared to the L-BRs, the L-IR shows a slightly higher CLD. It is due to the higher reactivity of the double bond in the isoprene structure [22]. Only the high molecular weight L-BR-3 shows a higher CLD, on a similar level as the L-SBR. It will result in a more ideal network with two and more crosslink units per chain. From L-BR-3 it can also been concluded that a stronger incorporation and higher CLD leads to a smaller free volume – or vice versa.

6.4. Conclusion

Different liquid polymers were selected and varied in type (L-BR, L-IR, L-SBR), molecular weight and microstructure (low and high 1,2-vinyl). The materials were comparatively introduced and compared to TDAE and Al-C5 resin. The curing was measured using a

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dynamic mechanical rheological tester, and the Shore hardness was compared. For the cured compounds, PALS was applied to determine the values of the free volume radius and its fraction. The results were compared to the T_g s of the compound, measured by DSC. The stress-strain analysis according to Mooney-Rivlin was used to provide further information about the CLD.

Compared to the reference, the non-reactive plasticizer and liquid polymer extended compounds show plasticizing effects in their rheological characteristics and hardness values. The T_g and free volume is affected according to the type of the material and its incorporation behavior into the main polymer network. For the un-extended reference, the CLD exhibit the lowest value together with the highest value of C_2 , indicating a high concentration of trapped entanglements.

The extending materials result either to increased or decreased free volume radii and fractions:

- Increased free volume radii and fractions for the different L-BRs and L-IR.
- Decreased or no effect of the radii and fractions for the L-SBR, Al-C5 and TDAE.

Generally, the CLD is low in the case of the materials resulting in high (L-BRs and L-IR) and high in case of low free volumes (L-SBR, Al-C5 and TDAE).

The CLD is therefore closely associated and caused by the concentration of the aromatic or cycloaliphatic groups between the extending material and main polymer. Consequently, the reactive butadiene segments of the main polymer can react more freely and unhindered.

All extending materials influence the crosslinking reaction by a lubrication effect between the polymeric chains. The different liquid polymers influence the crosslinking further with the co-crosslinking and physical interaction corresponding to their structures.

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CHAPTER 7

NETWORK FORMATION OF LOW MOLECULAR WEIGHT 'LIQUID' POLYMERS

Studied by Gel Permeation Chromatography and Stress-Strain Analysis
according to Mooney-Rivlin

Abstract

The rheological and mechanical properties of elastomers are defined by their different networks: The crosslink network and the filler network. The crosslink network is influenced by the polymer structure. The filler network – particularly in case of silica as filler – depends on the interaction between the filler particles and the polymer. Liquid polymers can affect these networks by their lower molecular weight and functional groups. The goal of the present work is to gain a better understanding of the network formation: 1. During the sulfur curing of pure liquid polybutadienes, and 2. Through differently added liquid polymer-silica-masterbatches in sulfur cured silica/SSBR mixtures. Gel permeation chromatography was measured of the pre-cured liquid polymer samples and indicate an association between sulfur content and chain length. Stress-strain analysis according to Mooney-Rivlin provides information about the interaction of liquid polymers with silica and the main polymer when it is added differently throughout the masterbatch approach.

7.1. Introduction

To achieve elastomeric-like properties, polymeric materials and their blends have to generate a network structure. According to Treloar there are three essential elements necessary besides the curatives: 1. the network should be composed of long-chain molecules, 2. the forces in between them should be low and 3. the chains should be connected at certain points [1]. For the last point, the connected points are either crosslink units or entanglements. In between, the polymer chains should be able to rotate and move freely. Most diene elastomers are crosslinked by the accelerated sulfur vulcanization throughout their allylic position [2]. Different chemical connections are formed e.g. monosulfidic, polysulfidic and carbon-carbon bonds. They are created between the different chains but also formed intramolecular. They exhibit different binding energies [3]. Entanglements are another form of connections between the different polymeric chains. They already exist in the untreated form of a single polymer or in a mixture of different polymers. The concentration of entanglements are related to the chain lengths and the Van der Waals forces between them. Due to the presence of entanglements, even an un-vulcanized material can show some similar elastic characteristics as vulcanized material, e.g. the response to short-term loading [1].

Elastomer blends typically contain fillers that generate a secondary network: The filler network. In silica-filled blends, the inter-particle strength is based on the generation of larger silica clusters. The filler network contributes to the final modulus of the filler-polymer composition. For carbon black-reinforced rubber, the strain dependence of the moduli was discovered by Payne [4,5]. The final modulus is the sum of the strain dependent filler-filler interactions (the filler network) and the strain-independent (simplified) filler-polymer interactions, the hydrodynamic effects and the polymer-polymer interactions (or the in-rubber structure with crosslinks and entanglements) [6]. The filler network deteriorates the elastic properties. For silica containing compounds, mostly bi-functional Silane Coupling Agents (SCA) are used to couple between the silica particles and the polymer chains. With this, an additional network is generated: a silica-silane-polymer network [7,8].

Liquid polymers can be used as a supplement to the plasticizer and polymer mixture. Their potential influences on the polymer and filler networks have been discussed in *chapters 3 to 6*. The incorporation of a liquid polymer to a higher molecular weight polymer reduces the average molecular weight of the polymer and therefore also the ideal rubber network (*chapter 3* and *chapter 4*). As shown in *chapter 5*, the statistical number of each reacted double bond along the polymer chain is reduced with the introduction of liquid polymer from every 40th to every 30th double bond. This is due to the dilution to a lower molecular weight average. Moreover, the probability to create network defects, in particular dangling ends, is increased. In *chapter 6* it is shown, that the crosslink density and entanglement density depend on the

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plasticization and the free volume of a polymeric compound. The addition of liquid polymer shows not only an effect on the polymer network but also on the filler network. For a given compound - if a non-reactive plasticizer is replaced by a liquid polymer - the polymeric content increases. The bound rubber content increases, too, due to the higher available amount of polymer that can be attached to the filler. To optimize also the filler-filler interactions, a new category of liquid polymers was developed: Functionalized liquid polymers which can hydrophobize the silica surface and create an additional network [9]. In *chapter 5* it is shown that an additional network is generated in the presence of the functionalized liquid polymers – the quality of this network depends on the type of silane coupling, the type of the liquid polymer and the choice of functionalization. The previous work provides a good inside view into the liquid polymer's compatibility, the co-reaction and influence on the polymer network, and the improvement of filler-polymer interactions. However, it is still unknown how the network generation progresses and which steps occur during the formation.

To obtain a better understanding of this, only the pure liquid polymers are mixed with different levels of curatives to evaluate the network formation. Heat-exposed samples were measured by Gel Permeation Chromatography (GPC) and rheometer to obtain information about their crosslinking progress.

To investigate the liquid polymer and silica network properties, different modified and unmodified liquid polymer pre-blends with silica and silica/silane were produced. Their Crosslink Densities (CLD) and entanglement contributions were comparatively evaluated by means of the Mooney-Rivlin method. They were further analyzed by their hardness values, rheometer torques and Payne effect values.

7.2. Experimental

7.2.1. Raw Materials

The same raw materials were used as listed in chapter 3.2.1. Further raw materials for the present study include tetrabenzylthiuramdisulfide (TBzTD), supplied from Flexsys. The low molecular weight polybutadienes were provided from Kuraray and are listed in Table 7.1. One silane-modified type (experimental type, no grade name available) and different unmodified, commercially available types were selected. The designation of the different liquid polymer types is as following: the "L" e.g. in Si-L-BR refers to liquid or low molecular weight polymer; "BR" refers to the type of polymer butadiene, "Si" refers to the functionality with an ethoxy silane group.

