

A versatile crosslinker and “de-linker” additive for modified bitumen

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Abstract

BA CR36 is a sulfur-rich alkyl polysulfide which acts as a liquid sulfur donor for sulfur-based crosslinking of polymers like SBS which are used to modify bitumen (PmB). It is readily dispersible in bitumen which allows a homogeneous distribution of the crosslinker in the binder matrix. Side reactions such as loss of sulfur due to hydrogen sulfide formation are reduced. The alkyl polysulfide combines acceptable safety characteristics with a high sulfur content. Under specific conditions the polysulfide BA CR36 acts also as a “de-vulcanising” agent, which selectively “de-links” reclaimed tyre rubber granules. The thermal treatment of the rubber particles with BA CR36 under relatively mild conditions cleaves selectively the sulfur bridges in vulcanised rubber. This “de-linking” of the rubber particles accelerates their swelling in bitumen and more homogeneous bitumen-rubber mixtures (CRmB) can be obtained. Mixing time of rubber crumb with bitumen in the manufacture process for CRmB is reduced and the energy consumption is lower. Comparative test results like DSR studies for both PmB and CRmB formulations involving the use of BA CR36 are presented.

1. INTRODUCTION

Increasing demands made on roads require the use of modifiers which increase the technical performance of conventional bitumen. The use of polymers to modify bitumen in road paving applications has been growing rapidly over the last decades, as authorities and paving contractors seek to improve road life in the face of increased traffic. Currently, the most commonly used polymer for bitumen modification is the elastomer styrene butadiene styrene (SBS), followed by other polymers, including reclaimed tyre rubber¹.

Stability and technical performance of **polymer-modified bitumen** (“PmB”) can be further enhanced by crosslinking an elastomer like SBS (styrene-butadiene-styrene copolymer) by use of sulphur². In the early eighties it was proposed to use organo-polysulphides as sulphur donors instead of elemental sulphur, in order to disperse the sulphur more homogeneously in the bitumen-polymer mixture³. In addition, the use of polysulphides helps to reduce hydrogen sulphide emissions⁴.

Reclaimed tyre rubber powder has been used as a modifier in the last decades mainly in the “Wet Process”, in which rubber granules are added to the binder to prepare a **rubber-modified bitumen** (“RmB”⁵). The tyre rubber shows elastic properties due to vulcanisation. Although this elasticity is beneficial when the rubber is dispersed in the bitumen, the crosslinked rubber is impossible to “dissolve” completely in the binder matrix. RmB is then either a) a high-viscosity, non-homogeneous material, which requires continuous agitation during storage, or b) a more homogeneous material in which the rubber polymers are sheared by high stress, digested by high temperatures (200-300°C), or de-vulcanised by means of de-vulcanising agents. Usually this “digesting” of the reclaimed tyre rubber comes with a loss of elastic properties.

This paper proposes the use of **C8-alkyl polysulphide**, in particular **C8-alkyl pentasulphide** (“BA CR36”), which turns out a) to be the optimal polysulphide for crosslinking of polymers in PmB, and, surprisingly, also b) efficiently and selectively de-vulcanises rubber and thus facilitates the production of RmB. If used properly, it is possible to maintain or even improve the elastic properties of RmB with this polysulphide.

2. POLYSULPHIDES AS SULPHUR DONORS IN PMB CROSSLINKING

Alkyl polysulphides have the following structure: R-S_x-R, with R = alkyl and S_x is a chain of x connected sulphur atoms (2-8)⁶. These alkyl polysulphides release reactive sulphur when heated. Depending on the type of alkyl group and the number of connected sulphur atoms x, the sulphur content varies from approx. 20 to 40%.

The sulphur donors enhance the elastic properties and hot storage stability of SBS-modified bitumen by crosslinking the polymer with bitumen components⁷. Crosslinking with organic sulphur donors is favourable compared to the use of more economic elemental sulphur if simple stirring devices, like a standard lab stirrer, are used to mix bitumen, polymer and the crosslinker.

In a lab experiment 3 % of a SBS copolymer (Kraton® 1101) was dissolved in bitumen 50/70 at 180°C. Crosslinking was started by adding either elemental sulphur (0.1%, w/w bitumen with polymer) or an alkyl polysulphide containing 40% sulphur (0.25%, w/w bitumen with polymer) at 160°C. The emitted H₂S is trapped by precipitation in Pb(Ac)₂ solution; mass of emitted hydrogen sulphide is determined as PbS by gravimetry. As can be seen in Table 1, by adding the polysulphide, compared to addition of elemental sulphur, a) the reaction starts faster (indication: onset of H₂S emission), and b) the loss of sulphur by H₂S emission is reduced by 50%.

Table 1. Crosslinking PmB with different sulphur sources with lab equipment

Crosslinker	Loss of sulphur [%]	Time until reaction started [min]
BA CR36	10.7	4
Elemental sulphur	20.6	18

There are differences in the **dynamic shear rheometer** (“DSR”) oscillating mode⁸ temperature sweep (parameter: phase angle δ) between PmB crosslinked with BA CR36 and elemental sulphur: The former shows an almost ideal sigmoid curve (low phase angle at lower temperatures, phase angle approaching 90°C for higher temperatures), whereas the latter shows a significantly higher phase angle (lower elasticity) for pavement service temperatures.

