Alternative chlorine-free peroxide for silicone rubber: Benefits with Aktisil Q

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1 Introduction

In solid silicone rubber, chlorine-containing peroxides are mainly used for extrusion articles. With the preferred di-(2,4-dichlorobenzoyl)peroxide - DCBP - vulcanization also works under oxygen supply. Due to its high reactivity, it also leads to rapid crosslinking.

Due to the emission of PCBs (polychlorinated biphenyls), which can only be broken down slowly both in the environment and in living organisms[1], such peroxides should be replaced by chlorine-free alternatives.

Usually these alternative peroxides lead to a slower crosslinking reaction. In addition, it has been reported that the processing of the compounds produced with them is problematic, as increased stickiness occurs both during mixing and during demoulding after vulcanization.

Hoffmann Mineral offers Aktisil Q, a funktional Neuburg Siliceous Earth that has been specially developed for use in silicone rubber.

Aktisil Q facilitates the processing of silicone rubber, since on the one hand it reduces or eliminates tackiness - depending on the dosage - and on the other hand it increases the stability of profiles during extrusion.

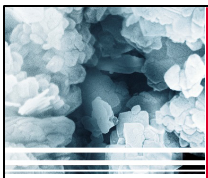
Apart from the markedly improved oil resistance, Aktisil Q scores especially with an excellent compression set.

In this paper the property profiles of DCBP and an alternative chlorine-free peroxide using Aktisil Q are presented.
Besides the rheological and mechanical properties, the processing properties are also examined.

[1] Source: Bayerisches Landesamt für Gesundheit und Lebensmittelsicherheit

2 Experimental

2.1 Formulation, mixing and preparation of specimens



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Formulation

		phr	
Elastosil R 401/40	polymer hardness: 40 Shore A	100	
Aktisil Q	filler Neuburg Siliceous Earth, methacrylic functionalized	0 – 100	
Perkadox PD-50S-ps DCBP	peroxide, chlorinated di-(2,4-dichlorobenzoyl)peroxide	1.5	-
Perkadox PM-50S-ps DMBP	peroxide, chlorine-free di-(4-methylbenzoyl)peroxide	-	1.07

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Fig.1

Elastosil R 401/40 is a polymer with a hardness of 40 Shore A that has already been used for numerous tests at Hoffmann Mineral. Besides a control compound without added filler, four different Aktisil Q loadings are compared: 25, 50, 75 and 100 phr. As mentioned at the beginning, Aktisil Q has been developed for use in silicone rubber. This is a Neuburg Siliceous Earth with a d_{50} of about 4 µm, treated with a methacrylic functional group.

Perkadox PD-50S-ps represents the chlorinated di-(2,4-dichlorobenzoyl)peroxide (DCBP), which is typically used for the production of extrusion articles. The chlorine-free alternative is Perkadox PM-50S-ps - di-(4-methylbenzoyl)peroxide (DMBP), whose dosage is adjusted according to the active oxygen content.

For the sake of simplicity, the two peroxides are named with the abbreviations presented below.

The compounds were produced on a laboratory rolling mill at a roll temperature of 20 °C in about 10 minutes. First, the polymer was rolled into a uniform sheet. Then - if contained - Aktisil Q was added and completely incorporated. With a spatula, the respective peroxide was applied to the compound and also incorporated.

To ensure identical production, all compounds were removed from the roll with a scraper, pupated, and then placed back on the roll in a reversed position. This process was repeated 10 times.

Figure 2 shows the experimental design.
At Hoffmann Mineral, all DCBP-containing vulcanizates have been prepared at 115 °C in recent years. This temperature was therefore also used in this test series. The DMBP was also tested at a temperature of 115 °C for direct comparison. In addition, the curing temperature for this peroxide was increased by 20 °C to 135 °C to compensate for the slower curing.

The curing time of 5 minutes was the same for all vulcanizates and, as is usual for silicone rubber, was post-cured for 4 hours at 200 °C. All the mechanical properties described below were therefore determined on post-cured test specimens.

