Paper #B04

New Struktol plasticizers for an improved service-life of tire curing bladders

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Abstract

Tire Curing Bladders are operated under severe service conditions during tire production. High temperatures and high pressures are applied as well as there is repeated flexing due to a high number of inflating and deflating cycles during the vulcanization cycles of the uncured tire.

This publication presents studies for a significant extension of the service-life of tire curing bladders. The beneficial use of Struktol's new plasticizer types is demonstrated.

Introduction

Tire Curing Bladders are used in the last step of tire production when the tire is finally shaped. The green tire is placed into the mold which is closed, subsequently the curing bladder is inflated by a heat transfer medium, for example steam, water or nitrogen to press the uncured tire outwards against the mold in order to define the final shaping. When the curing process is finalized, the bladder is deflated and released from the cured tire, the mold is opened and the tire is stripped out of it.

Tire curing bladders are subjected to repeated flexing cycles consisting of inflation and deflation loops. The applied service conditions, representing the curing temperatures, pressure, and steam used all contribute to a demanding and challenging surrounding framework.

For over 60 years castor oil has been the plasticizer of choice for the compounding of tire curing bladders. In 1958 a patent application was filed by Goodyear citing the replacement of mineral oil plasticizers by castor oil [1]. The authors claimed a significantly extended service-life for tire curing bladders if compounded with castor oil due to an intended incompatibility of castor oil with the non-polar butyl rubber matrix as a major advantage. Consequently, the release of the cured tire from the tire curing bladder improved. Accordingly, the function of castor oil as internal release agent was highlighted. Today still the vast majority of tire curing bladder formulations are compounded with castor oil.

However, in these days castor oil is considered more as a plasticizer than a release agent. Since a couple of decades bladder release coatings are applied onto the bladder surface in order to improve the release from the cured tire. This technology resulted in a further move to a higher number of curing cycles. In turn, the original function of castor oil as internal release agent now limits the total number of curing cycles because the plasticizer evaporates out of the rubber matrix at high (service) temperatures. If the number of curing cycles is too high, hardening effects might occur because the plasticizer leaves the rubber matrix and therefore a failure is stimulated.

Bladder producers and tire companies have a major interest to run a curing bladder as long as possible by extension of the service life in order to gain significant cost savings. An improvement of cycle life by 10 or 20% represents substantial saving opportunities due to less downtime and number of bladders used during tire production.

Approach

Considering the aforementioned, the main disadvantages of castor oil relate to higher volatility and evaporation at curing temperatures.

In order to solve this issue reactive plasticizers are investigated. If the plasticizer is connected to the rubber matrix, it is prevented from evaporating during service.

Regarding resin-cured tire curing bladder recipes, the plasticizer reacts with the crosslinking resin and thus is fixed to the butyl matrix. Accordingly, the material cannot leave the curing bladder. Consequently, a prolonged service life is expected which in particular is triggered by an improved flexing performance for freshly cured test specimen as well as after heat and steam aging experiments.

Struktol HT 815 and Struktol HT 820 were designed to overcome the described disadvantages in tire curing bladders. Both plasticizers are reactive polymers which differ in molecular weight/chain length, whereas the molecular weight of Struktol HT 820 is higher than Struktol HT 815. The number of reactive groups is equal.

Experimental

2 different butyl grades were investigated. Polymer of choice for tire curing bladders model recipes mainly is regular Butyl rubber. In addition, recipes containing butyl based Exxpro® polymer produced by ExxonMobil, which is a copolymer of butylene and methyl styrene, were evaluated. The rubber model formulations are presented in Table 1. In both recipes the plasticizer type as well as the loading were varied. The discussed compound containing Castor oil (6 phr) served as reference.