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Table 7.1: Main properties of the different liquid polybutadienes: The cis content of all types is comparable and indicated as high [10].

Synonym	Product Name	Functionality (Si per Chain)	Molecular Weight (M _n , g/mol)	1,2-vinyl ^A (mol%)	T _g (°C)	Viscosity (Pa*s at 38 °C)
L-BR-1	LBR-307	-	8,000	Low	-95	1.5
L-BR-2	LBR-305	-	26,000	Low	-95	40
L-BR-3	L-BR-361	-	5,500	High	-60	3.5
Si-L-BR	-	2 (Grafted)	6,000	High	-50	5.3

^A) Vinyl Content: Low 10 – 40 %, High 40 – 70 %

7.2.2. Preparation

Formation of Liquid Polymer Networks

100 phr of L-BR-1 or L-BR-2 is pre-heated to 80 °C and mixed on a laboratory disperser with curatives and additives. The formulation of the sample mixtures is shown in Table 7.2. For the GPC analysis the final mixtures were stored in an oven for 20 minutes at 160 °C.

Table 7.2: Formulation of the liquid polymer networks (concentration in phr)

Formulation	L-BR-x_1.5 ¹	L-BR-x_3.0 ¹	L-BR-x_4.5 ¹	L-BR-x_6.0 ¹
Liquid Polymer	100	100	100	100
Sulfur	1.5	3	4.5	6
Zinc Oxide	3	6	9	12
Stearic Acid	1.5	3	4.5	6
CBS	2	4	6	8
TBzTD	0.2	0.4	0.6	0.8
6PPD	1.5	1.5	1.5	1.5
Wax	1.5	1.5	1.5	1.5

¹) x = 1 for L-BR-1 and x = 2 for L-BR-2.

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Henceforth, the designation of the blends is according to the liquid polymer type and the sulfur content: For example “L-BR-1_1.5”.

Network Properties with Liquid Polymers and Silica (Silica Masterbatches)

Table 7.3 shows the formulations of different silica Masterbatches (MB) with L-BR-3 and Si-L-BR-4. For the “MB-Silica” types, L-BR-3, Si-L-BR or TDAE was mixed with silica. For the “MB-Silica-TESPD” types, L-BR-3, Si-L-BR or TDAE was mixed with silica and TESPD. The masterbatch mixing was executed on a Brabender internal mixer with a mixing chamber size of 350 ml. The mixer temperature was set to 140 °C to reach a silanization.

Table 7.3: Formulation of the silica masterbatches (concentration in phr)

Formulation	MB-SILICA	MB-SILICA-TESPD
TDAE, L-BR-3 or Si-L-BR	100	100
Silica	80	80
TESPD	0	24 (16 ¹⁾)

¹⁾ Concentration (deviant) for Si-L-BR

The liquid polymer and silane coupling agent were added according to the total number of ethoxysilane groups in the masterbatches: this corresponds to 6 phr SCA for TDAE and the unmodified L-BR-3 as a reference, and 4 phr SCA for the silane-functionalized Si-L-BR. Henceforth, the designation of the masterbatches is according to the three components. For example: “SILICA_TESPD_TDAE” contains 20 phr silica, 6 phr TESPD and 25 phr TDAE; “SILICA_Si-L-BR” contains 20 phr silica, no TESPD, and 25 phr Si-L-BR.

Network Properties with Liquid Polymers and Silica (Rubber Compounds)

Table 7.4 shows the SSBR/Silica based model formulation. TDAE, L-BR and Si-L-BR are either individually and directly added during the main mixing (DIRECT) or comparatively via their masterbatches according to Table 7.3.

The compounds were mixed in three stages according to the procedure described in chapter 3.2.2. The following exceptions are applied: no carbon black was used, the discharging time was set to 7:00 (minute:second).

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The compounds were cured on a Wickert press according to the procedure described in chapter 3.2.2.

Table 7.4 Formulation of the SSBR/Silica model compounds with different procedures of addition.

Formulation	DIRECT	MB-SILICA	MB-SILICA-TESPD
SSBR	100	100	100
Silica	70	50	50
TESPD	6 (4 ¹)	6 (4 ¹)	0
TDAE, L-BR-3 or Si-L-BR	25	0	0
MB-SILICA	0	45	0
MB-SILICA-TESPD	0	0	51 (49 ¹)
Zinc Oxide	3	3	3
Stearic Acid	1.5	1.5	1.5
Sulfur	1.5	1.5	1.5
Accelerator	2.0 CBS 0.2 TBzTD	2.0 CBS 0.2 TBzTD	2.0 CBS 0.2 TBzTD
Antidegradants	1.5 6PPD 1.5 Wax	1.5 6PPD 1.5 Wax	1.5 6PPD 1.5 Wax

¹Concentration (deviant) for Si-L-BR

Henceforth, the designation and description of the compounds is according to the three different procedures with varying additions.

The compounds in Table 7.4 were characterized according to their rheological and stress-strain properties (as described in the next chapter). One additional set of samples were produced without curatives (sulfur, zinc oxide and accelerator) and characterized by its curing characteristics.

7.2.3. Measurement and Analysis

Gel Permeation Chromatography (GPC)

The molecular weight was measured by GPC, the manufacturer and type of the device is Agilent 1200 Series with refractive index detector and UV detector, operating at 254 nm, columns: PLgel, 3 μ m, MIXED-E. The column temperature was set to 40 °C, tetrahydrofuran (THF) was used as solvent for the mobile phase at a flowrate of 1 ml/min. The molecular weight distributions were calibrated using a polystyrene (PS) solution with a molecular weight range from 162 to 27,810 g/mol.

Rheology

The hardness and the compounds' curing kinetics and Payne effect were performed according to the description in *chapter 3.2.3*. The frequency was set to 1.667 Hz.

Stress-Strain Analysis according to the Mooney-Rivlin Method

The method was performed according to the description in *chapter 6.2.3*.

7.3 Results and Discussion

7.3.1. Liquid Polymer Networks

Different concentrations of sulfur and curatives were added to two different liquid polymers, L-BR-1 and L-BR-2. The liquid mixtures were analyzed with a cure rheometer. The maximum torques after 20 minutes curing time indicate the final created crosslink network. The values are displayed in Figure 7.1.

The preceding work from *chapter 3* to *chapter 6* shows, that the combination of a low molecular weight liquid polymer with a conventional used high molecular weight main polymer reduces the maximum torques and the crosslink densities. This is due to the reduction of the overall molecular weight. Between the different polymer chains – assuming a constant concentration of sulfur – the statistical probability to form multiple crosslink units per chain is reduced.

In the present study, the influence of the molecular weight and concentration of sulfur is further considered. Figure 7.1a shows the maximum torque as a function of the sulfur content in phr. For both molecular weight types, at a certain concentration, the torque exhibits a rapid, increase due to a higher amount of created crosslinking points. In case of the lower molecular weight type, L-BR-1 (8,000 g/mol) the maximum torque increases from 0.1 dNm to 3.6 dNm

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for the corresponding concentration change from 4.5 phr to 6 phr. In case of the higher molecular weight type, L-BR-2 (26,000 g/mol), the torque increases from 0.07 dNm to 5.4 dNm for the concentration change from 1.5 phr to 3.0 phr. At this point, the formation of a network has started and progresses at an early stage, meaning that the polymer chains connect with each other and partially build larger segments. The torque values increase to a – still – small but significant degree. The appearance of the samples shows a solidification but they still contain liquid to pasty-like areas.