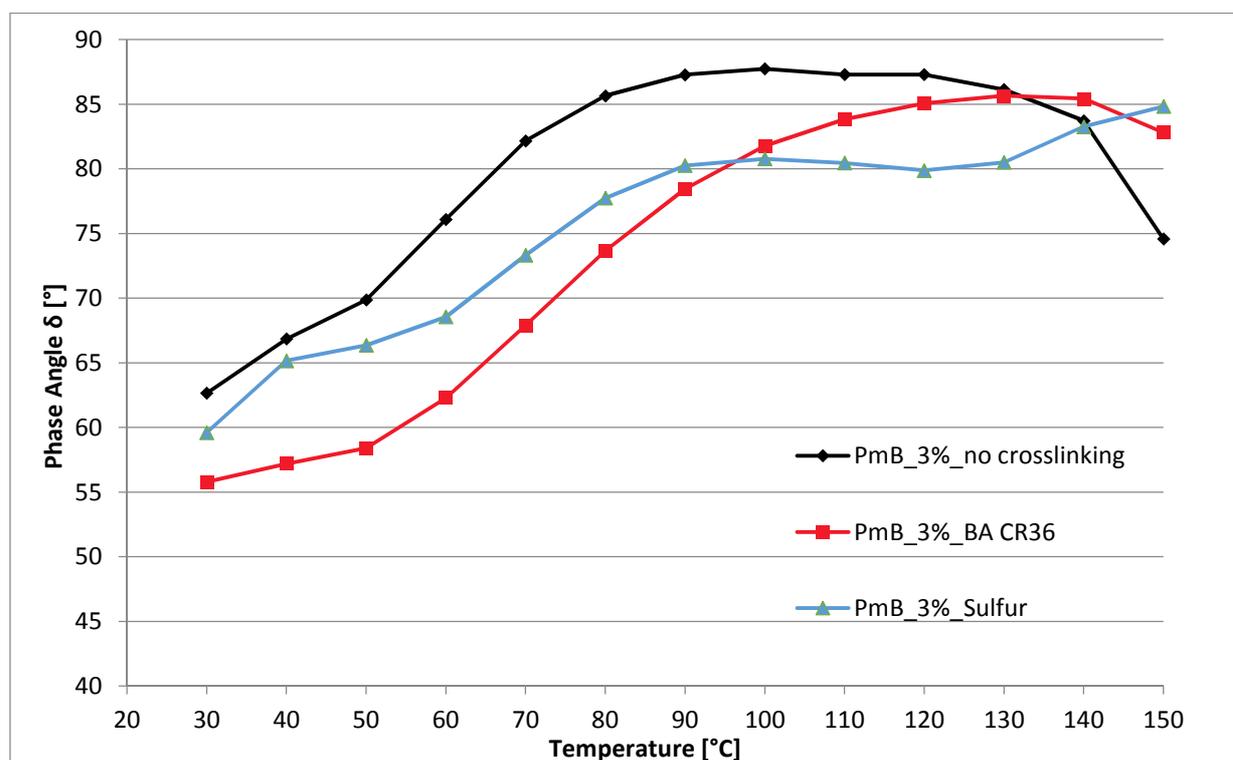


Figure 1. DSR temperature sweep of PmB crosslinked with C8-alkyl polysulphide “BA CR36” or elemental sulphur

The multiple stress creep recovery (“MSCR”) DSR test shows an increased recovery rate due to crosslinking by sulphur donors⁹. It is performed on a bitumen sample, 25 mm in diameter and 1 mm in thickness. The test is typically conducted at 60°C working temperature of the bitumen sample. For each cycle, a 1 s creep load is applied to the sample, followed by a 9 s rest period. Stress levels of 0.1, 1.6 and 3.2 kPa are applied successively and a total of 10 cycles are conducted for each stress level. By using higher levels of stress and strain, the response of the specimen captures not only the stiffening effects of the polymer, but also the elastic effects (see ¹⁰ as a reference for the MSCR test procedure).

In a lab study, different organic sulphur donors with different sulphur content were compared concerning their potential to increase the R value (recovery rate in percent) at 3 different stress stages. 4 different sulphur-releasing compounds were dosed according to their respective sulphur content **to achieve a concentration of 0.1% sulphur present in the reaction mixture.**

In the first experiment, SBS Copolymer Kraton® 1101 was dissolved in Nynas T 400 oil (12 g copolymer to 32 g oil), then the copolymer-oil pre-mix was added to bitumen 50/70 to yield a 3% copolymer solution (in bitumen and oil). Different types of alkyl polysulphides were used to crosslink the polymer. MSCR test demonstrated that, using the 40% sulphur containing C8-alkyl-polysulphide as a crosslinker, the thusly obtained PmB showed best elastic recovery rate (Table 2) of the modified binders, crosslinked by different types of sulphur donors.

Table 2. MSCR Results with Bitumen 50/70, 8% Nynas T400, 3% Kraton® 1101 crosslinked with 0.1% S

Crosslinker	0.25% C8-alkyl polysulphide with 40% S	0.32% C12-alkyl polysulphide with 32% S	0.46% C12-alkyl polysulphide with 22% S	0.59% sulphurized ester with 17 % sulphur
R value 0.1 kPa	33.84	26.63	12.07	21.92
R value 1.6 kPa	10.32	6.14	1.05	4.4
R value 3.2 kPa	2.68	0.34	0	0.05

The experiment was repeated with the better soluble Kraton® 1102 SBS copolymer, which required no solubilizer, and **at a higher concentration of sulphur (0.2%)**. Kraton® 1102 could be dissolved directly in 3% concentration in a 50/70 binder at 180°C. Also in this case, C8-alkyl polysulphide as a crosslinker gave the best MSCR recovery value (Table 3).

Table 3. MSCR Results with Bitumen 50/70, 3% Kraton® 1102 and 2 different alkyl polysulphides (0.2% S)

Crosslinker	none	0.50% C8-Alkyl-Polysulphide with 40% S	0.61% C12-Alkyl-Polysulphide with 32% S
R value 0.1 kPa	5.73	29.8	23.9
R value 1.6 kPa	3.26	21.3	15.6
R value 3.2 kPa	1.38	13.0	8.5

3. POLYSULPHIDE AS A DE-VULCANISING AGENT IN THE MANUFACTURE OF RUBBER-MODIFIED BITUMEN (“RMB”)

Alkyl poly- and -disulphides can cleave sulphur bridges formed by the vulcanisation process¹¹. C8-alkyl-polysulphide and comparable alkyl polysulphides are described as additives used in a process for the regeneration (de-vulcanisation) of sulphur-crosslinked vulcanised rubber¹². Reclaimed tyre rubber as fine granules are intensely mixed with alkyl polysulphide, the latter optionally mixed with carrier oil, so that the granule surface is covered with the polysulphide. The mixture is heated up to approx. 140°C which allows the polysulphide to penetrate the rubber particles and then to decompose. The resulting reaction of the polysulphide with the crosslinked polymer chains (see Fig. 2) is a re-arrangement; the alkyl groups of the polysulphide form a “capping group” for the ends of the broken sulphur bridge. In several patents¹³ the use of such “pre-treated” rubber is described with benefits for a) manufacture of rubberised bitumen, and b) the performance of thusly obtained rubber-modified bitumen.