Table 1: Regular Butyl formulation

	[phr]
Regular Butyl rubber [1]	100
Chloroprene rubber [2]	5
N-330 Carbon Black	50
Zinc oxide	5
Homogeniser [3]	5
Plasticizer	**6**
Crosslinking resin [4]	8
sum:	179

Table 2: Exxpro formulation

	[phr]
Exxpro polymer [5]	100
N-330 Carbon Black	50
Stearic acid	0,5
Plasticizer	**6**
Zinc oxide	3
Crosslinking resin [4]	3
MBTS accelerator	1,4
Magnesium oxide	0,1
sum:	164

[1] Butyl 268 (Exxon) or Butyl RB 301 (Arlanxeo), [2] Neoprene WRT (Denka Elastomer), [3] Struktol 40 MS Flakes (Struktol), [4] SP-1045 (SI Group), [5] Exxpro 3035 (Exxon).

Mixing was done in a HF Group 1.5E lab mixer. The final addition of the crosslinking chemicals was done on open mill.

For the first mixing stage, a fill factor of approx. 70% was chosen together with a rotor speed of 70 rpm and a starting temperature of 80 °C. Upside down mixing was applied. After 30 sec a sweep step was conducted and after 180 sec the compounds were dumped.

Vulcanization of the compounds was completed in a curing press. For regular butyl grades a temperature of 210 °C was applied for 13 min (2 mm test specimen) and 14 min (6 mm), respectively. Regarding Exxpro compounds 190 °C was chosen for 11 min (2 mm) and 12 min (6 mm).

MDR curves as well as Mooney viscosity and Mooney scorch evaluations were conducted on Alpha Technology machines. Tensile properties were measured with an Instron testing unit. Tension Set, Compression Set were evaluated according to existing norms with standard devices. Flex fatigue was determined in a De Mattia Fatigue Check machine from Gibitre Instruments S.r.l.. Evaluations of Flex fatigue at elevated temperatures were carried out in a De Mattia Fatigue Check Plus dynamic tester at Gibitre Instruments S.r.l. (Bergamo, Italy).

Results and Discussion

Bladder model recipe containing regular Butyl Polymer

Castor oil was replaced by 6 phr of Struktol HT 815 and Struktol HT 820, respectively. Also, a mixture of 4 phr castor oil and 2 phr Struktol HT 820 was evaluated, see Table 3.

Table 3: Investigated regular butyl rubber bladder compounds

recipe #6419-5	**25**	**26**	**28**	**29**
Regular Butyl rubber	100	100	100	100
Chloroprene	5	5	5	5
N-330 Carbon Black	50	50	50	50
Zinc oxide	5	5	5	5
Homogeniser	5	5	5	5
castor oil	**6**		**4**	
Struktol HT 820		**6**	**2**	
Struktol HT 815				**6**
Crosslinking resin	8	8	8	8
sum:	179	179	179	179

In terms of flow properties, the Mooney viscosity is not influenced by replacement of the plasticizer grades, see table 4. Furthermore, longer Mooney Scorch values are detected which might indicate a longer crosslinking process.

Regarding the Rheometer properties different delta torque values are detected in dependence of the applied plasticizer. The described drop in state of cure/delta torque is most pronounced for Struktol HT 815 (compound #29) whilst the difference between Struktol HT 820 (#26) and the reference compound which contains castor oil (#25) is negligible. For a mixture of 4 phr castor oil and 2 phr Struktol HT 820 almost no difference in delta torque is observed (#28), see Table 4.

Regarding those compounds containing the new reactive Struktol plasticizer grades, delta torque is decreased because during the curing process they also react with the crosslinking resin, which in turn reduces the total number of effective crosslinks contributing to the elastomer network.

As mentioned, the overall amount of reactive groups is highest for Struktol HT 815 because of the lower molecular weight compared to Struktol HT 820. This is clearly proven by a significant drop in delta torque compared to Struktol HT 820.