During mixing and vulcanization, the original molecular weight and structure of a polymer is altered [11]. Bartenev et al have defined a critical molecular weight at 1,000,000 g/mol. Molecules around this value or higher starts immediately with the formation of a three-dimensional network [12]. Everything below undergoes sub-sequential reaction steps prior to the network formation. The initial added sulfur is used for linking the single polymer chains into a growing and partially crosslinked structure. After achieving the critical molecular weight, the real network formation starts, meaning that the growing crosslinking segments start to connect with each other to an infinite network structure.

At this moment (when the critical molecular weight at 1,000,000 g/mol is reached), the formation progress is independent from the original molecular weight [12]. Considering this fact, the only difference between the two different liquid polymers is the required time until this network formation starts. In other words, the low molecular weight version exhibits a retarder function compared to the higher molecular weight version – until this particular breakeven point is reached and the network formation starts. In Figure 7.1 the range would be between the first significant increased values starting at 0.07 dNm or 0.1 dNm, respectively (indicating that the formation has started) and below 3.6 dNm or 5.4 dNm, respectively (indicating that the formation is in progress, but not completed). However, more gradual experiments would have been required to determine a narrower breakeven range.

The progress and speed is subjected to the initially added sulfur. In case of the low molecular weight version, more sulfur is required to reach this critical molecular weight. In Figure 7.1b the maximum torque is displayed as function of sulfur atoms per molecular chain, considering the initial molecular weights of the two liquid polymers.

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Figure 7.1 Maximum curing torque of the liquid polymers for different sulfur contents (a) and for different numbers of sulfur atoms per initial molecular chain (b). Cured for 20 minutes at 160°C.

The end torque depends on the sulfur per chain ratio. Compared to the overall measured values, L-BR-1 (6 phr sulfur) and L-BR-2 (3 phr sulfur) show comparable ranges for the maximum torque and sulfur per chain ratio as shown in Table 7.5. The sulfur content in the mixture of L-BR-1 has to be further increased to achieve the same proportional sulfur per chain ratio. With this, it can be assumed that the max. torque of L-BR-1 can be better adjusted. A plausible target concentration can be derived by the sulfur per chain ratio of L-BR-2. To achieve the same sulfur per chain ratio, the sulfur concentration in the compounds of L-BR-1 has to be increased to 9.4 phr (plus 3.4 phr) as shown in Table 7.5.

A similarity is seen for liquid polymer extended SSBR compounds from the results shown in *Chapter 6*. For SSBR as main polymer – with a significant higher molecular weight (assumed as 150,000 g/mol) – the sulfur content is 1.5 phr. This means that in average 35.2 sulfur atoms are attached to one polymer chain. If 15 or 30 phr L-BR-1 is added to SSBR, the sulfur per chain ratio drops to 30.8 or 27.5, respectively. The reduction is caused by the increase of polymer per volume unit but having the same amount of sulfur, meaning a less availability of sulfur per polymer. The torque is dropping correspondingly. For a proportional adjustment (35.2 sulfur per chain) the sulfur content should be increased to 1.7 or 1.9 phr, respectively (plus 0.22 or 0.42 phr) as shown in Table 7.5. Another example is the L-BR-2 wherein a lower adjustment is necessary compared to L-BR-1. The sulfur content has to be increased to 1.9 phr (for 30 phr L-BR-2). Within the ranges of the

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experimental series, it can be assumed that the maximum torque will be closer to that of the pure SSBR.

Table 7.5 Comparison of sulfur contents, sulfur per chain ratios and maximum torques for L-BR-1 and L-BR 2 with SSBR-based results obtained from chapter 6

Liquid Polymer	Sulfur Content (phr)	Total Polymer Content (phr) ¹	Combined M_w Average ² ($10^3 \cdot \text{g/mol}$)	Sulfur per Chain	Max. Torque (dNm)	Option for additional Sulfur (phr) ³
L-BR-2	3	100	26,000	11.8	5.4	-
L-BR-1	6	100	8,000	7.1	3.6	3.4
SSBR ⁴	1.5	100	150,000	35.2	7.5	-
SSBR/L-BR-1 ⁴	1.5	115	131,000	30.8	5.3	0.22
SSBR/L-BR-1 ⁴	1.5	130	117,000	27.5	3.9	0.42
SSBR/L-BR-2 ⁴	1.5	130	121,000	28.4	5.5	0.36

¹) 100 phr L-BR-1; 100 phr L-BR-2; 100 phr SSBR; 100 phr SSBR + 15 phr L-BR-1; 100 phr SSBR + 30 phr L-BR-1 or L-BR-2.

²) Content of L-BR * M_w + Content of SSBR * M_w .

³) Option to add additional sulfur to achieve the same sulfur per chain ratio as for L-BR-2 or SSBR, respectively.

⁴) Obtained from the results shown in *Chapter 6*.

Another important information is the molecular weight and structure before or at the initial moment of the network formation. GPC was used for the characterization of the samples containing different amounts of sulfur and curatives. As a pre-treatment, the samples were heat-exposed in an oven for 20 minutes at 160 °C. Herein, the heat transfer is less efficient compared to the rheometer measurement. It was intentionally considered to avoid fully-cured samples that couldn't be measured by GPC. The sample appearance remains liquid but shows a higher viscous and pasty-like consistence.

GPC is an exclusion measurement wherein a polymer solution passes through a column with a macroporous gel. The polymer solution is eluted by a constant flow of a solvent. At the end of the column the molecules are detected by a light scattering detector. The retention time corresponds to the elution volume, which is proportional to the molecular weight M_i . The intensity of the signal corresponds proportionally to the number of molecules w_i . Smaller molecule chains partially or fully permeate into the pores of the gel. The larger molecules passing faster through the column.

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In case of the sulfur extended pre-crosslinked liquid polymers, the solution transforms from a particle solution to a network solution. This leads to the fact that the single molecules are connected to each other faster, which means that the polymer is not fully diluted in the proper meaning of the GPC measurement. The flow and measured concentration is strongly affected. In practice, the reduced concentration has to be corrected depending on the polymer type [13]. A further constraint is given by the phenomenon that polymers build coils. In the GPC measurement these coils are diluted and flushed with the solvent. Depending on their individual structure, they are flushed differently. Polymers can be categorized as network solution (containing fully-flushed through coils) and particle solutions (un-flushed polymer coils).

Table 7.6 shows the number average, M_N and weight average, M_W calculated from the GPC measurement. With increased sulfur concentrations, both, the number average and the weight average do not change significantly. It is anyhow noteworthy that no changes could be determined: from the measurement principle, the first detected molecules are the larger ones and correspond to M_W . Furthermore, it can be presumed that larger molecules would be consumed first in the network and contribute more significantly to the formation progress. However, from the constant M_W and M_N values, this presumption seems to be less plausible. No clear conclusion can be made either the larger molecules are consumed first or all molecules are consumed randomly.

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Table 7.6 M_N and M_W obtained from the GPC for the different liquid polymers and different curative contents.

Type and Variation ¹	Molecular Weight (M_N , g/mol) ²	Molecular Weight (M_W , g/mol) ²
L-BR-1	9,717	10,014
L-BR-1_1.5 (<i>low Mw</i>)	9,867	10,025
L-BR-1_3.0 (<i>low Mw</i>)	9,760	10,018
L-BR-1_4.5 (<i>low Mw</i>)	9,731	10,014
L-BR-1_6.0 (<i>low Mw</i>)	9,752	10,017
L-BR-2	22,790	23,050
L-BR-2_1.5 (<i>high Mw</i>)	22,690	22,950
L-BR-2_3.0 (<i>high Mw</i>)	22,770	23,030
L-BR-2_4.5 (<i>high Mw</i>)	22,780	23,040
L-BR-2_6.0 (<i>high Mw</i>)	22,820	23,080

¹) Increased sulfur content with proportional adjustment of other curatives as described in 7.2.3.