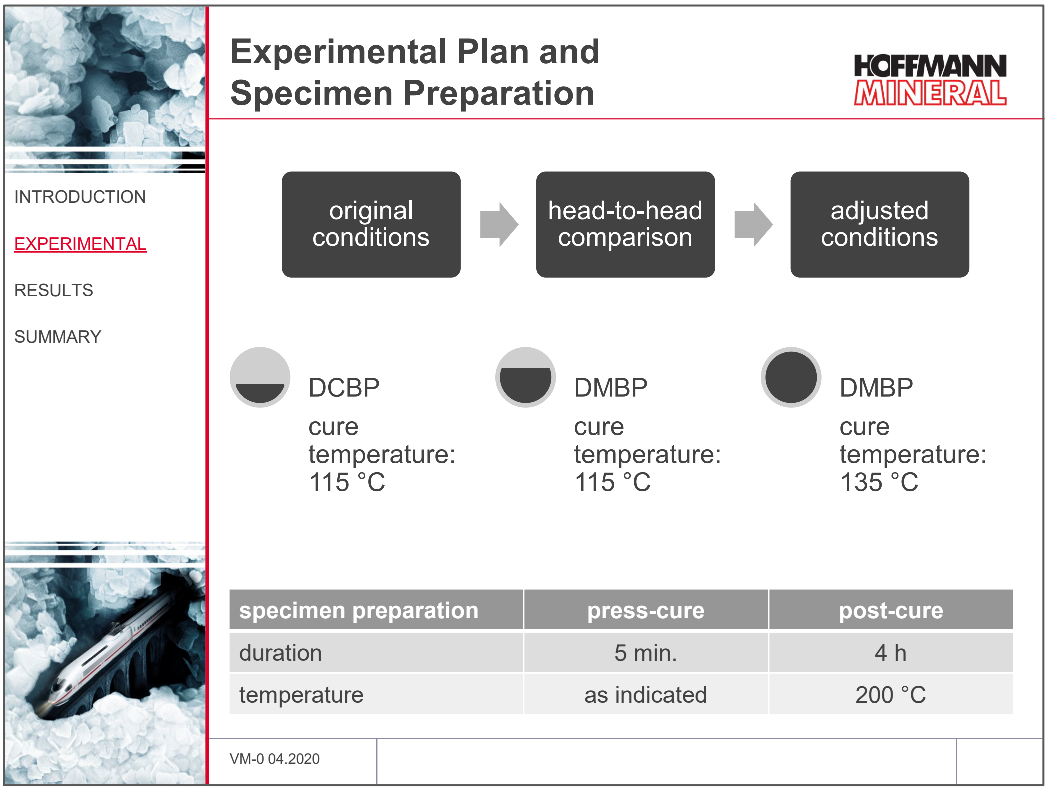


Fig. 2

2.2 Tests

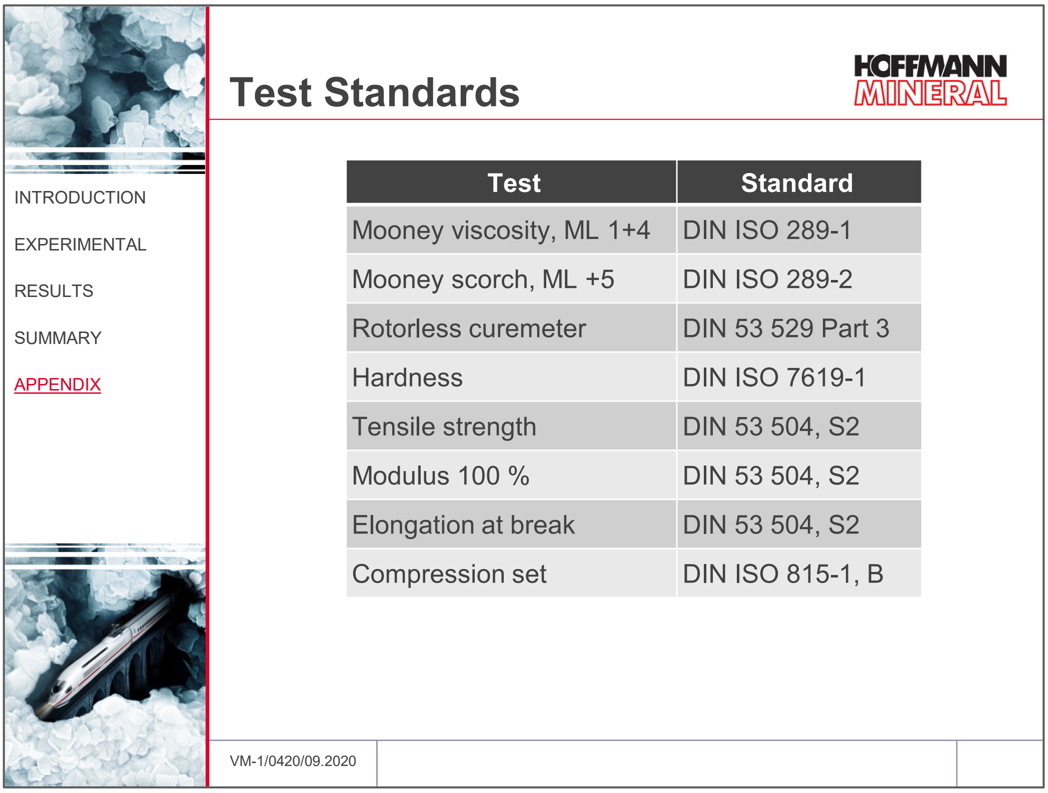


Fig. 3

The values shown in the following diagrams and at the end in the result tables refer to tests carried out in accordance with the standards listed in Fig. 3.

3 Results

3.1 Processing

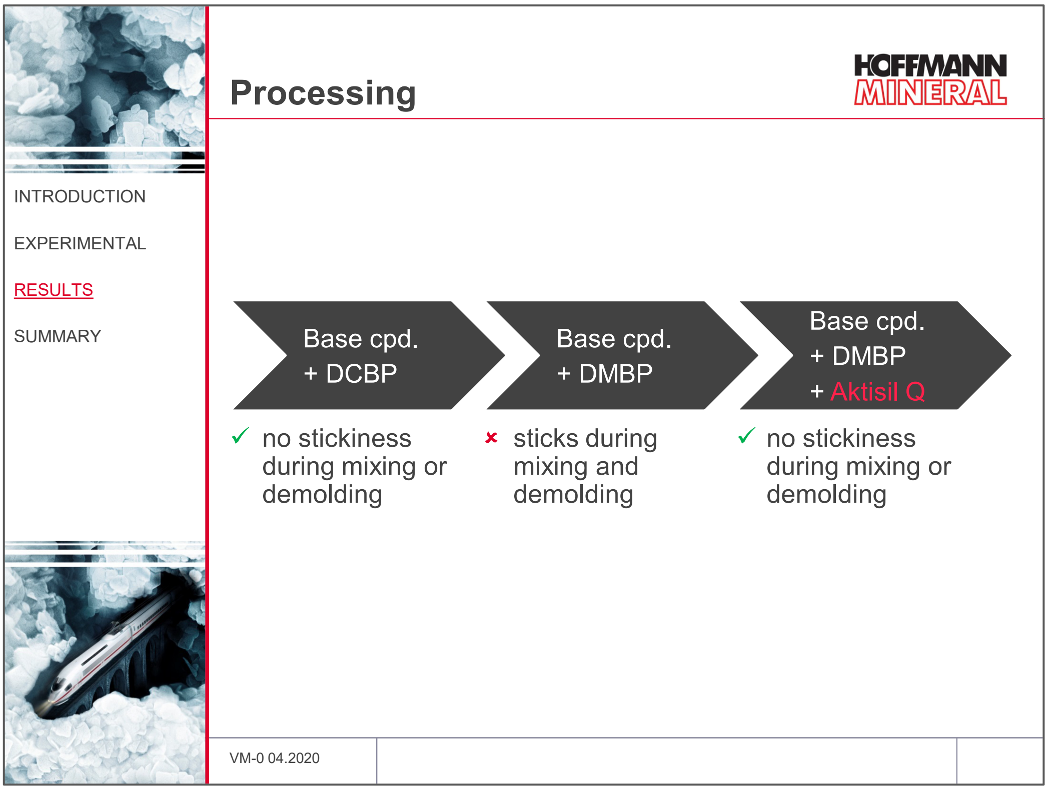


Fig. 4

If DCBP is added to the polymer, the compound does not stick either during mixing or when demolding after vulcanization. However, if DMBP is used instead of DCBP, it can be observed that the mixture tends to stick during mixing and demolding. Already 25 phr Aktisil Q can overcome this problem and prevent stickiness during mixing as well as during the curing process.