Table 4: Rheometer properties, Mooney Viscosity

recipe #6419-5		25	26	28	29
torque ML	[dNm]	1,88	2,04	1,92	2,04
torque MH	[dNm]	7,92	7,6	7,87	6,72
delta torque	[dNm]	6,04	5,56	5,95	4,68
Tc10	[min]	0,81	0,75	0,77	0,7
Tc50	[min]	11,62	12,46	11,92	11,87
Tc90	[min]	15,19	17,96	16,49	17,22
Mooney Scorch					
Ts5 @150°C	[min]	17,9	23,5	21,3	24,3
Mooney Viscosity					
ML(1+4) @100°C	[MU]	72	73	72	75

To expand the idea of a dependence of delta torque on the applied plasticizer grade, an effect on the physical properties might be expected, see table 5.

Table 5: Physical properties

recipe #6419-5		25	26	28	29
Shore Hardness A	[Sh A]	57	56	55	54
Tensile Strength	[MPa]	12,3	12,6	13,7	12,1
Elongation at Break	[%]	769	746	790	787
Modulus 100%	[MPa]	1,5	1,3	1,3	1,2
Modulus 300%	[MPa]	3,6	3,6	3,8	3,1
Modulus 500%	[MPa]	6,9	7,4	7,5	6,6
Tear Resistance					
Trouser	[kN/m]	17,7	16,7	17	16,7
Compression Set					
24h @100°C, 25%	[%]	27	26,4	23,9	31,1
Tension Set					
24h @100°C, 300%	[%]	17,3	17,9	14,8	20,6

Depending on the delta torque as referenced in Table 4, physical properties are affected. In particular, an impact on Modulus at low strain as well as Compression Set and Tension Set is observed whilst there is no big difference detectable in Tensile Strength, Elongation at Break and Tear Resistance.

However, a drop in Modulus strongly suggests a positive impact on flex fatigue performance, see Figure 1. Interestingly, the mixture compound #28 reveals best of class values for Compression Set/Tension Set.

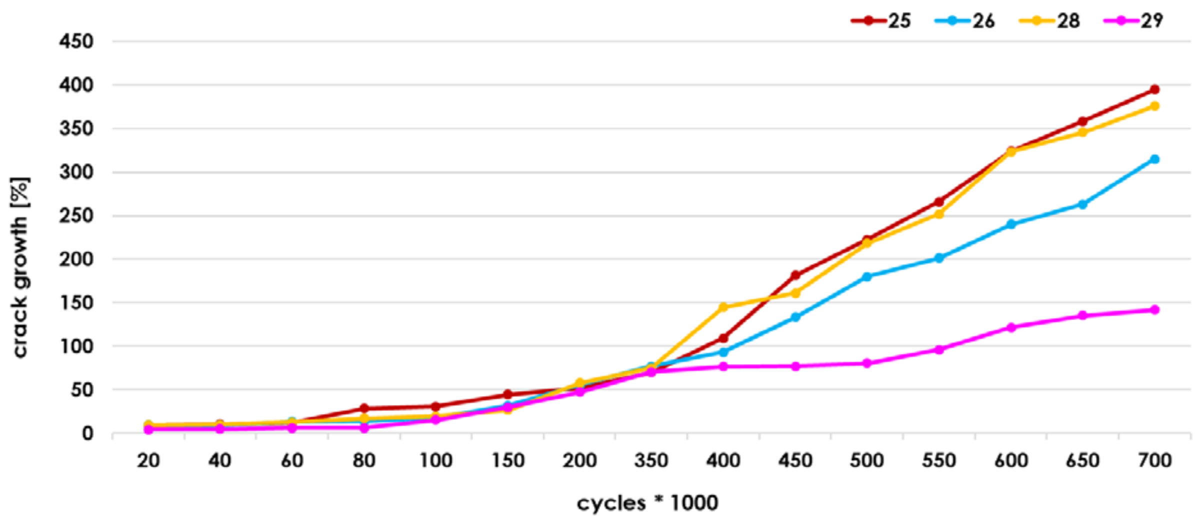


Figure 1: De Mattia flex fatigue test

A De Mattia experiment was conducted up to 700.000 flexing cycles. This test method is a well-recognized tool to judge the performance of bladder compounds because in a tire production this material is subjected to repeated flexing cycles. The crack growth percentage is plotted against the number of flexing cycles. The lower the crack growth value, the better bladder flex performance might be expected. Here, those compounds containing reactive plasticizer as full replacement (#26, #29) are superior to the reference (#25) which contains 6 phr castor oil. Regarding the mixture with 2 phr Struktol HT 820 (#28) a similar curve like castor oil is depicted.