²) Measured by GPC (values without curatives; L-BR-1: M_N 1,180 g/mol, M_W 9,790 g/mol; L-BR-2 M_N 710 g/mol, M_W 22,220 g/mol)

In the early progress of crosslinking, the molecule chains get connected to form branched structures, with a stronger tendency to build complex structures and a higher tendency to build coils or even gel-like particles. In these structures, the single polymer chains cannot be isolated by the solvent and they are consequently not detected. The real molecular weight of the cured liquid polymer samples can therefore been increased - even though the GPC measurement delivers constant values for M_N and M_W .

Figure 7.2 shows the molecular weight distribution curves. According to both the weight M_W and number average M_N , the signal intensity is reduced, corresponding to less molecules w_i that are passing through the column. What is measured are the remaining and unreacted liquid polymer chains, which are not yet consumed in the early moments of the network formation: The higher the sulfur concentration the lower the concentration of the remaining chains that are not consumed for the network formation. As a results of this, a lower intensity is measured by GPC.

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Figure 7.2 Molecular weight distribution of L-BR-1 (a) and L-BR-2 (b) and its sulfur extended compounds

The mechanism of sulfur vulcanization is still not fully understood. It depends on a wide multiplicity of occurring reactions, with a contribution of each single formulation ingredient [3]. This fact is also responsible for the broad spectrum and distribution of different sulfuric bonds. The crosslinking reactions can be a radical or an ionic initiated reaction [14]. For the accelerated sulfur vulcanization with tetraalkylthiuram sulfides (including TBzTD) and sulfenamides (including CBS) there is still no common understanding which reaction takes place [15]. It can be assumed that both reaction occur in parallel, depending on the molecular environment.

In case of a radical reaction mechanism, a fast initial vulcanization rate can be expected. The initial radicals react with the polymer chains, leading to polymer radicals, followed by a propagation reaction until no free radicals remain unreacted in the system. The reaction stops with termination reactions between initial or growing radicals.

To some extent, this mechanism can be compared to the progress of a polymerization. Over the conversion, the radical polymerization shows a constant polymerization degree due to the steady state of radical initiation and termination. In case of an ionic or polar initiated polymerization, the active polymer chains cannot react freely and unhindered with other polymer chains because of counterions and the electroneutrality. In this case a polymerization degree gradually increases with the conversion.[16]

In the present results the concentration w_i depends on the curative concentration, meaning that a progressing vulcanization reduces the concentration w_i . However, the reduced concentration w_i was measured only for three different formulations. From these results, the reduction of w_i cannot be correlated to the curative concentration. More formulations are

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necessary to plot a fine scale of w_i versus different curative contents. This information could support a conclusion about the crosslinking mechanism, whether it is ionically or radically initiated. The scope of the present study is to determine the dependence of the molecular weight and network formation. Therefore, only a limited number of formulations were planned which does not allow such conclusion.

As shown in Table 7.1, the values of M_N and M_W do not change. However, in both cases, assuming an ionic or radical initiated reaction it would be expected that a broader distribution is produced, which contains higher molecular weight fractions. However, it can be assumed that these fractions are not detected in the GPC measurement because of the tendency to build coils.

Figure 7.3 illustrates the network formation progress comparing a typical high molecular weight polymer with a low molecular weight liquid polymer. As proposed by Bartenev et. al.,[12] the network formation starts immediately in cases wherein the molecular weight of a polymer is around or above a certain level of 1,000,000 g/mol. In case of the liquid polymer – prior to the network formation – the polymer chains connect with each other until this critical molecular weight is reached.

Assuming a constant number of crosslink units per chain – or constant number of combined sulfur per chain – it results in a dense polymer network. These results show that liquid polymers are crosslinkable and consume sulfur accordingly.

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Figure 7.3 Possible curing progress of low molecular 'liquid' polymer (right) versus the 'solid' polymer like SSBR (left)

7.3.2. Networks with Liquid Polymers and Silica

For the investigation of the silica, possible formation of different networks with liquid polymers, unmodified and silane-modified types were compared. The liquid polymers were mixed with silica (MB-SILICA) or silica and silane coupling agent (MB-TESPD). These pre-mixes were named as "masterbatches". These masterbatches were added to the regular rubber compounds and compared to compounds where the single components were individually and directly added in the compounding step (DIRECT). The compounds were mixed in three stages. The curatives were added in the third stage. The rheometer torques were measured after the second stage (Figure 7.4a) and after the third stage (Figure 7.4b).

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In *Chapter 3* and *chapter 5* fundamental differences between TDAE, L-BR-3 and Si-L-BR were already observed which could be identified here as well. Figure 7.4b presents results which provide a further verification of the incorporation mechanism: it shows that the L-BR-3 reduces the average molecular weight and hinders an ideal crosslink network formation (visible by the lowest end torques), the silane-modified liquid polymer creates an additional network (visible by the highest end torques).

The results of the silica masterbatches provide further information. The main concept and questions behind the addition approach is: Does a preference of one material to react first with itself or another one change any of the characteristics? In most cases, the influences are small - but clear and plausible.

The unmodified L-BR-3 shows similar end torque values independent of the addition. All masterbatches are dry and still free-flowing powder-like, indicating that the liquid polymer or TDAE is adsorbed on the powder surface. Finally, it results possibly in a better hydrophobized silica surface, allowing a faster and more effective distribution of the modified filler in the latter mixing steps. In the masterbatches, the silane can react with the silica surface and react or interact earlier with the liquid polymer (compared to the reaction with the main polymer in the next step) to form a connection of silica-silane-L-BR. In the DIRECT case, the polymer active side of the silane coupling agent would be consumed mostly by the main polymer. However, in case of the masterbatches, the liquid polymer can be faster integrated into the filler-polymer networks because it has additional time to react with the silane and silica.

The samples obtained after the second mixing step doesn't contain curatives (sulfur, zinc oxide and accelerators). The results of these samples indicate predominately the reactions between silica, polymer and silane (Figure 7.4a). In this case, the torque results display mostly the contribution from the silica network.

The end torques are at a similar level independent of the order of addition. The silane-modified Si-L-BR shows some similarity but also some deviation to the L-BR. Both types of the masterbatch addition show a higher torque compared to the DIRECT addition. This indicates the formation of a denser network – based on the same reason for both types. However, herein the Si-L-BR/MB-SILICA without silane indicates also the creation of an slightly denser network compared to the Si-L-BR/MB-SILICA-TESPD (Figure 7.4a). The Si-groups on the liquid polymer can react preferably with the silica surface – not via the silane coupling agent. As explained in *chapter 5*, an additional network is generated containing the Si-L-BR. In case of this stimulated reaction between the Si-L-BR's Si-group and the silanol group of the silica, a direct bond can be created (additional network type C in Figure 5.8 of *chapter 5*) – instead of

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a reaction where only the silane coupling agent is incorporated between the silica and the liquid polymer. Consequently, this type shows a denser overall network.

Figure 7.4 Curing torques of the liquid polymers: with curatives, end torques (a); without curatives, end torques (b)

Figure 7.5 shows the Shore A hardness (a), Payne effect (b), and the entanglement contribution C_2 (c) and CLD (d) according to the stress strain analysis of Mooney-Rivlin. The Si-L-BR shows the highest hardness, followed by TDAE and L-BR.

In principle, the hardness measurement is a modulus measurement. The high value for Si-L-BR corresponds to its additionally generated network. The addition as masterbatch shows no effect on the hardness compared to the direct addition of silica, silane and liquid polymer. The general tendencies are also in accordance to the Payne effect results, which deliver further indications about the micro dispersion – based on the evaluation of the filler-filler and filler-polymer interactions.

