

# Use of liquid polymers

Understanding the structure-property relationship of low-molecular-weight liquid polymers in adjusted blends of sulfur-cured S-SBR-rich/silica formulations

by Anke Blume, Elastomer Technology and Engineering, Department of Mechanics of Solids, Surfaces and Systems, Faculty of Engineering Technology, University of Twente, Netherlands; and Marcel Gruendken, University of Twente and Kuraray Europe, Germany

In recent years, many patents on the use of liquid polymers in tires have been filed by tire producers.<sup>1-4</sup> These patents specifically cite a claimed improvement in the abrasion resistance of winter tires and a better balance of the low-temperature properties in winter tires.<sup>1,2</sup> The other application area of liquid polymers is in motorsport tires, where the wet and dry grip properties can be improved with the incorporation of liquid polymer.<sup>3,4</sup>

In previous work, the structure-property relationship of liquid polymers in winter tire tread formulations has been investigated.<sup>5</sup> In these studies, the structure of the liquid polymers was varied in terms of type (isoprene, butadiene and styrene butadiene), molecular weight and 1,2-vinyl content to understand the influence on the compound's characteristics and predict the in-rubber properties, by keeping the curing system consistent. All liquid polymers have a lower cross-link density (CLD) than treated distillate aromatic oil (TDAE). The higher-molecular-weight types have comparably greater CLD. When a low-molecular-weight-based material is introduced as a replacement for TDAE, the average molecular weight of the total compound is reduced, which is one explanation for this tendency.

However, only by adjusting the curing, cross-linking, hardness and the compound's  $T_g$  can the performance be comparatively evaluated. For example, the reduction in the CLD can be compensated for by adding additional sulfur to increase the number of cross-linking units per chain.<sup>5</sup> The present study further analyzes the influences and effects of adjusting the formulation.

First, a standard passenger car tire tread formulation was defined based on the previous study.<sup>5</sup> This formulation contained silica as a

**Table 1: Liquid polymers tested\***

Polymer	Product name	Monomer	Molecular weight (MN, g/mol)	1,2-vinyl (mol%)	TG (°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)

filler and S-SBR, BR and NR as the polymer composition, with TDAE as a standard plasticizer. The compound filled with only TDAE was used as a reference. The liquid polymer was used in place of the TDAE and the properties of it as an alternative plasticizer were studied.

The formulation was varied to adjust and compensate for the liquid-polymer-containing compound. Two different sulfur contents and two different S-SBR/BR ratios were used, and the addition of a polyterpene resin was also studied. With higher S-SBR content and the addition of resin, in-rubber properties such as wet grip and rolling resistance can be better balanced and potentially optimized.

## Raw materials

The following polymers were used:

- Sprintan 4601 S-SBR supplied by Trinseo;
- Buna CB24 high-cis BR supplied by Arlanxco;
- RSS3 natural rubber supplied by Saksham Gati.

The following fillers, all supplied by Evonik, were used:

- N330 carbon black;
- Ultrasil 7000 highly dispersible silica with Si266 organosilane, bis(triethoxysilylpropyl)disulfide (TESPD).

The following antioxidants were used:

- N-phenyl-N'-1,3-dimethylbutyl-p-phenylenediamine (6PPD) supplied by Flexsys;
- Antiozonant paraffinic wax supplied by Sasol.

The following additives, all supplied by Sigma-Aldrich, were used for vulcanization:

- Zinc oxide;
- Stearic acid;
- Sulfur.

Rubber accelerators used in all the formulations were the following:

- N-cyclohexyl-2-benzothiazolesulfenamide (CBS) supplied by Flexsys;
- Diphenyl guanidine (DPG) supplied by Sigma-Aldrich.

The following was used as a plasticizer:

- Vivatex 500 TDAE supplied by Hansen & Rosenthal.

The following was used for the comparison with different liquid polymers:

- Sylvagam TR90 polyterpene resin supplied by Kraton.

Different low-molecular-weight polymers from Kuraray were selected covering various types (butadiene, isoprene and styrene-butadiene), molecular weights and 1,2-vinyl content. The main properties of each of these grades are shown in Table 1. 'L' refers to liquid or low-molecular-weight polymer; 'BR', 'SBR' refer to the type of polymer: butadiene, isoprene or styrene-butadiene rubber, respectively. The number refers to the molecular weight (MN) of the polymer.