Because tire curing bladders are operated at high temperatures in a steam atmosphere, also properties after steam ageing were investigated, see Figure 2.

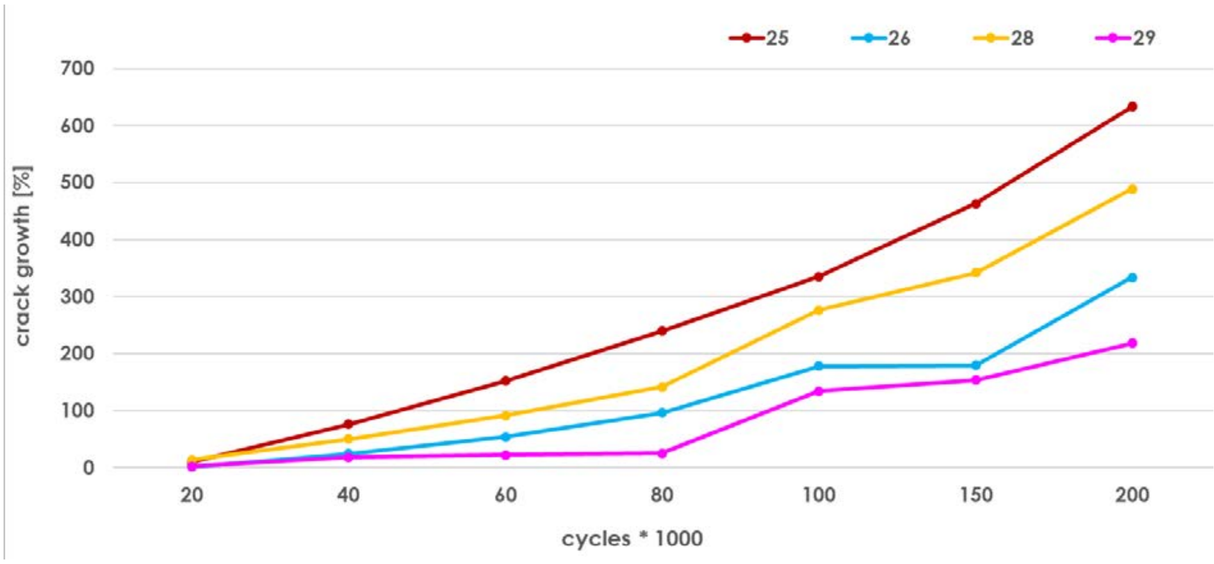


Figure 2: De Mattia flex fatigue test after steam ageing (48 h @190 °C)

After steam ageing, the flex fatigue performance benefits are even more pronounced. Those compounds containing the reactive plasticizer clearly outperform the reference compound (#25). Regarding the mixture compound #28 which contains 2 phr reactive plasticizer, in contrast to the results observed without ageing treatment a lower crack growth percentage is found. Again, this clearly indicates benefits, detected already at low concentrations of Struktol HT 820.

An increased performance also is reported for the physical properties after steam ageing, see Table 6.