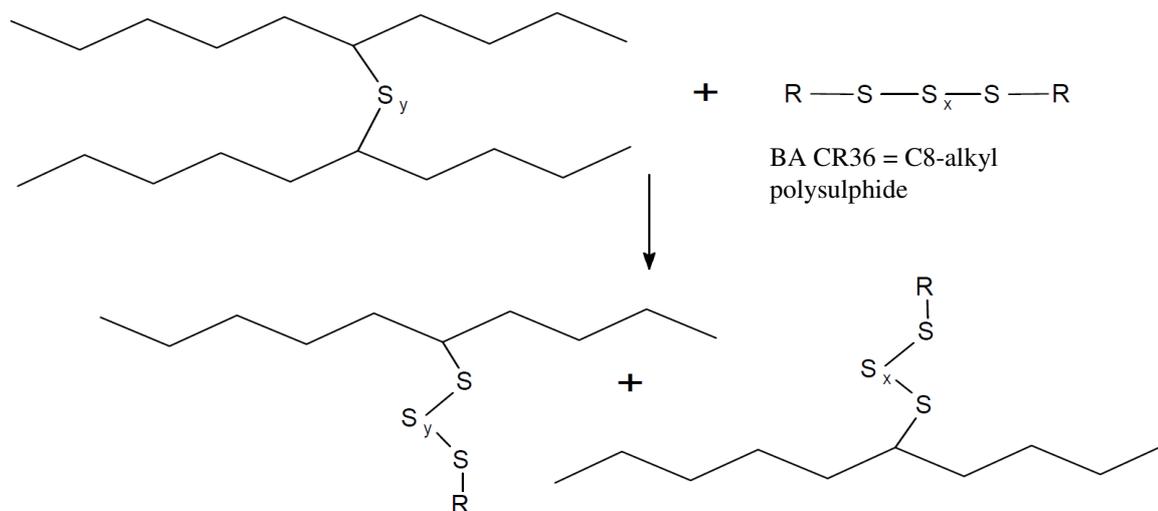


Figure 2. Cleaving sulphur bridges by means of alkyl polysulphides

If the rubber is treated with polysulphide under optimal conditions (thermal treatment, agitation), mixing with bitumen gets easier, because a) the viscosity is generally lower, and b) the viscosity maximum is reached faster.

In a lab experiment, fine dispersions of 30% rubber in bitumen were prepared at 170°C by stirring at this temperature for 2 hours. In one case, pure rubber particles (0.4-0.6 mm grain size) derived from truck tyres (supplier: MRH Mülsener Rohstoff- und Handelsgesellschaft mbH, blue curve in Fig. 3) were used, in the comparative case the same rubber particles, but treated with 2.5% BA CR 36 (C8-alkyl polysulphide) at 140°C for 40 minutes prior to being added to the bitumen (red curve in Fig. 3), were used. **The stirring apparatus and the agitator used can be regarded as a modified rotational viscosimeter¹⁴, so for convenience the viscosity of the rubber-bitumen “solution” is monitored by torque needed to keep stirring velocity constant.**

The curves clearly demonstrate that the pre-treatment with polysulphide generally reduced the viscosity of the rubber-bitumen mix, and accelerated swelling of the rubber particles in the bitumen matrix. The time until swelling is finished is indicated by the time needed to reach the viscosity maximum, which is 70 minutes for the non-treated

rubber particles, and approx. 17-18 minutes for the treated particles. The viscosity maximum is reached at 52-53 Ncm torque for the non-treated, and at 30 Ncm for the treated rubber particles.

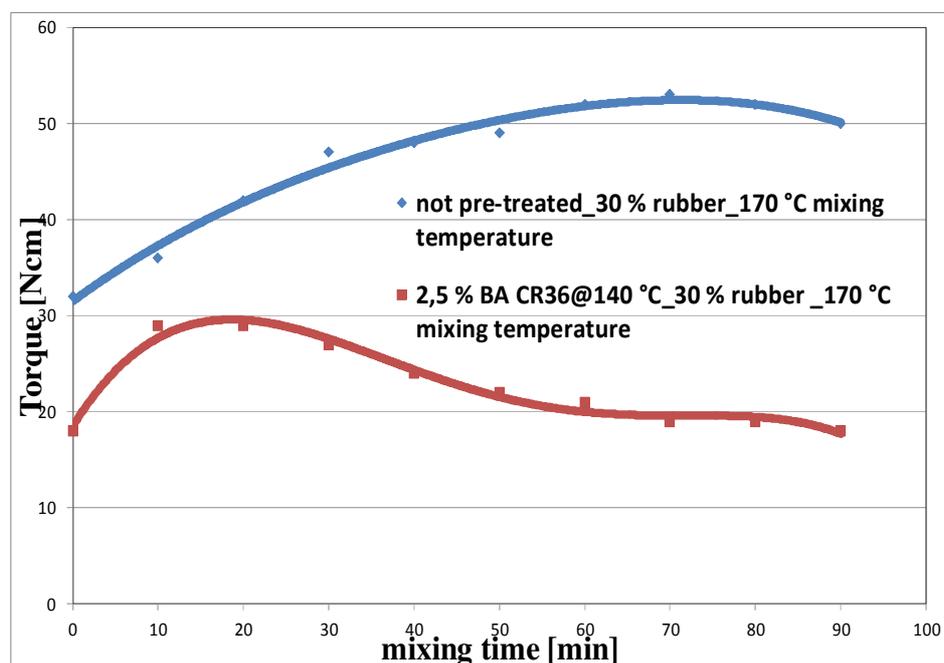


Figure 3: Viscosity development in rubber-bitumen mixes by monitoring torque needed to keep stirring velocity constant. Rubber was either non-treated, or treated with BA CR36

The purpose of rubber vulcanisation is to improve elasticity¹⁵. A de-vulcanised reclaimed rubber may be easier to be dispersed in bitumen, but what are the consequences of the de-vulcanisation for the viscoelastic properties of rubber-modified bitumen? The addition of elastomers like SBS or rubber usually results in increased complex modulus and viscosity, improved elastic response and enhanced cracking resistance at low temperatures¹⁶. Addition of de-vulcanised crumb rubber increases the viscosity significantly less than adding vulcanised rubber¹⁷.

In a comparative study (Fig. 4) crumb rubber-modified bitumen were prepared, using a) native, non-treated rubber, derived from truck tyres, 0.4 mm to 0.6 mm diameter, and b) the same type of rubber, treated with 2.5% C8-alkyl-polysulphide BA CR36 at 140°C for 40 minutes. The rubber particles were added to the binder at 170°C, and the mixture was stirred with a standard lab stirrer for 2 h at this temperature to achieve an even dispersion.

The phase angle of the corresponding modified bitumen was lower (indicating more elastic behaviour) for both types of rubber than the phase angle for the bitumen 50/70 used to prepare the modified samples.

The binder modified with non-treated rubber had a lower phase angle for all temperatures than the treated one, the difference smaller at road service temperature (30-60°C) than at temperatures close to asphalt mixing conditions (150°C). Using the treated rubber particles, the drop in elastic behaviour, as indicated by the higher phase angle, seems to arise from the de-vulcanisation. Nevertheless, the loss of elasticity at service temperature seems to be a move in the wrong direction.