Si-L-BR shows the lowest Payne effects followed by L-BR and TDAE. It is a further plausible assumption that the silane group of Si-L-BR reduces the filler-filler network and consequently reduces the Payne effect.

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Figure 7.5 Shore A hardness (a), Payne effect values (b), entanglement contribution C_2 (c) and crosslink density (d) for the cured samples

The Payne effect shows a different tendency depending on the additions, if Si-L-BR is added individually and directly during the main mixing step (DIRECT) or if it is added as a masterbatch. For the MB-SILICA – wherein the silica is combined only with the Si-L-BR –, the Payne effect is high. For the DIRECT addition and MB-SILICA-TESPT – wherein the silane is additionally added –, the Payne effect is slightly lower. For Si-L-BR, both, the CLD and the amount of entanglements, are comparably high which seems to be associated with the Payne effects.

The following tendency and association can be drawn with the different addition ways for the Si-L-BR:

- DIRECT: low end torque, low Payne effect, low CLD and a high amount of entanglements.

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- MB-SILICA: high end torque, high Payne effect, high CLD and a low amount of entanglements.
- MB-SILICA-TESPD: medium end torque, medium Payne effect, medium CLD and a medium amount of entanglements.

This is based on the creation of an additional network and the fact that the connection between silica, silane coupling agent, liquid polymer and main polymer (network of 'main polymer'–'liquid polymer'–silica according to the description in *Figure 5.7 in Chapter 5*) are differently achieved.

It was shown in a recent study about the combined mechanism of terminated silane-functionalized liquid polybutadiene and silane coupling agents [17] that both materials work well synergistically in a silica-based SSBR/BR formulation. The fact that the DIRECT addition reaches the lowest Payne effect in the present research further suggests that the combination of silane coupling agent and Si-L-BR reaches the optimum results.

7.4. Conclusion

This chapter discusses the network formation with low molecular weight 'liquid' polymers. The first part of the evaluation is the network formation of pure liquid polybutadienes by sulfur curing. The second part is an evaluation of different liquid polymer types in sulfur cured silica/SSBR compounds: Silica, liquid polymers; and silica, liquid polymer and silane coupling agent were pre-mixed to masterbatches. These masterbatches were added to the compounds during the main mixing step. The results were compared to compounds where the single components (silica, liquid polymer and silane coupling agent) were added individually and directly during the main mixing step. Four different liquid polymers were analyzed wherein one type contains a silane-functionalization.

For the first evaluation (pre-cured liquid polymer samples), the network formation was followed by rheometer and gel permeation chromatography. The results indicate an association between the sulfur content and the chain length. Comparing the liquid polymers L-BR-1 and L-BR-2, the low molecular weight L-BR-1 needs three times more sulfur to achieve a similar sulfur-to-chain ratio. To obtain the same sulfur-to-chain ratio in a liquid polymer extended SSBR compound compared to an unextended compound, additional sulfur in the range of 0.2 to 0.4 phr has to be added. The comparably low adjustment is due to the fact that the majority of chains are based on the high molecular weight SSBR. With increased curative contents the GPC shows a reduced concentration w_i and constant molecular weight distribution. In this

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study it provides a qualitative information of the vulcanization speed and progress. In combination with other evaluations it could be used to determine the vulcanization mechanism.

For the second analysis, the stress-strain according to Mooney-Rivlin is measured and compared to the Shore hardness and Payne effect. The results provide information about the interaction of liquid polymers with silica and the main polymer when it is added differently throughout the masterbatch approach. The lowest Payne effect values are shown for the Si-L-BR, indicating higher filler-polymer interactions and an improved micro-dispersion. The values are in accordance with high CLD values for Si-L-BR and high entanglement densities, indicating that an additional network is created. The direct addition of Si-L-BR during the main mixing step reaches the lowest Payne effect compared to other additions. It indicates that both, TESP and Si-L-BR, are necessary for the building of the additional network. Both materials work synergistically.

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SUMMARY

LOW MOLECULAR WEIGHT 'LIQUID' POLYMERS IN TIRE TREAD APPLICATIONS

LIQUID POLYMERS - A NEW INGREDIENT IN TIRES

The present work focusses on liquid polymers as a new ingredient category in tire applications and their interactions with the main polymers and fillers. Commonly, the tire industry uses the term "alternative plasticizers" for liquid polymers and resins, which means plasticizers that are not "classical", like paraffinic oils or (Treated) Distillated Aromatic Extracts (DAE, TDAE). The liquid polymers and resins are used either to replace or to supplement traditional plasticizers. According to the definition and the plasticization concept, they are mainly used for two reasons: reducing the glass transition temperature (T_g) and reducing the modulus. Besides, the plasticizers are used to reduce the viscosity in order to improve the processability. However, in today's tire tread formulations, a combination of different plasticizers are used to achieve modifications beyond this original purpose. The hydrocarbon resins for example show an anti-plasticization effect with an increase in T_g . This effect is typically used to improve the wet grip performance. Liquid polymers are used to modify the main polymer with the same chemical composition. From the industry they are marketed as co-vulcanizable plasticizer, however, this marketed behavior is not yet described in the literature.

The goal of this work is to obtain a better understanding about the behavior of liquid polymers in tire tread compounds. An understanding on their influences should be established. The first part covers a literature study with the present state-of-the-art and the practical use as plasticizing and reinforcement-supporting material. The second part (explained in the following paragraphs) is the experimental part that investigates the liquid polymer's structure-property relationship, the influence of silane-functionalization and analysis of the free volumes and networks.

FROM THE LIQUID STATE TO A CONTRIBUTION TO THE RUBBER NETWORK

The structure-property relationship was investigated with different liquid polymers in a winter tire tread (SSBR-rich/Silica) and a racing tire tread (ESBR/CB) formulation. The structure of the liquid polymers such as type (isoprene, butadiene and styrene butadiene), molecular weight and 1,2-vinyl content was varied to understand the influence on the compounds'

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characteristics. It was further used to predict the in-rubber properties. The study includes mainly an investigation of the curing characteristics and final Crosslink Densities (CLD), the mechanical and dynamical properties and filler interactions. Compared to TDAE, all liquid polymers show lower levels of CLD. When the lower molecular weight-based material is introduced, the average molecular weight in the total compound is reduced. It is independent from the material which is replaced by the liquid polymer, e.g. the replacement of a non-reactive plasticizer, a main polymer or a combination of both. Elastomeric properties depend on the established crosslinking network after the vulcanization, or on the degree an ideal network is created. The potential to build such an ideal network decreases with increasing amount of liquid polymer in the compound. One reason for this is the creation of dangling ends. Furthermore, the liquid polymer reduces the average molecular weight and broadens the molecular weight distribution of the total polymer composition. This was further confirmed by different hydrogenated L-SBRs in ESBR/CB compounds. With the hydrogenated type, the curing torque and CLD becomes similar to that of the reference compound with TDAE. It indicates that the material is less reactive due to the fewer available double bonds.

From a statistical probability (based on the molecular weight between crosslinks) it can be assumed that the liquid polymer is integrated or at least partially connected to the main polymer network. It could be further confirmed in the experiments that liquid polymers allow several crosslink connections per polymer chain: In case of the low molecular weight types (5,000 to 6,000 g/mol), two to three crosslink units per chain, in case of the high molecular weight type (30,000 g/mol) around fourteen crosslink units per chain.