Table 6: Physical properties after steam ageing (48 h @190°C)

recipe #6419-5		**25**	**26**	**28**	**29**
Shore Hardness A	[Sh A]	74	65	66	63
change	[Sh A]	17	9	11	9
Tensile Strength	[MPa]	12,8	13,8	14,2	13,3
change	[%]	4,1	9,5	3,6	9,9
Elongation at Break	[%]	590	640	644	670
change	[%]	-23,3	-14,2	-18,5	-14,9
Modulus 100%	[MPa]	2,3	1,8	2,1	1,6
change	[%]	53,3	38,5	61,5	33,3
Tear Resistance	[kN/m]	16,6	17,9	16,4	19
change	[%]	-6,2	7,2	-3,5	13,8

Steam ageing tests are frequently conducted and well established because the applied parameters are close to the service conditions at which curing bladders are operated in a tire plant. Therefore, the generated results for the reactive plasticizers Struktol HT 815 and Struktol HT 820 are at a premium.

Under steam conditions the beneficial properties of reactive plasticizers in combination with the requirements of an extended service-life are a perfect match.

Due to the crosslinking of Struktol HT 815 and Struktol HT 820 they cannot evaporate out of the test specimen. Looking at the change in Shore Hardness A, the expected hardening effect is strictly limited for compounds #26 and #29. In particular, the reference compound which contains 6 phr of castor oil suffers from a huge increase in Shore Hardness A.

Having the aforementioned in mind, the excellent De Mattia results following steam ageing are due to the reduced evaporation of plasticizers, respectively lower stiffness increase, which is directly reflected in better Flex fatigue resistance.

For further evidence of the benefits of reactive plasticizers in tire curing bladder compounds a Flex fatigue test was carried out in a special De Mattia device consisting of an Environmental chamber in which the sample holding system is mounted. The temperature was adjusted to 160°C during the test.

Again, the well-known model recipe was chosen with a reference (#25) and 2 compounds #26 & #27 containing the reactive plasticizer Struktol HT 815, see Table 7. By means of a higher filler loading the Shore Hardness A was balanced in compound #27 compared to #26. Accordingly, the impact of a higher stiffness in a Flexing experiment was investigated.

Table 7: Compounds investigated in a De Mattia device equipped with an environmental chamber

recipe #6419-7	**25**	**26**	**27**
Regular Butyl rubber	100	100	100
Chloroprene	5	5	5
N-330 Carbon Black	50	50	53
Zinc oxide	5	5	5
Homogeniser	5	5	5
castor oil	**6**		
Struktol HT 815		**6**	**6**
Crosslinking resin	8	8	8
sum:	179	179	182

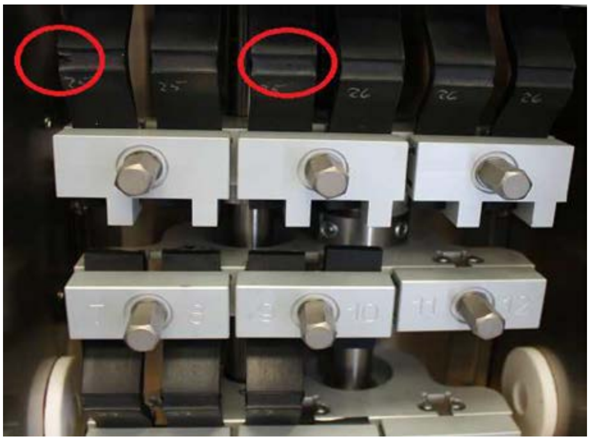
Interestingly, the outcome of the De Mattia experiment in the environmental chamber at 160 °C resulted in the expected benefits of Struktol HT 815 and Struktol HT 820 and strongly underlined the advantages of the reactive Struktol plasticizers over castor oil, see Table 8

Table 8: De Mattia Fatigue Check Plus results at 160 °C (performed by the manufacturer Gibitre Instruments S.r.l., Bergamo/Italy)