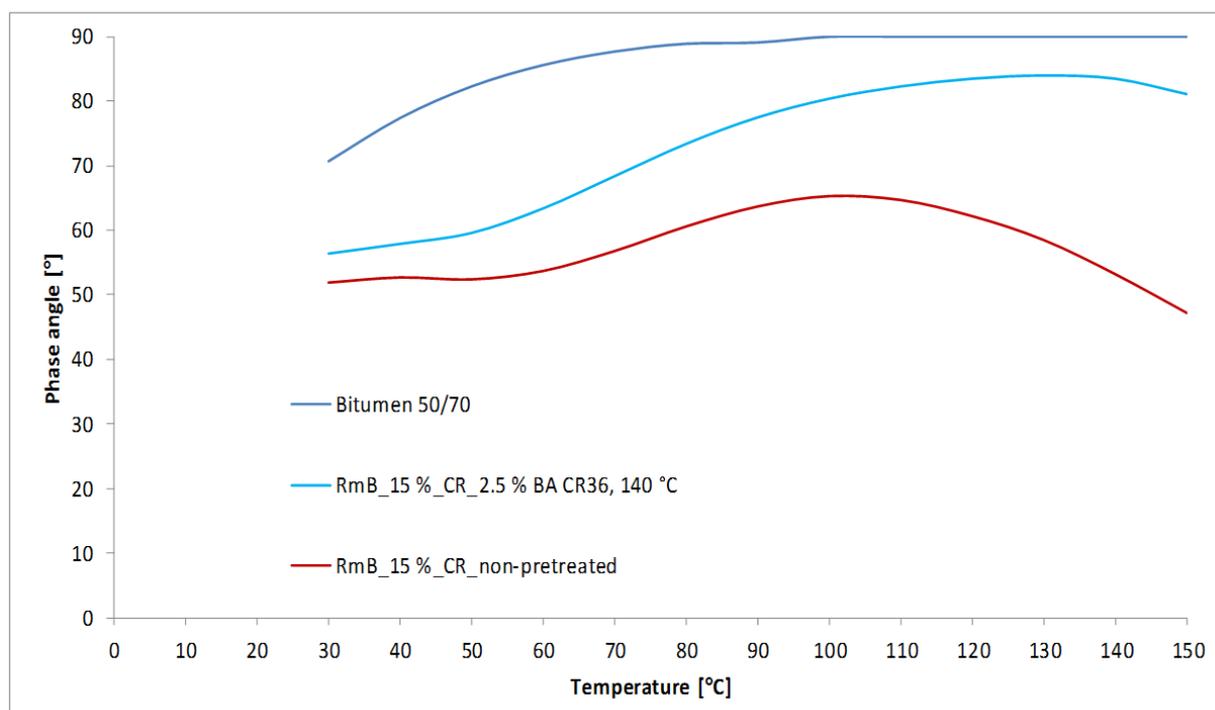


Figure 4. DSR temperature sweep of bitumen 50/70 and crumb-rubber(CR)-modified (15% rubber w/w) bitumen (RmB)

At the asphalt mixing plant a more viscous behaviour (phase angle close to 90°C) is preferred. The undesired phase angle drop in case of using the non-treated rubber could be explained by network formation at high temperatures due to not finished swelling of the rubber particles, even after 2 h stirring of the rubber – bitumen mix.

It was assumed that, by optimisation of the thermal treatment process, the loss of elastic behaviour as indicated by increase of phase angle can be reduced. In a trial rubber (particle size 0.2 mm to 0.4 mm) derived from truck tyres (supplier: MRH) was mixed with the C8-alkyl polysulphide under intense agitation in the rubber recycling plant, then thermally treated (140°C) for 15-20 minutes.

The rubber particles, both treated (as described) and non-treated, were then added to bitumen 50/70 at 170°C to achieve a fraction of 15% rubber. Mixing was achieved by vigorous stirring at the same temperature for 1 h, followed by maturing the dispersion without stirring for another hour at 170°C.

Fig. 5 shows a comparison of temperature-sweep shear modulus and phase angle data of the rubber-modified bitumen types obtained either with standard non-treated rubber particles, or those treated with the polysulphide as described above. Stirring and maturing phases in minutes are given by 2 numbers separated by slash / (e. g. 60/60).

The shear modulus (logarithmic scale) in the temperature sweep is a bit more flat if a treated rubber is used to modify bitumen, but the more interesting point is the phase angle maintaining its low value until 50°C is reached, and rise with higher temperatures (60°C, 70°C) being moderate compared to non-treated rubber. The significant difference of treated vs non-treated rubber is remarkable, because exactly at pavement temperatures of 50°-70°C, which can be reached in the summer, a high resistance to deformation, i.e. highly elastic behaviour, is advantageous to prevent rutting.

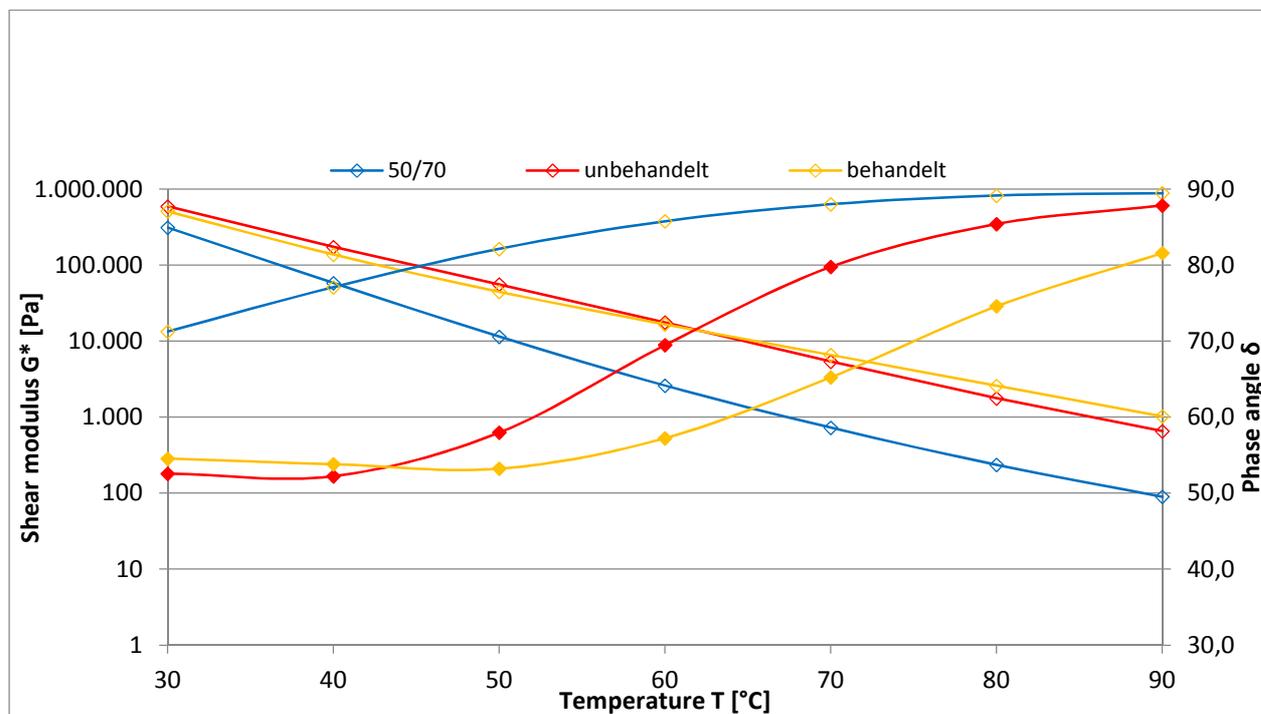


Figure 5: Complex shear modulus G^* and phase angle δ of bitumen 50/70 and rubber- (treated and non-treated) modified bitumen (15%, 60 min stirring, 60 min maturing, 60/60, at 170°C)

The same behaviour is seen if the rubber has a much shorter time to be digested into the bitumen.