## Preparation of blends and sample plates

Table 2 shows the ingredients for an S-SBR-rich/silica formulation representing a winter tire tread. Deviations from the contents [shown

**Table 2: Reference compound details**

Formulation	Concentration
S-SBR	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)

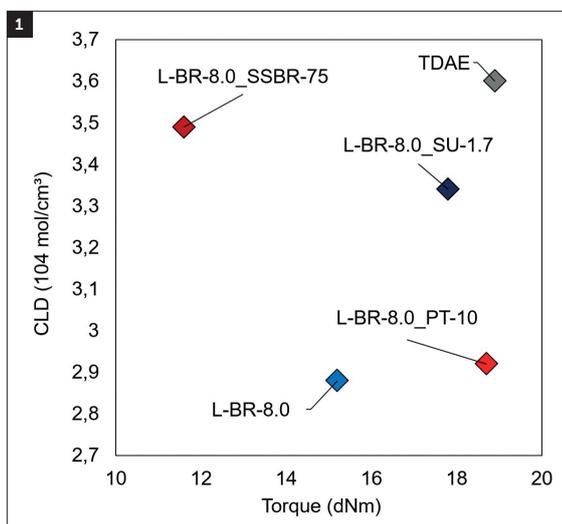
in Table 2] are indicated in the name and legends as follows: L-BR-8.0\_Su-1.7 = 1.7phr sulfur content, L-BR-8.0\_S-SBR-75 = 75phr of S-SBR with a corresponding reduction of BR to 15phr. L-BR-8.0\_PT-10 = 10phr polyterpene resin with a corresponding reduction of the L-BR-8.0 to 15phr.

The compounds were mixed in three stages. The first two steps were executed in a Brabender internal mixer with a chamber size of 350ml. Fill factor was set to 70%.

The steps for the first mixing stage were as follows:

- Polymer added;
- After one minute of mixing, 50% of the carbon black, silica and silane (both only for the S-SBR-rich formulation) and TDAE or low-molecular-weight polymer were added;
- After three minutes 20 seconds the remaining 50% of silica

Figure 1: CLD vs maximum torque of the silica/S-SBR compounds



was added (only for the S-SBR-rich formulation);

- At 6 minutes 20 seconds, the zinc oxide, stearic acid, wax and 6PPD were added, and discharged at 7 minutes 20 seconds.

The initial temperature of the mixer was set to 50°C. The target temperature for the compound at the end of the mixing cycle was 140°C to ensure silanization with the silane coupling agent.

The second mixing stage involved homogenization and silanization of the compound, 16 hours after the first mixing stage.

After each mixing stage the compound was sheeted out on a two-roll mill.

The third mixing stage was carried out on the same two-roll mill. The amount of accelerators and sulfur was recalculated according to the mass of the compound after the second mixing stage.

The compounds were cured in a Wickert laboratory press at 160°C and 100 bar, according to the optimal vulcanization time ( $t_{90}$ ) of each compound. The cured specimens were cut to measure 100 x 100mm, and 2mm in thickness.

The liquid polymer was used to replace the TDAE as an alternative plasticizer to study its influence on the in-rubber properties.

## Evaluation

The compound's curing kinetics were determined with an Alpha Instruments RPA 2000 dynamic mechanical rheological tester. The increase in torque at 160°C and 0.5% strain was measured over a period of 20 minutes. The frequency was applied at 1.667Hz. The  $t_{90}$  of the compounds was determined. The tensile properties of the cured compounds were determined using a Zwick Z020 tensile tester according to ISO 37. The Shore A hardness was measured using a Zwick hardness tester according to ASTM D2240.

The dynamic measurements of the cured compounds were carried out using a DMA2000 dynamic spectrometer. For storage ( $E'$ ) and loss modulus ( $E''$ ) as a function of temperature, measurements were performed between -80°C and +80°C with a heating rate of 2°C/min at a dynamic strain of 0.1%, static strain of 1% and a frequency of 10Hz. The  $\tan \delta$  was taken as an indicator for the abrasion resistance ( $\tan \delta$  at

-50°C), wet grip performance ( $\tan \delta$  at 0°C) and rolling resistance ( $\tan \delta$  at 70°C), in the knowledge that only the prediction of the rolling resistance seems to be reliable.

The CLD was determined by a swelling test. To remove low molecular-weight soluble substances (for example, residues, decomposition products, fatty acids and antioxidants) prior to the swelling, the samples were extracted with acetone and subsequently immersed in tetrahydrofuran, for three days in each solvent, following three days drying in a vacuum oven. Then samples of approximately 0.4g were swollen to equilibrium in toluene for seven days at ambient temperatures. After that, the samples were dried to constant weight for three days at 50°C in a vacuum oven. The CLD was measured according to the Flory-Rehner equation:<sup>10</sup>

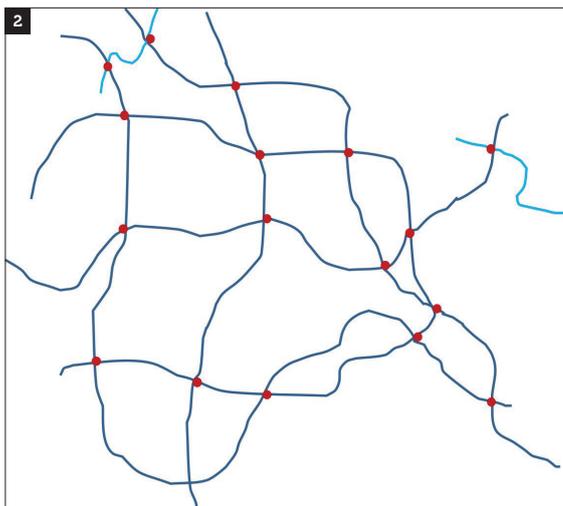
$$v = - \frac{\ln(1-V_r) + V_r + \chi V_r^2}{V_0 (V_r^{\frac{1}{3}} - \frac{2V_r}{f})}$$