Client: SCHILL + SEILACHER "STRUKTOL" GmbH											
START TEST (De Mattia Flexon Check test: @300RPM / 160°C / Run 57mm / Samples 76mm)											
STEP N°	CYCLES INCREMENT	CYCLES SUBTOTAL	(PRODUCT #25)			(PRODUCT #26)			(PRODUCT #27)		
			#1	#2	#3	#4	#5	#6	#7	#8	#9
1	50	50	OK	OK	OK	OK	OK	OK	OK	OK	OK
2	100	150	OK	OK	OK	OK	OK	OK	OK	OK	OK
3	200	350	OK	OK	OK	OK	OK	OK	OK	OK	OK
4	400	750	OK	OK	OK	OK	OK	OK	OK	OK	OK
5	1000	1750	OK	OK	OK	OK	OK	OK	OK	OK	OK
6	2000	3750	OK	OK	OK	OK	OK	OK	OK	OK	OK
7	4000	7750	OK	OK	OK	OK	OK	OK	OK	OK	OK
8	8000	15750	OK	OK	OK	OK	OK	OK	OK	OK	OK
9	16000	31750	OK	OK	OK	OK	OK	OK	OK	OK	OK
10	32000	**63750**	**CRACKED**	OK	**CRACKED**	OK	OK	OK	OK	OK	OK
11	8000	71750	**CRACKED**	OK	**CRACKED**	OK	OK	OK	OK	OK	OK
12	16000	87750	**CRACKED**	OK	**CRACKED**	OK	OK	OK	OK	OK	OK
13	32000	119750	**CRACKED**	OK	**CRACKED**	OK	OK	OK	OK	OK	OK
14	64000	**183750**	**BROKEN**	**CRACKED**	**CRACKED**	OK	OK	OK	OK	OK	OK
15	128000	311750	**BROKEN**	**CRACKED**	**CRACKED**	OK	OK	OK	OK	OK	OK
16	256000	567750	**BROKEN**	**CRACKED**	**CRACKED**	OK	OK	OK	OK	OK	OK
17	512000	1079750	**BROKEN**	**CRACKED**	**CRACKED**	OK	OK	OK	OK	OK	OK
18	1024000	2103750	**BROKEN**	**CRACKED**	**CRACKED**	OK	OK	OK	OK	OK	OK
18.5	CHECK	**3344000**	**BROKEN**	**CRACKED**	**CRACKED**	**BROKEN**	**BROKEN**	**BROKEN**	**BROKEN**	**BROKEN**	**BROKEN**
END OF THE TEST											

The reference compound revealed initial cracks after 64.000 and 184.000 flexing cycles, see Picture 1. Compounds #26 and #27 remained in a stable condition up to approx.

2.100.000 bending cycles. Accordingly, Struktol HT 815 impressively outperformed the widely used plasticizer castor oil.



Picture 1: De Mattia test specimen after approx. 64.000 cycles operated at 160 °C

Bladder model recipe containing Exxpro polymer

Regarding the use of Exxpro polymer in tire curing bladder applications an increased service-life due to the fully saturated polymer backbone is postulated. Exxpro model recipes in general also contain heat reactive crosslinking resin types, see Table 1.

Both, a full replacement with Struktol HT 815 as well as a blend with castor oil (3 phr) was investigated against a reference compound (6 phr castor oil).

Overall, similar benefits as reported with regular butyl rubber were observed. Most important results are summarized in a spider graph, see Figure 3. The higher the percentage, the better.