FROM SILANE-FUNCTIONALIZATION TO ADDITIONAL NETWORKS

A further investigation covers silane-functionalized 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. Another important aspect is how it interacts with the silane. Different liquid polymers were combined with different bifunctional silanes and mercaptosilanes. The curing kinetic, crosslinking density and Payne effect were measured to evaluate the strain dependence of the mixtures and to estimate the filler-polymer and filler-filler interactions. The dynamic mechanical properties were evaluated to describe the materials comprehensively and to predict their in-rubber performance in passenger car tires.

The curing curves and CLD give 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 reaction between the 'main polymer', the 'liquid polymer' and the silica. Also reactions

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between the liquid polymer and the silane or liquid polymer and the silane and silica can take place. This reduces the filler-filler interactions by a strong hydrophobation of the silica surface.

It is assumed that the generation of these networks occurs in parallel and with different probabilities according to the individual microstructure of the liquid polymers, the types of silane and the concentrations. These reactions are also competing with the generation of the known networks, the silica-silica network, the polymer-polymer network as well as the silica-silane-polymer network.

For silane-functionalized higher molecular weight liquid polymers it can be assumed that primarily the following additional networks are created: 'main polymer'-'liquid polymer'-silane and 'main polymer'-'liquid polymer'-silane-silica. A strong contribution to the polymer network and an efficient hydrophobation of the silica can be expected from the evaluation. For the silane-functionalized lower molecular weight types, the polymer chains can move more freely with a higher possibility to connect directly to the silica. With this, more 'main polymer'-'liquid polymer'-silica connections can be created. In the presence of mercaptosilanes, the connection between silica-'main-polymer'-'liquid polymer'-silane-silica can be assumed as the most probable one. The triethoxysilyl groups of the functionalized liquid polymer as well as the silane can react with the silica. The thiol group of the silane can react preferably 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 show a dependence on the intensity of the networks. From the DMA evaluation, the E' shows the highest values for a compound including a mercaptosilane and a high molecular weight silane-functionalized liquid polymer. However, the silane-functionalized lower molecular weight types indicate overall more favorable in-rubber properties (evaluated by DMA) in regards of wet grip and rolling resistance balance.

PLASTICIZATION, FREE VOLUMES AND NETWORK FORMATION

Different liquid polymers were introduced in SSBR compounds and compared to TDAE and a cycloaliphatic resin. Positron Annihilation Lifetime Spectroscopy was used to investigate the free volume of cured compounds. The T_g 's of the compounds were compared to the stress-strain analysis results which were evaluated according to Mooney-Rivlin. The liquid polymers, resin and TDAE were added on-top to the SSBR main polymer. They show plasticizing effects on the rheological characteristics and hardness values. The measured T_g and free volume depend on the structure of the extended material and its incorporation behavior into the polymer network. Compared to the extended version, the reference with only SSBR as the main polymer exhibits the lowest CLD together with the highest amount of trapped entanglements. The different liquid polymers, resin and TDAE result either in an increased or

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decreased free volume: For the on-top addition to SSBR main polymer, an increased free volume was observed for the butadiene (L-BR) and isoprene (L-IR) types. In contrast to this, a decrease is shown for the styrene-butadiene (L-SBR), the cycloaliphatic resin and TDAE.

Generally, the CLD is lower in the presence of the liquid polymers that create higher free volumes (L-BR's and L-IR). However, the CLD is higher for the L-SBR, TDAE and the cycloaliphatic resin. The CLD is therefore closely associated with the concentration of the aromatic or cycloaliphatic groups between the extending liquid polymers, TDAE and resin and the main polymer. Together with the SSBR main polymer, different π electron systems can interact via non-covalent π - π interactions. This results in π - π stacking and therefore a strong concentration of the different aromatic π systems (between SSBR, L-SBR, TDAE, resin). The free volume along the polymer chain is filled up more effectively. Consequently, the reactive butadiene segments (between the concentrated aromatic groups of the SBRs and TDAE or with the cycloaliphatic groups from the resin) of the main polymer can react freely and unhindered with sulfur and with each other. All extending materials influence the crosslinking reaction by a lubrication effect between the polymeric chains: The mobility of the polymer chains is increased that allows a fast re-entanglement due to lower restrictions. Another reason for the more effective crosslinking may be associated to a better distribution of the curatives inside the compound due to the liquefaction. The different liquid polymers influence the crosslinking further by co-crosslinking and physical interaction corresponding to their structures.

The last part of this work focusses on how the liquid polymer is incorporated into the polymer network and into the filler-polymer network. Different liquid polymer types were mixed with varying concentrations of curatives, cured and analyzed by GPC and rheometer torque. For the filler and filler-polymer network, different pre-silanized silica/liquid polymer blends were prepared, mixed and cured with the other formulation ingredients. Their CLD and entanglements were evaluated according to the Mooney Rivlin method.

The results indicate a dependence between the sulfur content and the chain length. To obtain the same sulfur-to-chain ratio in a liquid polymer extended compound, additional sulfur has to be added. In an SSBR compound the addition of 0.2 to 0.4 phr of sulfur can be estimated – depending on the chosen liquid polymer's molecular weight and its concentration in the compound. The GPC results further suggest that the crosslink reactions are mainly radically initiated.

The results of this work provide new information about liquid polymers, their interactions with main polymers, curatives, silica and silane coupling agents and their influence on the in-rubber properties. The addition of liquid polymers affects the crosslink network and the filler-filler and

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filler-polymer network. Based on these findings future liquid polymer containing formulations can be adjusted in a better way to realize the full potential of this new type of polymers.

SAMENVATTING

LAGE MOLECULAIRE MASSA VAN 'VLOEIBARE' POLYMEREN BIJ LOOPVLAKTOEPASSINGEN

VLOEIBARE POLYMEREN - EEN NIEUW BESTANDDEEL IN BANDEN

Dit onderzoek is gericht op vloeibare polymeren als een nieuwe categorie van bestanddelen voor bandentoepassingen en hun wisselwerking met hoofdpolymeren en vulstoffen. In de bandenindustrie wordt meestal de term 'alternatieve weekmakers' gehanteerd voor vloeibare polymeren en harsen; het gaat dan om de niet 'traditionele' weekmakers zoals paraffineolie of (Behandelde) Gedistilleerde Aromatische Extracten (DAE, TDAE). Vloeibare polymeren en harsen worden gebruikt om traditionele weekmakers te vervangen of aan te vullen. Afhankelijk van de definitie en het weekmaakconcept worden ze overwegend om twee redenen gebruikt: het verlagen van de glastransitietemperatuur (T_g) en het verminderen van de modulus. Daarnaast worden de weekmakers gebruikt voor een verlaging van de viscositeit om de verwerkbaarheid te verbeteren. Voor de samenstelling van de huidige loopvlakken wordt echter een combinatie van verschillende weekmakers gebruikt om modificaties te realiseren die verder gaan dan dit oorspronkelijke doel. Zo vertonen koolwaterstofharsen een anti-weekmaakeffect met een verhoogde T_g . Dit effect wordt doorgaans gebruikt om de grip op een nat wegdek te verbeteren. Vloeibare polymeren worden gebruikt om het hoofdpolymeer te modifieren bij dezelfde chemische samenstelling. Vanuit de industrie worden deze op de markt gebracht als co-vulkaniseerbare weekmakers; deze marktbenadering wordt echter nog niet genoemd in de vakliteratuur.

Doel van dit onderzoek is om meer inzicht te verkrijgen in het gedrag van vloeibare polymeren in loopvlakcompounds. We moeten begrijpen wat de invloed van deze polymeren is. Het eerste deel omvat een literatuurstudie inzake de huidige technische stand van zaken en het praktische gebruik als ondersteunend materiaal voor weekmaking en versterking. Het tweede deel (dat in de volgende alinea's wordt toegelicht) is het experimentele gedeelte waarin het verband tussen de structuur en eigenschappen van het vloeibare polymeer, en de invloed van silaan-functionaliserings worden onderzocht; tevens worden de vrije volumes en netwerken geanalyseerd.