3.2 Rheological properties

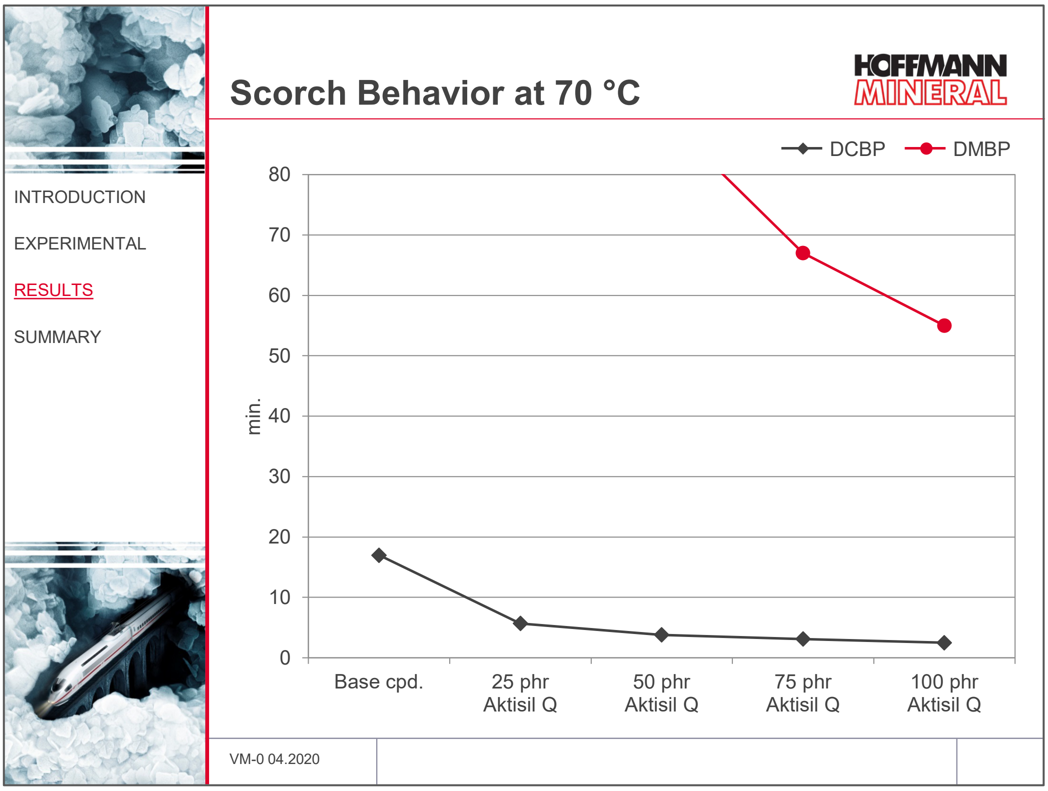


Fig. 5

The replacement of DCBP by DMBP leads to a significantly improved scorch safety, as Fig. 5 shows.