If the test described in Fig. 5 is repeated but with a much shorter mixing time (5 minutes mixing, 15 minutes maturing at 170°C, 5/15, Fig. 6) both binder samples show a more viscous behaviour at lower temperatures, but the rubberized bitumen with C8-alkyl polysulphide-treated rubber requires higher temperature to reach a given level of phase angle (i. e. maintains its elastic behaviour up to a higher temperature). It is reasonable to assume that the treated rubber particles swell faster than the non-treated ones, indicating their potential use in the “Dry Process”; i. e. mixing aggregates, standard type bitumen and rubber particles in the asphalt mix plant.

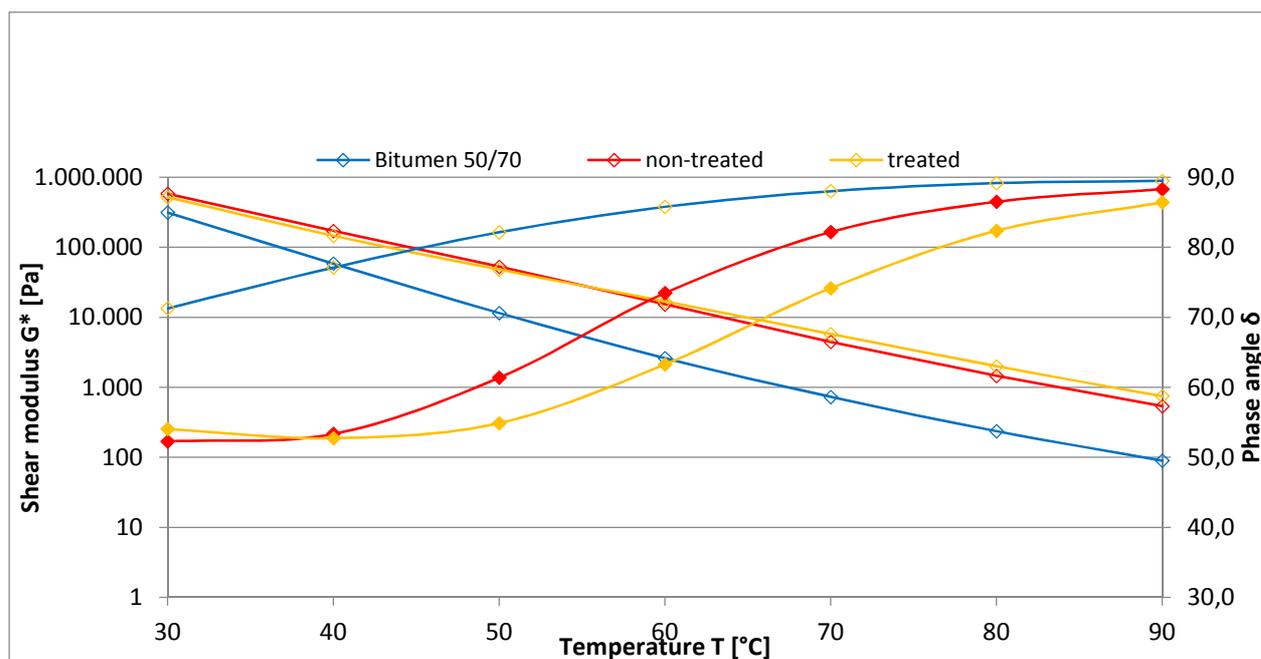


Figure 6. Complex shear modulus G^* and phase angle δ Bitumen 50/70 and rubber-(treated, non-treated)-modified bitumen (15%, 5min stirring, 15 min maturing, 5/15, at 170°C)

Table 4 gives comparative data for bitumen, modified with treated as well as non-treated rubber and for the unmodified bitumen 50/70. The operational temperature range is extended by the rubber pre-treatment: the softening point is increased, and the stiffness at low temperatures is reduced. Remarkable is the gain in elastic recovery (DIN EN 13398) by pre-treating the rubber with polysulphide, from 43% (non-treated rubber) to 72% (treated rubber). The table also includes the requirements of the “Empfehlungen zu gummimodifizierten Bitumen und Asphalten” (“Recommendations to rubber-modified bitumen and asphalts”) of the German FGSV” (2012; see¹⁸).

Concerning elastic recovery, the 50% recommended by FGSV can be achieved only by the pre-treatment of the rubber particles. The same applies to the recommended value for the phase angle δ of max. 65° in the oscillating DSR test mode at 60°C (see Fig’s 5 and 6 with different stirring and maturing phases for the rubber-bitumen mix).

Table 4. RmB key data, comparison made by rubber, non-treated vs treated

Property	Rubber non-treated 60/60	Rubber non-treated 5/15	Rubber treated 60/60	Rubber treated 5/15	50/70	Recommendation RmB 25/55-50(60) (FGSV)
Softening point RaB, °C	61.6	60.2	65.6	62.4	49.0	≥ 50 (60)
Needle penetration, 0.1 mm	33	35	38	36	59	25-55
Elastic recovery, %	43	30	72	54	8	≥ 50
Stiffness at -16°C, MPa	130	137	103	114	168	≤ 200 (≤150)
Stiffness at -25°C, MPa	314	289	248	288	434	
m-Value at -16°C	0.328	0.339	0.339	0.316	0.389	≥ 0.3
m-Value at -25°C	0.245	0.238	0.253	0.251	0.276	
S: Critical temperature, °C	-24.3	-25.6	-28.2	-25.6	-20.5	
M: Critical temperature, °C	-19.0	-19.4	-19.9	-18.1	-23.1	

The gain in elastic behaviour by pre-treating the rubber particles with polysulphide is further supported by DSR MSCR data.

The R value is the percentage of deformation recovery; and J is a measure of the amount of residual strain left in the specimen after repeated creep and recovery, relative to the amount of stress applied. J is currently perceived as the best rheological parameter for the assessment of the susceptibility of the binder to resist permanent deformation in asphalt mixture. The lower the J value is the greater proportion of the stress the binder is able to absorb, and the less susceptible to plastic deformation it is¹⁹.