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VAN VLOEIBARE TOESTAND NAAR EEN BIJDRAGE AAN HET RUBBERNETWERK

Het verband tussen structuur en eigenschappen werd bij verschillende vloeibare polymeren onderzocht in het loopvlak van een winterband (SSBR-rich/Silica) en in het loopvlak van een raceband (ESBR/CB). De structuur van de vloeibare polymeren zoals type (isopreen, butadieen en styreen-butadieen), moleculaire massa en 1,2-vinylgehalte werd gevarieerd om inzicht te krijgen in de invloed op de eigenschappen van de compound. Tevens werden deze gegevens gebruikt om de eigenschappen in het rubber te voorspellen. De studie omvat overwegend een onderzoek van de uithardingseigenschappen en uiteindelijke Crosslink Densities (CLD), de mechanische en dynamische eigenschappen en wisselwerking met vulstoffen. In vergelijking met TDAE vertonen alle vloeibare polymeren lagere CLD-niveaus. Bij gebruik van een materiaal met een lagere moleculaire massa vermindert de gemiddelde moleculaire massa van de compound als geheel. Dit geldt ongeacht het materiaal dat door het vloeibare polymeer wordt vervangen, dus de vervanging van een niet-reactieve weekmaker, een hoofdpolymeer of een combinatie van beide. De elastomerische eigenschappen hangen af van het crosslink-netwerk dat tot stand komt na vulkanisatie, of van de mate waarin een ideaal netwerk wordt opgebouwd. De mogelijkheid voor de opbouw van zo'n ideaal netwerk neemt af naarmate de hoeveelheid vloeibaar polymeer in de compound toeneemt. Eén van de onderliggende redenen is de vorming van losse keteneinden. Bovendien vermindert het vloeibare polymeer de gemiddelde moleculaire massa en verbreedt het de verdeling van de moleculaire massa van de polymeersamenstelling als geheel. Dit werd tevens bevestigd door verschillende gehydrogeneerde L-SBR's in ESBR/CB-compounds. Bij het gehydrogeneerde type worden het uithardingsmoment en de CLD gelijk aan die van de referentiecompound met TDAE. Dit geeft aan dat het materiaal minder reactief is vanwege het geringere aantal dubbele verbindingen.

Vanuit een oogpunt van statistische waarschijnlijkheid mag (op basis van de moleculaire massa tussen vernettingen) worden verondersteld dat het vloeibare polymeer is geïntegreerd in, of althans gedeeltelijk verbonden met het hoofdpolymeernetwerk. Tijdens de experimenten kon verder worden bevestigd dat bij vloeibare polymeren verschillende vernettingspunten per polymeerketen mogelijk zijn, namelijk 2 tot 3 crosslinks per keten bij de types met een lage moleculaire massa (5.000 tot 6.000 g/mol), en circa 14 vernettingspunten per keten bij de types met een hoge moleculaire massa (30.000 g/mol).

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VAN SILAAN-FUNCTIONALISERING NAAR AANVULLENDE NETWERKEN

Ook silaan-gefunctionaliseerde vloeibare polymeren in SSBR/silica-compounds maakten deel uit van het onderzoek. Een van de belangrijkste vragen is of dit materiaal het silicaoppervlak hydrofobeert, en of het wordt opgenomen in het hoofdrubbernetwerk. Een ander belangrijk aspect is de wisselwerking met silaan. Verschillende vloeibare polymeren werden gecombineerd met bifunctionele silanen en mercaptosilanen. De uithardingskinetiek, vernettingsdichtheid en het Payne-effect werden gemeten om de spanningsafhankelijkheid van de mengsels te meten en om de wisselwerking tussen vulstof-polymeers en vulstof-vulstof in te schatten. De dynamische mechanische eigenschappen werden geëvalueerd om de materialen uitvoerig te beschrijven en hun werking binnen het rubber van banden van personenauto's te voorspellen.

De uithardingscurven en CLD leveren een duidelijke indicatie op van de opbouw van een aanvullend netwerk, dat wordt gegenereerd door het silaan-gefunctionaliseerde vloeibare polymeer. Het aanvullende netwerk is gebaseerd op een koppelingsreactie tussen het 'hoofdpolymeers', 'vloeibare polymeers' en silica. Er kunnen ook reacties optreden tussen het vloeibare polymeers en silaan of vloeibare polymeers, en tussen het silaan en silica. Dit vermindert de wisselwerkingen tussen de vulstoffen als gevolg van een sterke hydrofobering van het silica-oppervlak.

Aangenomen wordt dat het genereren van deze netwerken zich parallel voordoet en met wisselende waarschijnlijkheden, afhankelijk van de individuele microstructuur van de vloeibare polymeren, de types silaan en de concentraties. Tevens wedijveren deze reacties met het genereren van de bekende netwerken; het silica-silicaneetwerk, het polymeers-polymeernetwerk en het silica-silaan-polymeernetwerk. Voor silaan-gefunctionaliseerde vloeibare polymeren met een hogere moleculaire massa kan worden aangenomen dat de volgende aanvullende netwerken primair worden gecreëerd: 'hoofdpolymeers'-vloeibaar polymeers'-silaan en 'hoofdpolymeers'-vloeibaar polymeers'-silaan-silica. Op grond van de evaluatie mag een substantiële bijdrage aan het polymeernetwerk worden verwacht, evenals een efficiënte hydrofobering van het silica. Bij de silaan-gefunctionaliseerde types met een lagere moleculaire massa kunnen de polymeerketens zich vrijer bewegen, met grotere kansen om zich rechtstreeks met het silica te verbinden. Op die manier kunnen er meer 'hoofdpolymeers'-vloeibaar polymeers'-silicaverbindingen tot stand worden gebracht. Gezien de aanwezigheid van mercaptosilanen mag worden aangenomen dat de verbinding tussen silica-'hoofdpolymeers'-vloeibaar polymeers'-silaan-silica het meest voor de hand ligt. De tetraethoxysilaan-groepen van het gefunctionaliseerde polymeers kunnen, net als het silaan, reageren met het silica. De thiolgroep van het silaan reageert bij voorkeur met de 1.2-

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vinylgroepen van het vloeibare polymeer. Dit resulteert in een lang en flexibel aanvullend netwerk.

De microdispersie en mechanische eigenschappen blijken afhankelijk te zijn van de intensiteit van de netwerken. Op basis van de DMA-evaluatie geeft E' de hoogste waarden voor een compound die een mercaptosilaan bevat en voor een silaan-gefunctionaliseerd vloeibaar polymeer met een hoge moleculaire massa. Silaan-gefunctionaliseerde types met een lagere moleculaire massa daarentegen geven over de gehele linie gunstigere rubbereigenschappen te zien (geëvalueerd via een DMA) als het gaat om de balans tussen grip op natte oppervlakken en rolweerstand.