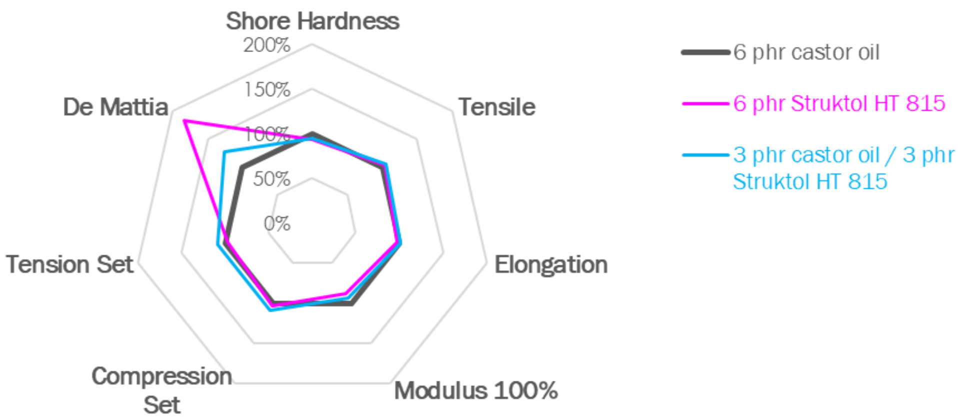


Figure 3: Spider graph depicting the most important properties in an Exxpro model recipe

Regarding the physical properties a slight drop in Shore Hardness A is detected. On the other side, compression set and tension set are equal to the reference compound containing castor oil. The De Mattia experiment revealed a very much improved Flex fatigue performance if Struktol HT 815 is used.

After steam ageing, same trends as previously reported for regular butyl model recipes are observed, see spider graph, Figure 4.

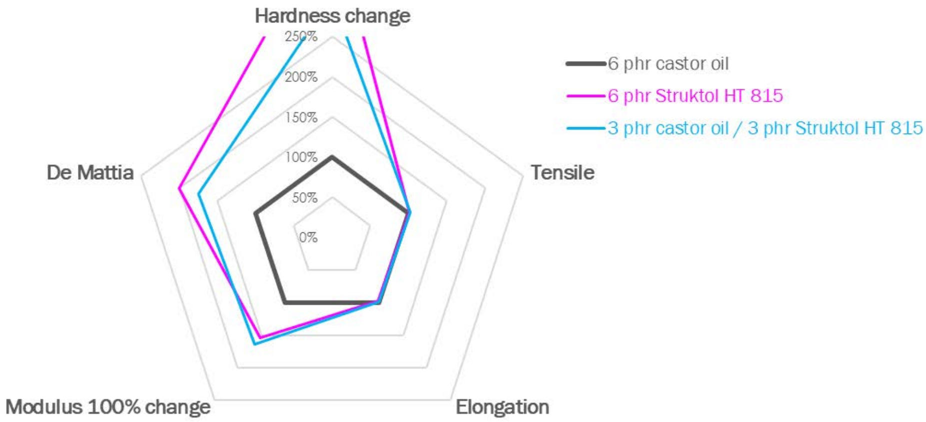


Figure 4: Spider graph depicting the most important properties after steam ageing (48 h at 190 °C) in an Exxpro model recipe

Again, hardness increase as well as modulus increase are less pronounced for Struktol HT 815. No increase in Shore Hardness A was observed for 6 phr Struktol HT 815. Regarding 3 phr castor oil/3 phr Struktol HT 815 an increase of 1 Hardness point was detected. The reference compound (6 phr castor oil) revealed a Hardness increase by 4 Shore A units. Consequently, flex fatigue performance is shifted towards an excellent De Mattia result for those compounds containing Struktol HT 815 (#26, #27), which overall will end in a higher number of curing cycles per curing bladder, directly attributable to an improved control of evaporated plasticizer.

Conclusions

The advantages of the new reactive plasticizers grades Struktol HT 815 and Struktol HT 820 in tire curing bladders are described. Struktol HT 815 and Struktol HT 820 offer a basket of benefits if used as a replacement of the well-known plasticizer castor oil. Due to the reaction with the crosslinking resin during the curing step a connection to the rubber network is established. Therefore, the new reactive plasticizer grades are prevented from evaporating out of the tire curing bladder during service which is a big advantage over low molecular weight, chemically incompatible castor oil.

Under consideration of the applied service conditions (high temperatures, pressure and steam) in a tire plant, Struktol HT 815 and Struktol HT 820 are well suited plasticizer candidates because they benefit from a limited drop in physical properties, in particular Modulus and Hardness after steam ageing. As a consequence further improvements in flexing performance are realized which translate into an extended service-life.