As shown in Table 5, the polysulphide-treated rubber particles, with different mixing and maturing times as indicated, show higher deformation recovery and a higher capacity of the binder to absorb stress (lower J value).

Table 5. RmB DSR MSCR comparative data with rubber, non-treated and treated

DSR MSCR	Rubber non-treated 60/60	Rubber non-treated 5/15	Rubber treated 60/60	Rubber treated 5/15	50/70
R (0,1 kPa), %	22.0	19.8	47.2	29.8	0.8
R (1,6 kPa), %	14.6	11.1	40.8	22.6	-0.6
R (3,2 kPa), %	9.9	7.0	31.8	15.6	-1.1
J (0,1 kPa), 1/kPa	0.352	0.429	0.183	0.290	3.649
J (1,6 kPa), 1/kPa	0.393	0.486	0.212	0.331	3.838
J (3,2 kPa), 1/kPa	0.442	0.542	0.259	0.388	3.973

Bitumen ageing is a process involving oxidation and loss of lightweight constituents that leads to hardening of the material. There are two types of ageing, namely, short-term aging and long-term ageing. Short-term ageing occurs during the mixing period of aggregate and bitumen in the asphalt mixing plant, while long-term ageing occurs in a longer time period during the service life of the asphalt pavement.

Rubber addition can help to reduce the hardening rate and oxidation susceptibility of bitumen. Rubber also helps in lowering viscosity build-up with ageing²⁰.

In this context of potentially improving the ageing behaviour of bitumen by the addition of rubber, the impact of the C8-alkyl polysulphide treatment as described (2.5% polysulphide added to rubber particles, thermal treatment at 140°C for 15 min under agitation) was investigated. Interestingly, the rubber-modified bitumen with non-treated rubber showed the highest increase of the softening point by RTFOT ageing (10 K, versus 6.4 K for non-modified bitumen 50/70 and only 2.4 K for the RmB with treated rubber (see Table 6).

Table 6. Ageing behaviour of RmB with non-treated and treated rubber

		Bitumen 50/70	RmB non- treated (60/60)	RmB treated (60/60)
Not aged	Softening Point RaB [°C]	49.0	65.6	67.2
RTFOT	Softening Point RaB [°C]	55.4	75.8	69.6
	Increase RaB RTFOT [K]	6.4	10.2	2.4
RTFOT + PAV	Softening Point RaB [°C]	65.4	76.4	72.8
	Increase RaB RTFOT + PAV[K]	16.4	10.8	5.6

The small increase in softening point of the rubber-modified bitumen with treated rubber in short-term ageing is favourable after PAV ageing. The overall (RTFOT + PAV) ageing is smallest for the RmB with treated rubber (5.6 K).

Besides elastic and ageing properties there are other performance aspects of bitumen which determine the suitability of rubberized bitumen in asphalt pavements, e. g. adhesion to aggregates.

Open-porous asphalts with an air-void ratio of 15-20% were initially proposed to provide drainage and reduce surface water and spray during heavy rainfall, but they turned out also to reduce traffic noise at roadsides²¹. Regarding noise reduction, rubberized asphalt pavements provide more favourable conditions as conventional ones, an advantage of about 1-3 dB. This noise reduction performance seems to be constant from period of construction to at least 45 months later²².

Such open-graded mixes are especially susceptible to pavement failures caused by stripping by water due to their permeability compared to dense-graded mixes²³. Polymer-modified as well as rubber-modified binders typically yield greater film thicknesses, which have been shown to protect against moisture damage²⁴.

In the following study the effect of polysulphide treatment on the bitumen-aggregates adhesion was investigated using reclaimed rubber particles as a bitumen modifier.

Rubber granules (passenger car / truck tyres) of 0.8 mm – 2 mm particle size (supplier: Genan GmbH, Germany) were treated at 130°C for 40 minutes with Shell Flavex® 595 oil or a mixture of both alkyl polysulphide and oil (40%/60%). The rubber particles, treated and non-treated, were added to bitumen 70/100 to obtain a 15% rubber-modified bitumen (2 h mixing time).

The adhesion of the resulting modified bitumen was tested with the Rolling Bottle test (DIN EN 12697-11) at room temperature using mineral Andesite (from Baumholder quarry, Germany, size 8/11 mm), as aggregate. Mixing temperature of the binder with the aggregates was 175°C. After cooling down, the aggregates were immersed in water of a specific temperature (20±5°C), and kept in a rolling bottle for a defined time (6h, 24 h). The ratio bitumen (70/100) to aggregates was 16g binder to 500g aggregates.

Table 7 shows the results obtained with a) the rubber particles as they are, b) rubber particles treated with 13% extender oil Shell Flavex® 595, and c) particles treated with 13% of a solution of the C8-alkyl polysulphide (40%) in extender oil (60%).

The binder with the relatively coarse rubber granules shows only a modest adhesion to the Andesite aggregates; the coverage after 24 h is low with only 35%. The values are an average of the visual assessment by 3 operators. Adding extender oil improves the adhesion, but the best result is obtained by a mixture of polysulphide and extender oil. It is also possible to achieve adhesion improvements by adding the polysulphide solution to the already finished rubberized bitumen (last row in Table 7, data marked with an asterisk *).

Table 7. Adhesion properties of non-treated vs treated rubber particles (DIN 12697-11, "Rolling Bottle test")

RmB with bitumen 70/100	BA CR36 [% rel. rubber]	Shell Flavex® 595 [% rel. rubber]	Coverage (av) after 6 h (%)	Coverage (av) after 24 h (%)
15% Rubber	0	0	85	35
15 % Rubber	0	13	90	50
15 % Rubber	5.2	7.8	90	60
15 % Rubber	0 (+5.2*)	0 (+7.8*)	85 (95*)	35 (65*)

4. Conclusions

C8-alkyl polysulphide BA CR36 is among the polysulphides tested in the comparative study the most efficient crosslinker for PmB. The presented data indicate efficient de-vulcanisation of reclaimed tyre rubber, without loss of elastic recovery.