$v$  is the CLD per unit volume (mol/cm<sup>3</sup>).  $V_r$  is the volume fraction of the rubber in a swollen sample.  $V_0$  is the solvent molar volume (in the case of toluene = 106.9cm<sup>3</sup>/mol),  $f$  is the functionality of the polymer ( $f=4$ , assumption for the formation of tetra-functional cross-links) and  $\chi$  is the Flory-Huggins polymer-solvent interaction parameter. For an SBR/toluene system,  $\chi$  is 0.378, as reported by George et al.<sup>9</sup> The SBR/toluene system was selected due to the high content of SBR in the formulation. The morphology is thus dominated by the S-SBR and the interpretation mostly considers this fact.

The abovementioned 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.<sup>10</sup> However, due to the fact that the filler content and the filler system are the same for all compositions, the cross-link densities were calculated without the Kraus correction. Similar effects can be assumed in all samples. The Kraus correction can be neglected for the comparison within this study.

## Results

Figure 1 shows the CLD and maximum torques of the L-BR-8.0 and the different adjustments of the



S-SBR-rich/silica compounds. As presented in the previous study,<sup>5</sup> substitution of TDAE by a liquid polymer results in lower values of both properties. Assuming that TDAE does not contribute to the cross-linking network, the total reactive polymer composition increases in the liquid polymer blends. This can be attributed 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 co-reacts with the base polymer. This most likely occurs with a lower statistical probability than the base polymers reacting with each other.

With the increase of sulfur content to 1.7phr in L-BR-8.0-SU-1.7, it can be seen that the maximum torque and CLD are closer to the reference compound with TDAE. This is one option to compensate in the formulation containing a liquid polymer. Another concept is to use a different polymer ratio (increase of 10phr S-SBR from the reference) to S-SBR/BR/NR (=75/15/10) with L-BR.8.0\_S-SBR-75. This also shows an increase in the CLD. This could be due to the higher reactivity of the S-SBR than 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 with the blend ratio of S-SBR/BR, the combination of L-BR/polyterpene resin shows a slightly higher CLD and a more

Figure 2: Cross-linking network built with liquid polymer assuming it is a combination with one or two polymer chains<sup>5</sup>

pronounced increase in maximum torque. At least partially, this tendency can be attributed to the non-reactivity of the resin, meaning that the base rubber cures more effectively.

In all liquid-polymer-containing blends, the potential to create a less ideal network – in particular through dangling ends – seems to be increased.<sup>6,7</sup> In such a case, the liquid polymer is assumed to be connected with the main polymer but does not fully contribute to the mechanical properties. To contribute to the modulus, for example, according to the ideal network theory, at least two cross-linking units are required to connect a chain. Figure 2 shows the possible incorporation of liquid polymer into the vulcanized network. It is possible that the liquid polymer can be connected with one or more cross-linking units per chain with the base polymer.

The mechanical properties are shown in Table 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. The adjusted formulations generally increase the hardness and moduli and lower the elongations. The results can be interpreted as showing 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 tensile strength and elongation reduction is caused by exceeding an optimum cross-linking structure and density for a liquid-polymer-based compound – with the creation of shorter polysulfidic connections.<sup>11</sup>

## Conclusion

In this study, low-molecular-weight liquid polymers were added to an S-SBR/BR/NR blend filled with silica, representing a winter tread compound.

This formulation was adjusted with varying concentrations of sulfur and different S-SBR/BR ratios and liquid polymer/polyterpene ratios. The aim was to gain a better understanding of the influence of using liquid polymers in this application.

As shown in previous work, the overall CLD is reduced with the incorporation of liquid polymer into the formulation. This can be partially attributed to the liquid polymer's co-reaction with the base polymer. With an increase in the sulfur content and change in the S-SBR/BR ratio, the maximum torque and CLD values are closer to that of the reference compound with TDAE. Therefore it can be assumed that these are two possible options to adjust the CLD. Another option to increase the CLD is combining it with polyterpene resin – attributed to the non-reactivity of the resin – and particularly the T<sub>g</sub>, to improve the performance balance of the in-rubber properties. The adjusted formulations increase the hardness and moduli, and lower the elongations. **tire**

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Table 3: Comparison of cross-linking and mechanical properties of the silica/S-SBR compounds

	CLD (104 mol/cm <sup>3</sup> )	Torque (dNm)	Shore A Hardness	M100 (MPa)	M300 (MPa)	Tensile strength (MPa)	Elongation (%)
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
_S-SBR-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