WEEKMAKING, VRIJE VOLUMES EN NETWERKOPBOUW

Er werden verschillende vloeibare polymeren opgenomen in SSBR-compounds, en vergeleken met TDAE en een cycloalifatische hars. Positron Annihilation Lifetime Spectroscopy werd ingezet om het vrije volume van uitgeharde compounds te onderzoeken. De T_g - waarden van de compounds werden vergeleken met de stress-strain-analyseresultaten, die volgens de Mooney-Rivlinmethode werden geëvalueerd. De vloeibare polymeren, hars en TDAE werden toegevoegd aan het SSBR-hoofdpolymeer. Deze hebben weekmakende effecten op de reologische karakteristieken en hardheidswaarden. De gemeten T_g en het vrije volume hangen samen met de structuur van het uitgebreide materiaal en de manier waarop het opgaat in het polymeernetwerk. In vergelijking met de uitgebreide versie vertoont het referentiemateriaal met uitsluitend SSBR als hoofdpolymeer de laagste CLD, in combinatie met de grootste hoeveelheid ingesloten verstrengelingen. De verschillende vloeibare polymeren, hars en TDAE resulteren in een toegenomen of afgenomen vrij volume; bij de toevoeging aan het SSBR-hoofdpolymeer werd een verhoogd vrij volume vastgesteld voor de types butadieen (L-BR) en isopreen (L-IR). Bij styreen-butadieen (L-SBR), cycloalifatische hars en TDAE was echter een afname te zien.

In het algemeen is de CLD lager bij aanwezigheid van vloeibare polymeren die grotere vrije volumes creëren (L-BR's en L-IR). Daarentegen is de CLD hoger bij L-SBR, TDAE en cycloalifatische hars. De CLD wordt daarom nauw in verband gebracht met de concentratie van de aromatische of cycloalifatische groepen tussen de uitbreidende vloeibare polymeren, TDAE en hars, en het hoofdpolymeer. Verschillende π -elektronsystemen kunnen, samen met het SSBR-hoofdpolymeer, interageren via niet-covalente π - π -interacties. Dit resulteert in π - π -stapeling en derhalve in een sterke concentratie van de verschillende aromatische π -systemen (tussen SSBR, L-SBR, TDAE, hars). Het vrije volume in de gehele polymeerketen wordt effectiever opgevuld. Als gevolg daarvan kunnen de reactieve butadieensegmenten

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(tussen de geconcentreerde aromatische groepen van de SBR's en TDAE, of bij de cycloalifatische groepen van de hars) van het hoofdpolymeer zonder enige belemmering reageren met zwavel, en onderling. Alle uitbreidende materialen zijn vanwege een smerend effect tussen de polymeerketens van invloed op de vernettingsreactie; de mobiliteit van de polymeerketens wordt verhoogd, zodat snelle herverstrengeling mogelijk is vanwege verminderde restricties. Een andere reden voor de effectievere vernetting zou verband kunnen houden met een betere verdeling van de uithardingsstoffen in de compound als gevolg van liquefactie. De verschillende vloeibare polymeren beïnvloeden de vernetting verder door co-crosslinking en de fysieke wisselwerking die inherent is aan hun structuren.

Het laatste deel van dit onderzoek is gericht op de manier waarop het vloeibare polymeer wordt opgenomen in het polymeernetwerk en het vulstof-polymeernetwerk. Verschillende types vloeibaar polymeer werden vermengd met wisselende concentraties van uithardingsstoffen, en vervolgens uitgehard en geanalyseerd via GPC en een rheometertest. Voor het vulstof- en vulstof-polymeernetwerk werden verschillende voorgesilaniseerde mengsels van silica en vloeibaar polymeer geprepareerd, gemengd en uitgehard met de overige bestanddelen van de samenstelling. De CLD en verstrengelingen van de mengsels werden geëvalueerd volgens de Mooney Rivlin-methode.

Uit de resultaten blijkt een verband tussen het zwavelgehalte en de lengte van de keten. Om dezelfde zwavel/keten-verhouding te bereiken in de met vloeibaar polymeer uitgebreide compound, dient extra zwavel te worden toegevoegd. Aan een SSBR-compound kan naar schatting 0,2 tot 0,4 phr zwavel worden toegevoegd, afhankelijk van de moleculaire massa van het gekozen vloeibare polymeer en de concentratie in de compound. Daarnaast suggereren de GPC-resultaten dat de vernettingsreacties overwegend radicaal in gang worden gezet.

De uitkomsten van dit onderzoek leveren nieuwe informatie op over vloeibare polymeren, hun wisselwerking met hoofdpolymeren, uithardingsstoffen, silica en silaanverbindingen, en hun invloed op rubbereigenschappen. De toevoeging van vloeibare polymeren is van invloed op het crosslinknetwerk en de netwerken van vulstof-vulstof en vulstof-polymeer. Op basis van deze bevindingen kunnen formules met vloeibaar polymeer voortaan efficiënter worden samengesteld om het potentieel van dit nieuwe polymeertype volledig te benutten.

ABBREVIATIONS

ASTM	American Society for Testing and Materials
BR	Butadiene Rubber
BRC	Bound Rubber Content
BET	Brunauer–Emmett–Teller
CB	Carbon Black
CBS	n-Cyclohexyl-2-Benzothiazole-Sulfenamide
CED	Cohesive Energy Density
CLD	Crosslink Density
DAE	Distillated Aromatic Oil
DMA	Dynamic Mechanical Analysis
δ	Solubility Parameter
DSC	Differential Scanning Calorimetry
DPG	Di-Phenyl Guanidine
E'	Storage Modulus
E''	Loss Modulus
ESBR	Emulsion Polymerized Styrene Butadiene Rubber
EPDM	Ethylene-Propylene-Diene Monomer Rubber
f_v	Fractional Volume
G'	Storage Modulus
ΔG	Storage Modulus Difference (Payne Effect)
GPC	Gel Permeation Chromatography
HSE	Health Safety and Environment
ISO	International Organization for Standardization
IR	Isoprene Rubber or Polyisoprene
L-BR	Liquid Butadiene Rubber of Liquid Polybutadiene

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L-FR	Liquid Farnesene Rubber or Liquid Polyfarnesene
L-IR	Liquid Isoprene Rubber or Liquid Polyisoprene
LP	Liquid Polymer
L-SBR	Liquid Styrene Butadiene Rubber or Liquid Styrene-Butadiene Copolymer
M100	Tensile Modulus at 100 % Strain
M300	Tensile Modulus at 300 % Strain
M_W	Molecular Weight (weight average)
M_N	Molecular Weight (number average)
MES	Mild Extracted Solvent
MWD	Molecular Weight Distribution
NR	Natural Rubber
NSA	Nitrogen Surface Area
o-Ps	ortho-Positronium
PALS	Positron Annihilation Lifetime Spectroscopy
Ps	Positronium
R	Gas Constant; Free Volume Radius
r^2	Coefficient of Determination
REACH	Registration, Evaluation, Authorization of Chemical Substances
RPA	Rubber Process Analyzer
RR	Rolling Resistance
SBR	Styrene Butadiene Rubber or Styrene-Butadiene Copolymer
Si	Silane
Si-L-BR	Silane-Modified Liquid Butadiene Rubber
SSBR	Solution Polymerized Styrene Butadiene Rubber
STSA	Statistical Thickness Surface Area
Su	Sulfur

ABBREVIATIONS

<i>tanδ</i>	Loss Angle
τ_3	ortho-Positronium Lifetime
TDAE	Treated Distillated Aromatic Oil
TESPD	Bis(triethoxysilylpropyl)disulfide
TESPT	Bis(triethoxysilylpropyl)tetrasulfide
T_g	Glass Transition Temperature
TBzTD	Tetrabenzylthiuramdisulfide
TEM	Transmission Electron Microscopy
VGC	Viscosity-Gravity-Constant
WG	Wet Grip
ZnO	Zinc Oxide
6PPD	N-Phenyl-N'-1,3-dimethylbutyl-p-phenylenediamine

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- “Network Formation of Low Molecular Weight ‘Liquid’ Polymers”, M. Gruendken, D. Koda, A. Blume, (ready to be submitted)

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