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6. REFERENCES

- ¹ Serhiy Pyshyev, Volodymyr Gunka, Yuriy Grytsenko and Michael Bratychak, POLYMER MODIFIED BITUMEN: REVIEW, in: CHEMISTRY & CHEMICAL TECHNOLOGY Lviv Polytechnic National University, Vol. 10, No. 4 p 634, 2016
- ² US 4145322 and US 4242246
- ³ EP 0096638
- ⁴ US 7608650
- ⁵ Davide Lo Presti, Recycled Tyre Rubber Modified Bitumen for road asphalt mixtures: A literature review, Construction and Building Materials 49 (2013) 863–881
- ⁶ Thomas Rossrucker and Achim Fessenbecker: Sulfur Carriers; in: Rudnick et al, Lubricant Additives: Chemistry and Applications, Second Edition, CRC Press 2009, p 252
- ⁷ Feng Zhang, Jianying Yu, Shaopeng Wu, Journal of Hazardous Materials, Volume 182, Issues 1–3, 15 October 2010, Pages 507-517, <https://doi.org/10.1016/j.jhazmat.2010.06.061>
- ⁸ Dr. Hans M. Wyss, Ryan J. Larsen, Prof. David A. Weitz, G.I.T. Laboratory Journal 3-4/2007, pp 68-70, , Darmstadt
- ⁹ Weidong Huang, Naipeng Tang, Construction and Building Materials 93 (2015) 514–521
- ¹⁰ <https://www.fhwa.dot.gov/pavement/materials/pubs/hif11038/hif11038.pdf>
- ¹¹ V.V. Rajan, W.K. Dierkes, R. Joseph, and J.W.M. Noordermeer; Science and technology of rubber reclamation with special attention to NR-based waste latex products; Progress in Polymer Science, 31(9):811 - 834, 2006
- ¹² EP-B-2164895
- ¹³ WO2011138412, WO2015189399 and WO2017032661
- ¹⁴ <https://www.pavementinteractive.org/reference-desk/testing/binder-tests/rotational-viscometer/>
- ¹⁵ Shinzo Kohjiy: Chemistry, Manufacture and Applications of Natural Rubber, Elsevier Woodhead Publishing; 2014, p 250
- ¹⁶ Zhu, J., Birgisson, B., Kringos, N. (2014) Polymer modification of bitumen: Advances and challenges. European Polymer Journal, 54: 18-38, <http://dx.doi.org/10.1016/j.eurpolymj.2014.02.005>, page 13
- ¹⁷ Nuha Salim Mashaan, Asim Hassan Ali, Mohamed Rehan Karim, and Mahrez Abdelaziz: A Review on Using Crumb Rubber in Reinforcement of Asphalt Pavement; <http://dx.doi.org/10.1155/2014/214612>
- ¹⁸ FGSV Nr 724; http://www.fgsv-verlag.de/catalog/_pdf-files/Inhaltsuebersicht_Strassenbautechnik.pdf
- ¹⁹ Lucie Benešová and Jan Valentin 2017 , IOP Conf. Ser.: Mater. Sci. Eng. 236, 2016
- ²⁰ Mohd Rasdan Ibrahim, Herda Yati Katman, Mohamed Rehan Karim, Suhana Koting, and Nuha S. Mashaan, A Review on the Effect of Crumb Rubber Addition to the Rheology of Crumb Rubber Modified Bitumen, Advances in Materials Science and Engineering, Volume 2013, Article ID 415246, <http://dx.doi.org/10.1155/2013/415246>
- ²¹ Zetterling T, Nilsson NA. Implementation of the pro-elastic road surface. In: Proceedings of international tire/road noise conference, 1990:p.315–25
- ²² S. Mavridoua, and F. Kehagiab, Environmental Noise Performance of Rubberized Asphalt Mixtures: Lamia’s case study, Procedia Environmental Sciences 38 (2017) 804 – 811
- ²³ Taylor, M., and N. Khosla. “Stripping of Asphalt Pavements: State-of-the-Art”, Transportation Research Record 911, National Research Council, TRB, Washington, D.C., 1983. pp. 150-158
- ²⁴ Gorkem, C., & Sengoz, B. (2009). Predicting Stripping and Moisture Induced Damage of Asphalt Concrete Prepared with Polymer Modified Bitumen and Hydrated Lime. Construction and Building Materials, 23, 2227-2236

Annex

ANNEX: PRODUCTION AND INVESTIGATION OF RUBBER-MODIFIED ASPHALT WITH “BA CR36”

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The next step for testing the impact and the suitability of the new developed product “BA CR36” as a modifier of asphalt pavements is the production of rubber-modified asphalt (RmA). In this trial the “dry process”, which is the mostly used technique in Germany, was applied. The RmA with “BA CR36” as modifier was produced large-scale in an asphalt mixing plant and the mix composition and some performance properties were tested afterwards. To classify the results, a common used commercial product was also tested as a “Benchmark” (BM). In addition, there were studies on the aged material to estimate the long-term impact.

The used bituminous mixture is an asphalt concrete for an asphalt surface course with grain size 8 mm following EN 13108, Part 1 with an usual bitumen content of 7.1 M.-%. As a special feature, in the mixture is a high amount of aggregates > 2 mm, which is called “grit” and follows the German specification [1]. As aggregate, a quartz porphyry was used and the non-modified binder has a penetration from 50 to 70 1/10 mm. In the RmA blend with the new product “BA CR36” is a percentage of 15 M.-% rubber. Additional parameters like grain size distribution, mix composition, conventional characteristics and volumetric properties from both rubber-modified asphalts were determined. All these characteristic values fulfil the requirements of the German specification [2, 3].

After the investigation of the mix compositions of both RmAs, some performance proportions were determined to estimate the behaviour during service temperatures. First proportions were established when delivered condition (not aged) exist and then executed in the aged state. The ageing process of the bituminous mixture follows the CEN / TS 1697-52, procedure A1, where the mixing is aged in an oven at 100 °C with oxygen supply and daily blend. The effect of the successful ageing was detected with the Softening Point Ring and Ball, because it decreases in comparison to the delivered condition for both products. This result was also verified with the rheological performance of the binder.

The behaviour of low service temperatures were examined with the Thermal Stress Restrained Specimen Tests (TSRST), according to the German technical test specification [4], which corresponds to the European standard EN 12697, part 46. An image from the experimental setup is shown in Figure 1 (left). In the test, the specimen (prism with dimensions 40 x 40 x 160 mm³) is held in constant length, while test temperature is constantly reduced, starting at 20 °C with a constant cooling rate of -10 K/h. Meanwhile the thermal-shrinkage of the specimen is retained due to the constant length of the specimen. Therefore thermal stress is applied by temperature cooling and cryogenic tensile stress is arising which leads to low temperature cracking, when cryogenic tensile stress reaches its maximum. The test is stopped as soon as the specimen fractures. One test includes three specimens. Failure stress and failure temperature represent the important parameters of this test. The lower the failure temperature, the better the behaviour. In Germany, there are recommendations for the failure temperature depending on the frost action zone [4]. There are three frost action zones, which assign different areas in accordance with the altitude of the ground. The recommendation for zone I amounts to ≤ -15 °C, for zone II to ≤ -20 °C and for zone III to ≤ -25 °C.