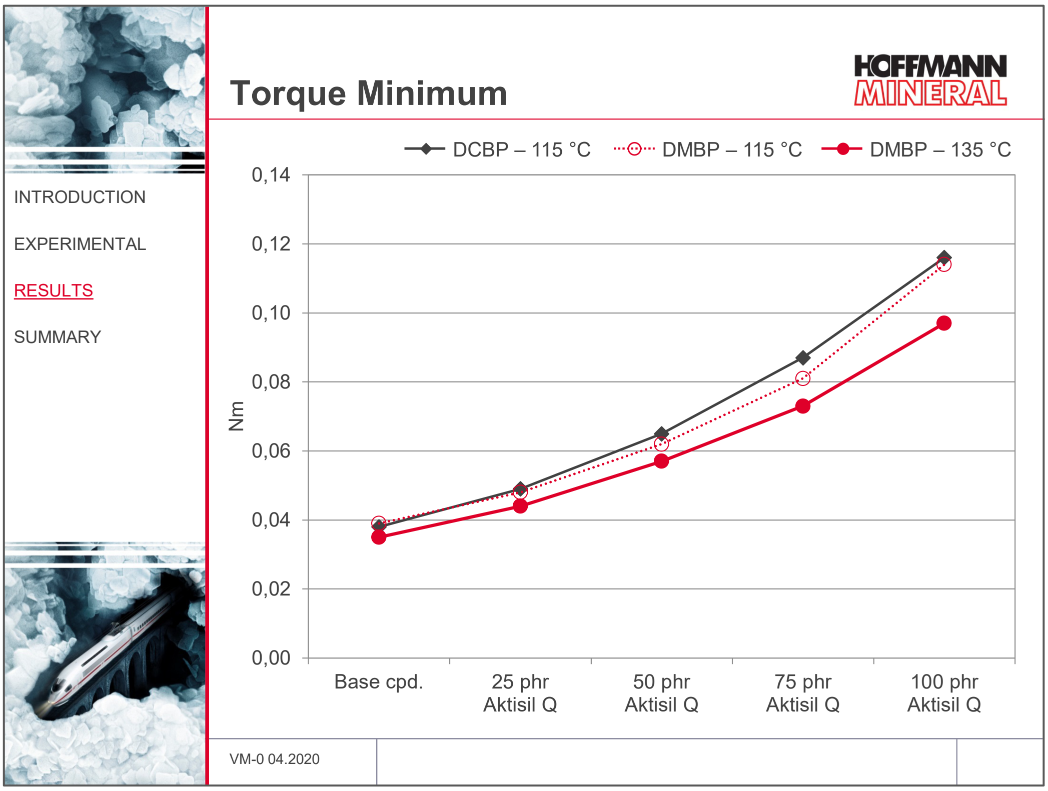


Fig. 6

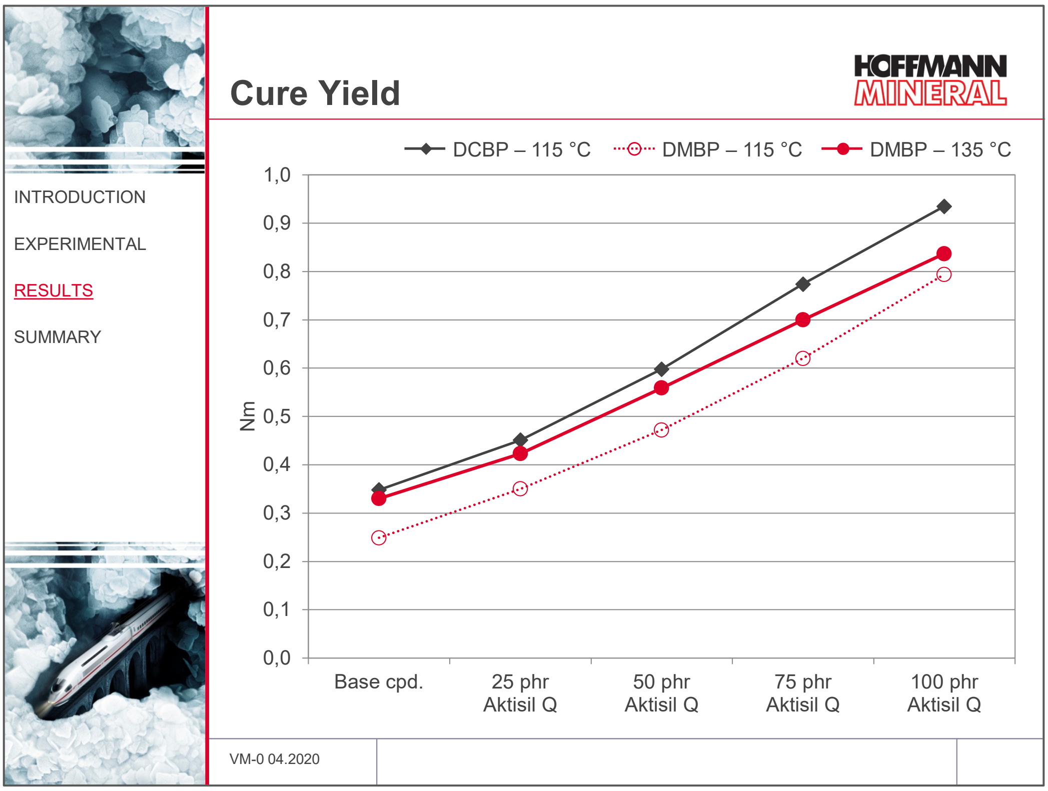


Fig.7

Due to the higher temperature, the viscosity with DMBP drops slightly compared to DCBP, as can be seen from the values of the torque minimum in Fig. 6. Fig. 7 shows the cure yield which is higher with both peroxides when the Aktisil Q content is increased. The somewhat lower yields of the higher filler loading with DMBP at 135 °C compared with DCBP, however, do not result in any disadvantages in the mechanical properties, as the further results will show.

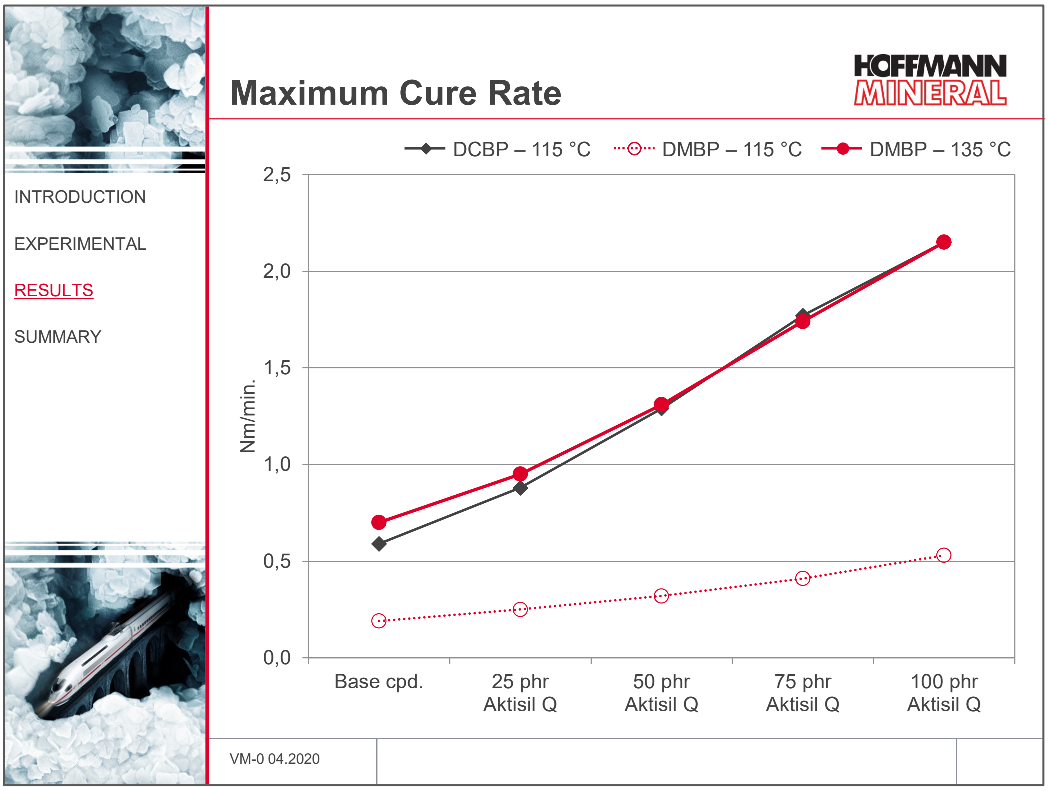


Fig. 8

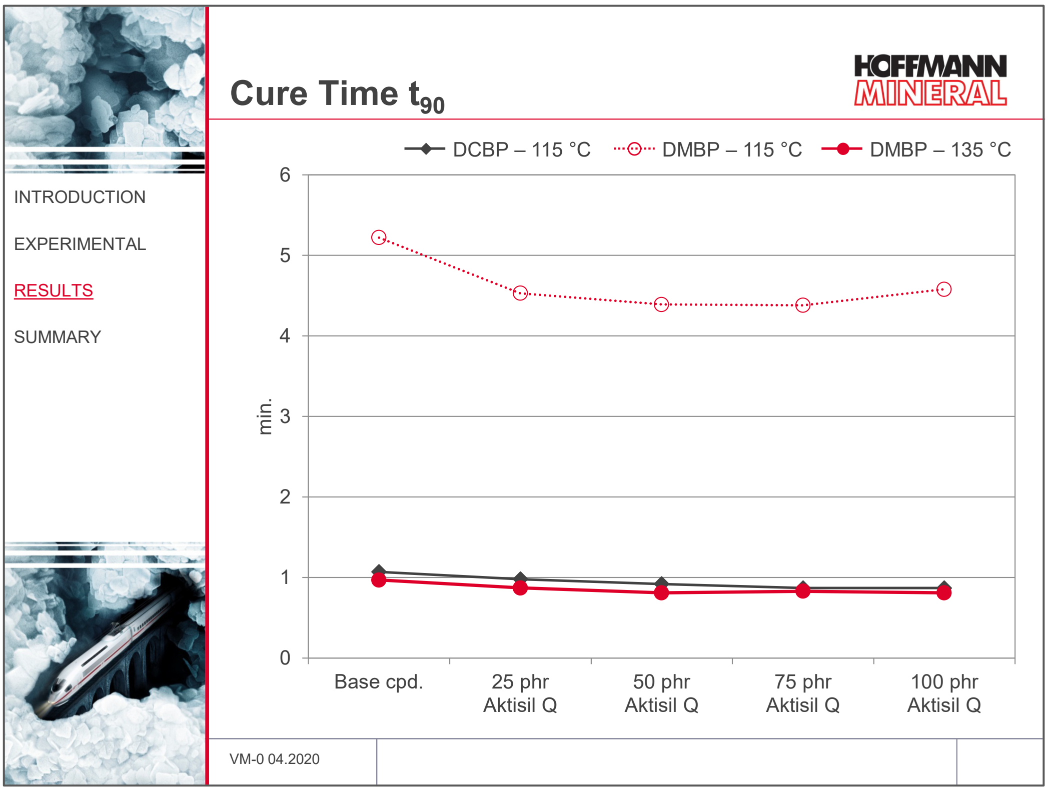


Fig. 9

As expected, the replacement of DCBP by DMBP without temperature adjustment leads to a significantly slower curing (Fig. 8). Although 100 phr Aktisil Q and DMBP at 115 °C can achieve a cure rate comparable to the "unfilled" base compound and DCBP, a further acceleration of the crosslinking reaction is not possible under these conditions. However, by raising the temperature to 135 °C, the maximum cure rate with DMBP can then easily be matched to that of DCBP.

Correspondingly, practically identical conversion times t_{90} are then obtained (Fig. 9).

3.3 Mechanical properties

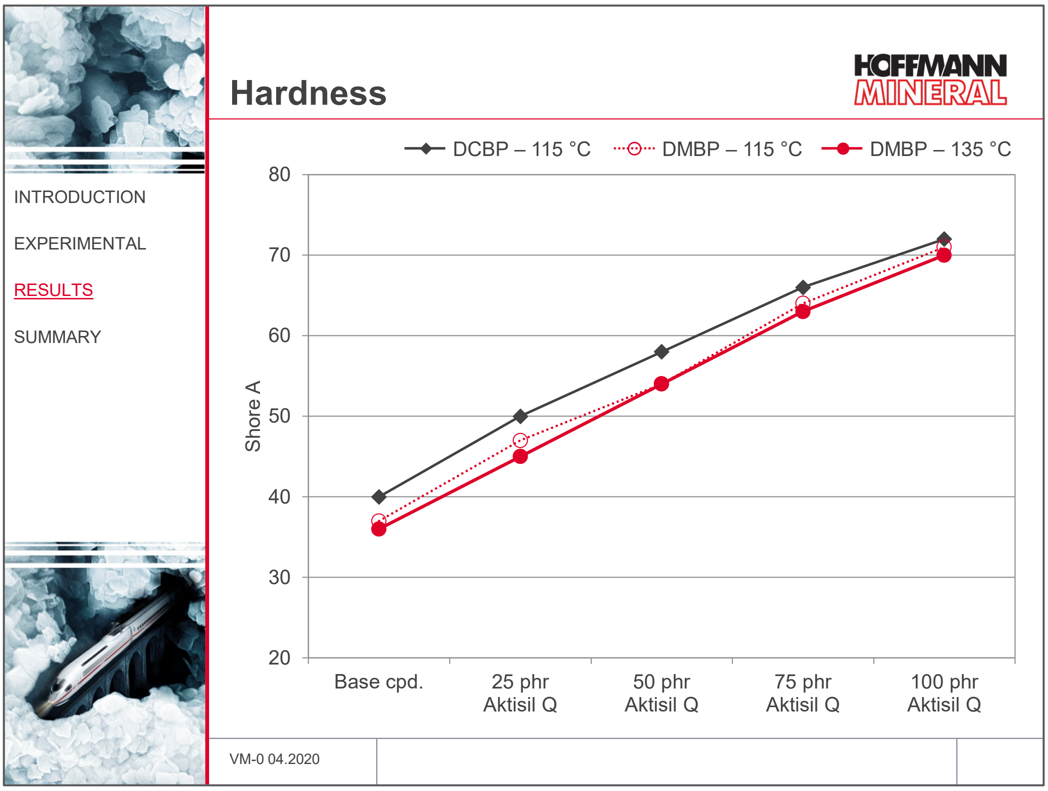


Fig. 10

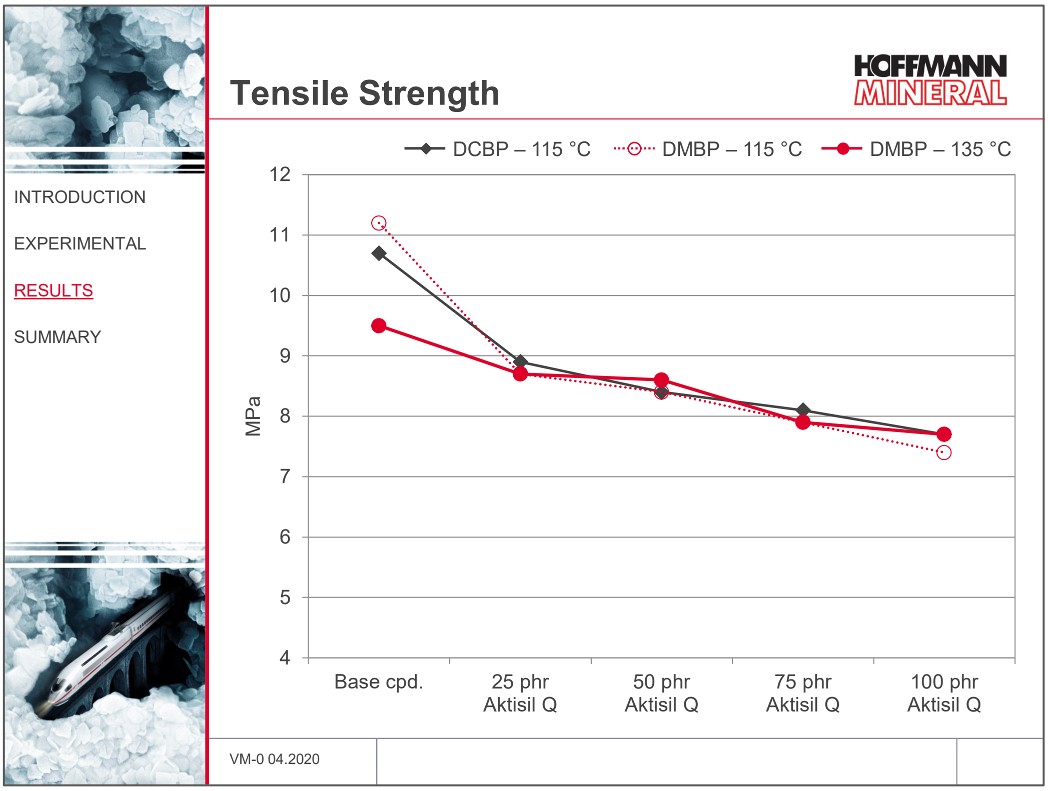


Fig. 11

The replacement of DCBP by DMBP has a slightly reducing effect on hardness (Fig. 10). With the higher Aktisil Q loadings, however, the level is then noticeably leveled out again. The tensile strength also decreases due to the peroxide exchange and the temperature increase in vulcanization (Fig. 11). However, this can only be observed with the "unfilled" base polymer. If the vulcanizates contain Aktisil Q, the peroxide exchange no longer has any effect.