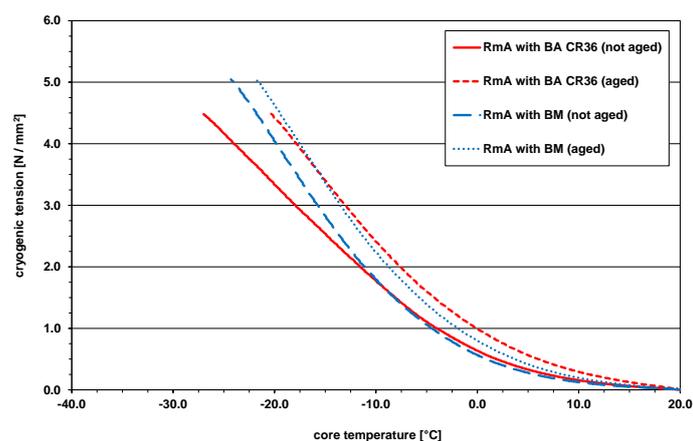


Figure 1: Left: Test stand for TSRST with fixed specimens; Right: Graphical representation of cryogenic tensile stresses depending on the core temperature (averages) for both RmAs (not aged and aged)

In Figure 1 (right) are presented the cryogenic tensile stresses depending on the core temperature. Every graph presents an average of three specimens. The results of both RmAs show, that there is a good behaviour at low service temperatures. The RmA with “BA CR36” shows a slightly better performance when delivered condition exists as the mixture with the BM. In addition, all failure temperatures comply the recommendations in frost action zone II. After the ageing, there is not any significant difference between the failure temperatures, which are still under -20 °C.

The performance at high service temperatures was determined with the uniaxial cyclic compression test (Figure 2, left) according to the German technical test specification for testing asphalt for road construction [5]. The test corresponds to the European standard EN 12697, part 25 as a special case of triaxial testing without lateral confinement. The test provides a possibility to determine the deformation behaviour with an axle-load-simulating dynamic load. Thereby cylindrical specimens (here: Marshall Specimens) are subjected to a repeated sinusoidal haversine load with rest periods onto their base area at isothermal test conditions (50 °C). The loading pulse lasts for a duration of 0.2 seconds, the rest period lasts for 1.5 seconds. Normally 10,000 loading cycles are applied if the axial strain does not exceed the limit of 40 ‰. The stress arrangement is defined by a minimum stress σ_u (0.025 MPa) and a maximum stress σ_o (0.35 MPa). Some deformations are elastic or visco-elastic and decrease during the rest period, others stay irreversible. These irreversible deformations are recorded and evaluated for each loading cycle and result in an impulse creep curve. The most characteristic parameters are the number of loading cycles n , the strain ϵ in ‰ and the strain rate ϵ^* in $\text{‰} \cdot 10^{-4}/n$. These parameters are either determined at the inflection point or if this stage has not been achieved, at the end of the test ($n = 10,000$). Asphalts with a high resistance to permanent deformation have a low strain rate.

In Figure 2 (right) are presented the impulse creep curves as averages of three specimens. The results show that both products have a good deformation resistance before and after ageing. The strain rate is around $2.0 \text{‰} \cdot 10^{-4}/n$ which is rather low, the strain is on a low level and for all mixtures quite similar (around 9.0 ‰), and the impulse creep curves have not an inflection point ($n = 10,000$ load cycles are achieved).

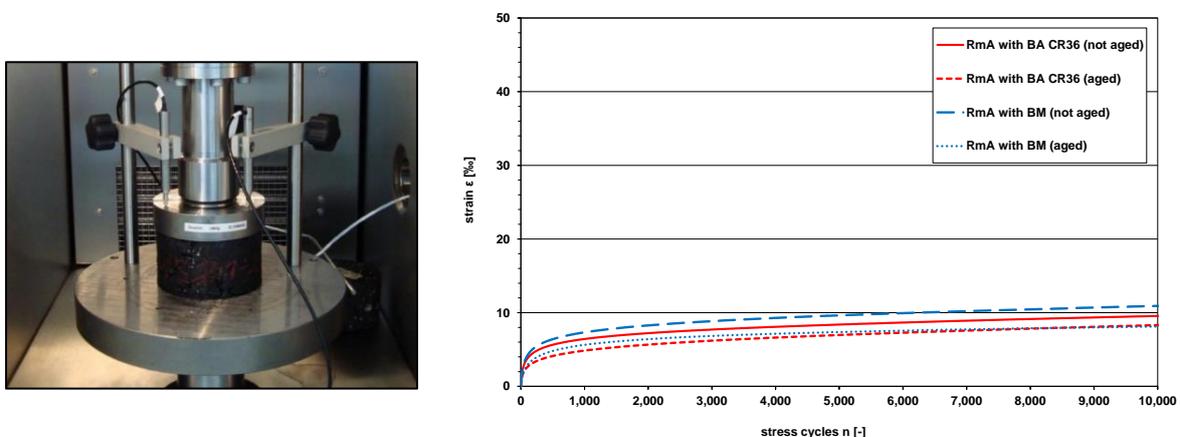


Figure 2: Left: Test stand for cyclic compression test with Marshall Specimen; Right: Graphical display of the impulse creep curves (averages) for both RmAs (not aged and aged)

As consequence of the good results with the rubber-modified asphalt with “BA CR36” there was build a 100 m unilateral test track in the black forest in south Germany in July 2020 to examine the performance from the laboratory in situ. It was used the same formulation as before and bituminous mixture and drill cores were removed from the pavement to test the composition again. As the material tested large-scale there were also all German requirements fulfilled in situ. During the incorporation, the RmA showed a good workability, which was confirmed from the results of the drill cores because they have a degree of compaction of 100 %. Now, the pavement is under observation and the long-term behaviour is observed.

It can be concluded, that the new developed product “BA CR36” is comparable with a common used commercial product with experience as modifier for asphalt pavements. Based on the investigated properties, there is a good performance at low and high service temperatures and no evident degradation with ageing. It is expected that there is also a good long-term behaviour obviously.

REFERENCES

- [1] Road and Transportation Research Association: Working paper for plan and implementation from asphalt surface course containing grit asphalt concrete for application in pavements with special stresses (AP AC D SP), 2019
- [2] Road and Transportation Research Association: TL Asphalt-StB: Technical conditions of delivery for bituminous mixture for building traffic areas, 2007
- [3] Road and Transportation Research Association: ZTV Asphalt-StB: Additional technical terms and guidelines for building asphalt traffic areas, 2007
- [4] Road and Transportation Research Association: Working paper for low temperature behaviour from asphalt, Part 1: Tension and Cooling Tests, 2012
- [5] Road and Transportation Research Association: TP Asphalt-StB, Part 25 B 1: Uniaxial Cyclic compression test - Determination of the deformation behaviour of roll asphalt at high temperatures, 2012