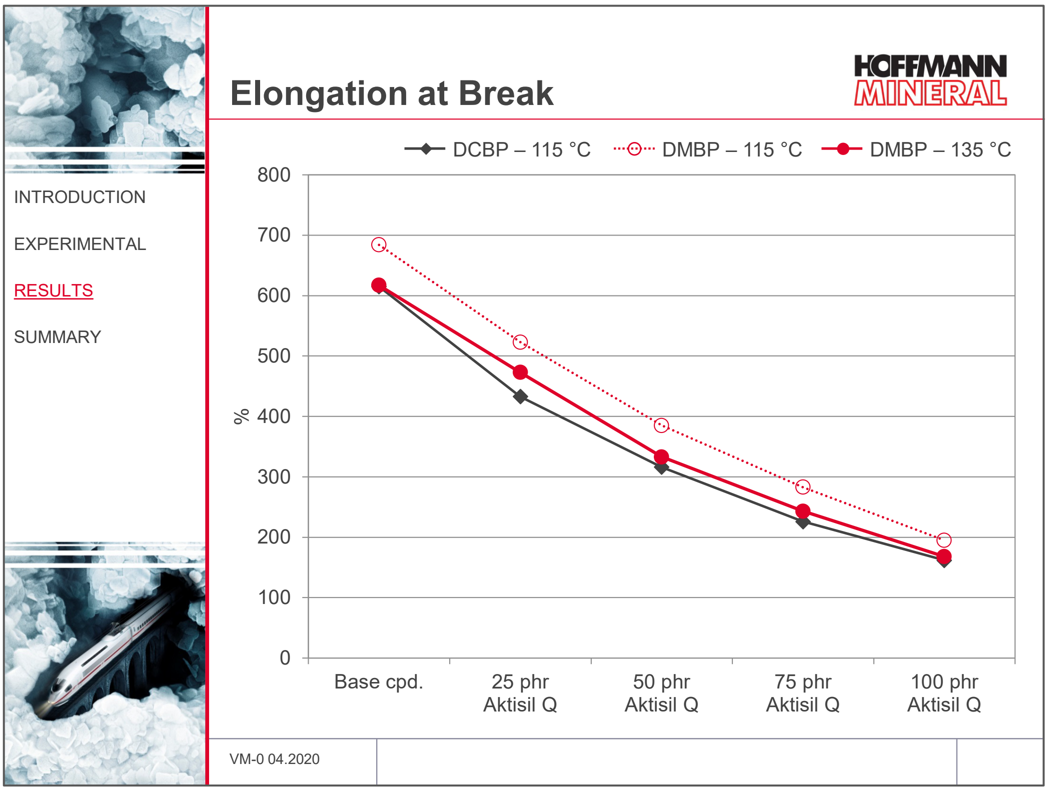


Fig. 12

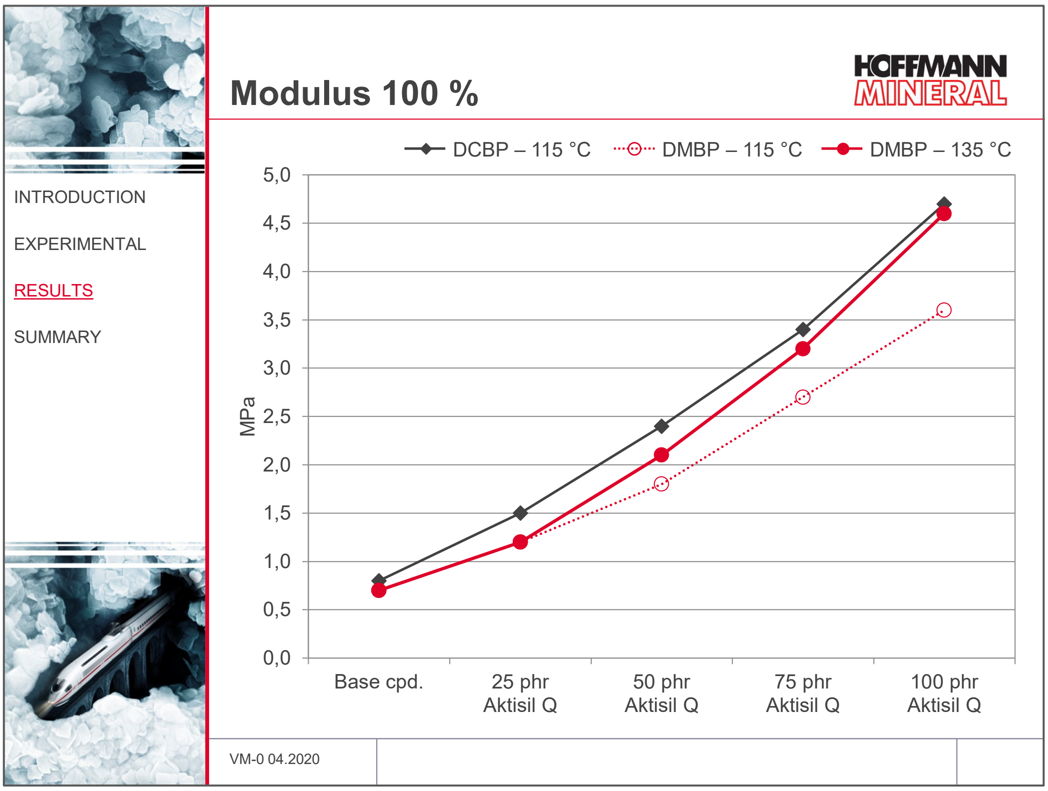


Fig. 13

In a direct comparison of the two peroxides, the DMBP at 115 °C gives slightly higher elongation at break values compared to DCBP, and reduced modulus values, especially in the higher filler loadings (Fig. 12 + Fig. 13). With the adjusted curing temperature, there are practically no differences between the two peroxides.

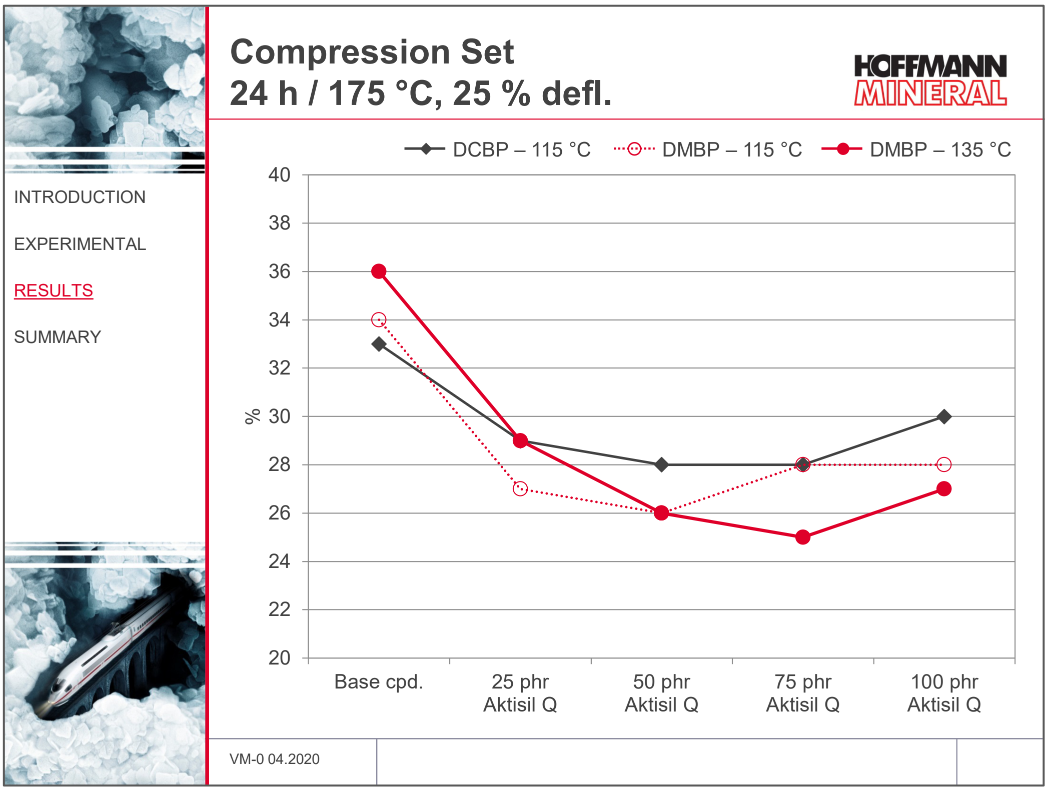


Fig. 14

The replacement of DCBP by DMBP and the simultaneous increase of the curing temperature have a positive effect on the compression set when Aktisil Q is included, as shown in Fig. 14. Already at a level of 50 phr, Aktisil Q can reduce the good level of compression set in this constellation even further.

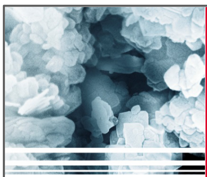
This finally shows that the slightly reduced cure yield with the higher Aktisil Q contents (see Fig. 7) has no negative impact on the mechanical properties - especially the compression set.

4 Summary

Replacement of the chlorinated DCBP by the chlorine-free alternative DMBP using Aktisil Q and simultaneous increase of the curing temperature:

- makes processing easier by eliminating stickiness
- increases the scorch safety
- leads to a comparably fast cross-linking
- gives comparable tensile properties
- slightly improves the compression set

These results thus show that with Aktisil Q a chlorine-free peroxide can be used while eliminating its limitations, and the advantages of the chlorine-containing peroxide are retained.



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DCBP (Perkadox PD-50S-ps), 115 °C

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		Base cpd.	25 phr Aktisil Q	50 phr Aktisil Q	75 phr Aktisil Q	100 phr Aktisil Q
Rheology						
Mooney viscosity, ML 1+2, 70 °C	MU	16	19	24	33	58
Mooney scorch, ML +5, 70 °C	min.	17	5.7	3.8	3.1	2.5
Rotorless curemeter M_{min}, 115 °C	Nm	0.04	0.05	0.07	0.09	0.12
Rotorless curemeter M_{max}-M_{min}, 115 °C	Nm	0.35	0.45	0.60	0.77	0.94
Rotorless curemeter V_{max}, 115 °C	Nm/min.	0.59	0.88	1.29	1.77	2.15
Rotorless curemeter t_{90}, 115 °C	min.	1.07	0.98	0.92	0.87	0.87
Mechanical properties – press-cure 5 min. / 115 °C; post-cure 4 h / 200 °C						
Hardness	Sh. A	40	50	58	66	72
Tensile strength	MPa	11	8.9	8.4	8.1	7.7
Modulus 100 %	MPa	0.8	1.5	2.4	3.4	4.7
Elongation at break	%	615	433	316	226	162
Tear resistance Trouser tear	N/mm	5.7	1.9	2.5	1.8	1.5
Tear resistance Graves	N/mm	22	9.3	7	6.4	6.1
Compression Set, 24 h / 175 °C, 25 % defl.	%	33	29	28	28	30

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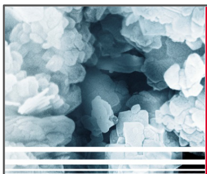

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DMBP (Perkadox PM-50S-ps), 115 °C

HOFFMANN MINERAL

		Base cpd.	25 phr Aktisil Q	50 phr Aktisil Q	75 phr Aktisil Q	100 phr Aktisil Q
Rheology						
Mooney viscosity, ML 1+2, 70 °C	MU	16	19	23	27	36
Mooney scorch, ML +5, 70 °C	min.	> 90	> 90	> 90	67	55
Rotorless curemeter M_{min}, 115 °C	Nm	0.04	0.05	0.06	0.08	0.11
Rotorless curemeter M_{max}-M_{min}, 115 °C	Nm	0.25	0.35	0.47	0.62	0.80
Rotorless curemeter V_{max}, 115 °C	Nm/min.	0.19	0.25	0.32	0.41	0.53
Rotorless curemeter t_{90}, 115 °C	min.	5.2	4.5	4.4	4.4	4.6
Mechanical properties – press-cure 5 min. / 115 °C; post-cure 4 h / 200 °C						
Hardness	Sh. A	37	47	54	64	71
Tensile strength	MPa	11	8.7	8.4	7.9	7.4
Modulus 100 %	MPa	0.7	1.2	1.8	2.7	3.6
Elongation at break	%	684	523	385	283	195
Tear resistance Trouser tear	N/mm	7.0	7.3	3.6	2.3	1.8
Tear resistance Graves	N/mm	38	9.3	8.4	7.2	6.5
Compression Set, 24 h / 175 °C, 25 % defl.	%	34	27	26	28	28

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Table of Results
DMBP (Perkadox PM-50S-ps), 135 °C

HOFFMANN MINERAL

		Base cpd.	25 phr Aktisil Q	50 phr Aktisil Q	75 phr Aktisil Q	100 phr Aktisil Q
Rheology						
Rotorless curemeter M_{min}, 135 °C	Nm	0.04	0.04	0.06	0.07	0.10
Rotorless curemeter M_{max}-M_{min}, 135 °C	Nm	0.33	0.42	0.56	0.70	0.84
Rotorless curemeter V_{max}, 135 °C	Nm/min.	0.70	0.95	1.31	1.74	2.15
Rotorless curemeter t_{90}, 135 °C	min.	0.97	0.87	0.81	0.83	0.81
Mechanical properties – press-cure 5 min. / 135 °C; post-cure 4 h / 200 °C						
Hardness	Sh. A	36	45	54	63	70
Tensile strength	MPa	9.5	8.7	8.6	7.9	7.7
Modulus 100 %	MPa	0.7	1.2	2.1	3.2	4.6
Elongation at break	%	617	473	333	243	168
Tear resistance Trouser tear	N/mm	7.0	4.9	5.1	2.3	1.7
Tear resistance Graves	N/mm	35	10	8.1	7.1	6.4
Compression Set, 24 h / 175 °C, 25 % defl.	%	36	29	26	25	27

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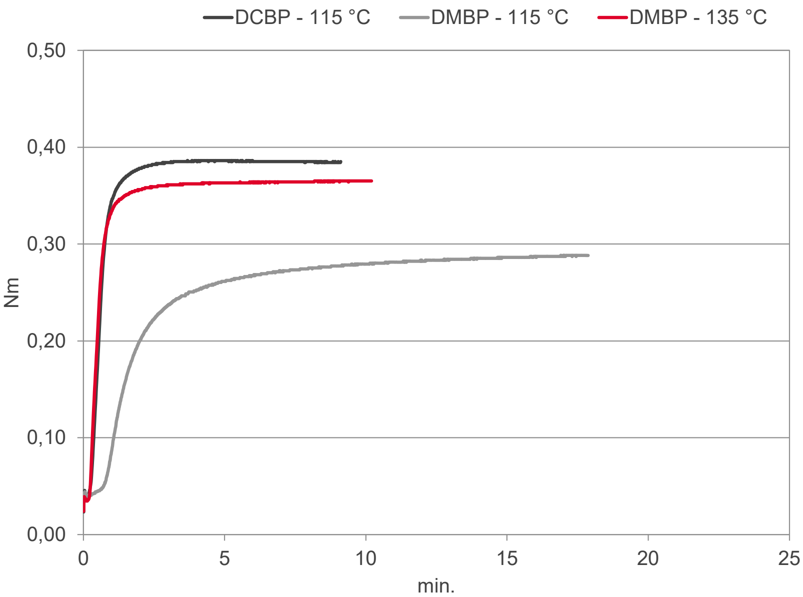
Cure Properties
Base compound

HOFFMANN MINERAL



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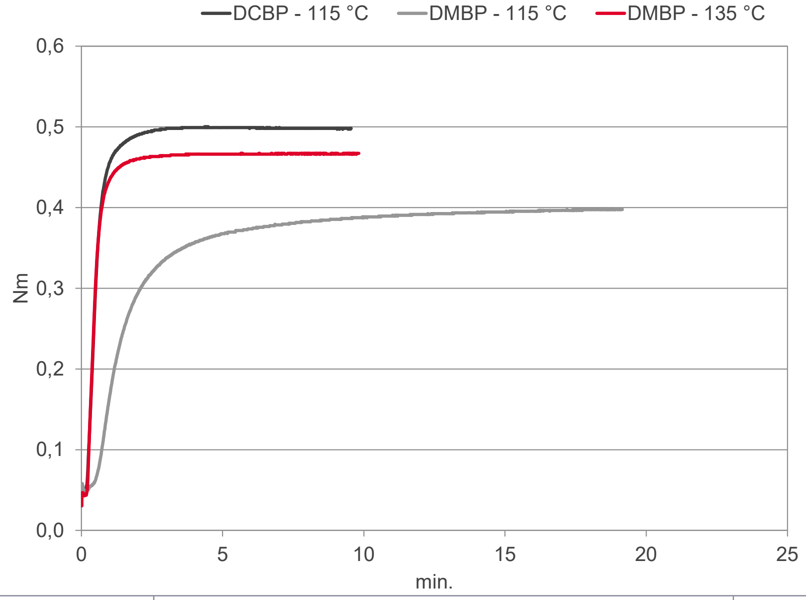
Cure Properties
25 phr Aktisil Q



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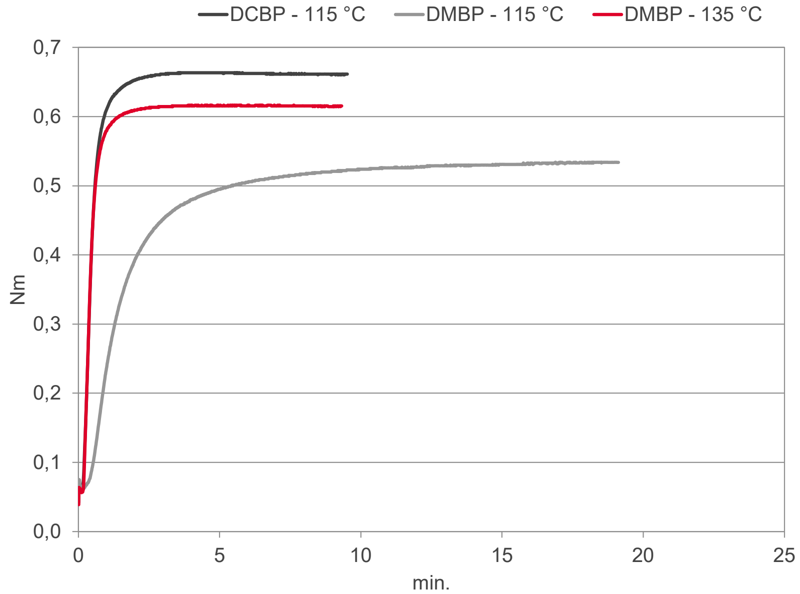
Cure Properties
50 phr Aktisil Q



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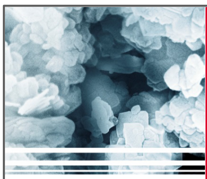

Cure Properties
75 phr Aktisil Q

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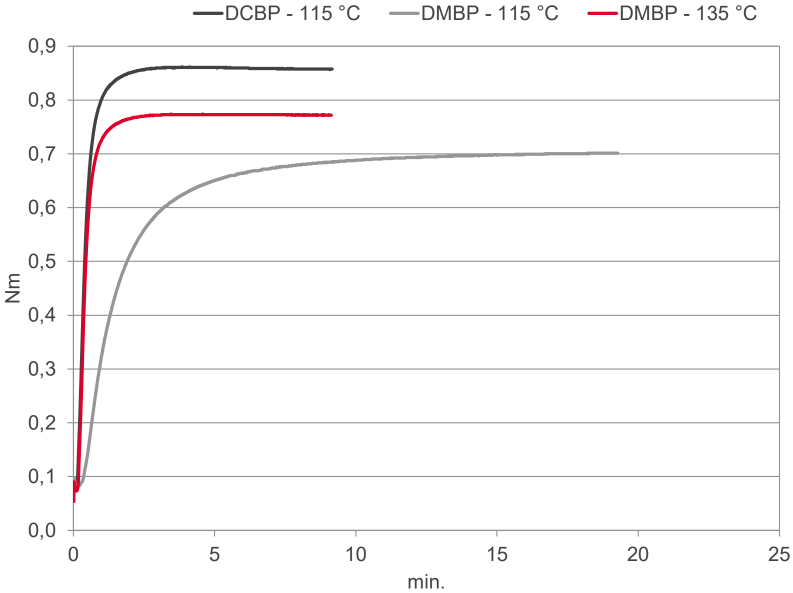

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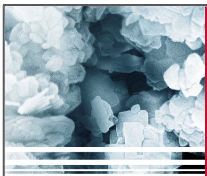

Cure Properties
100 phr Aktisil Q

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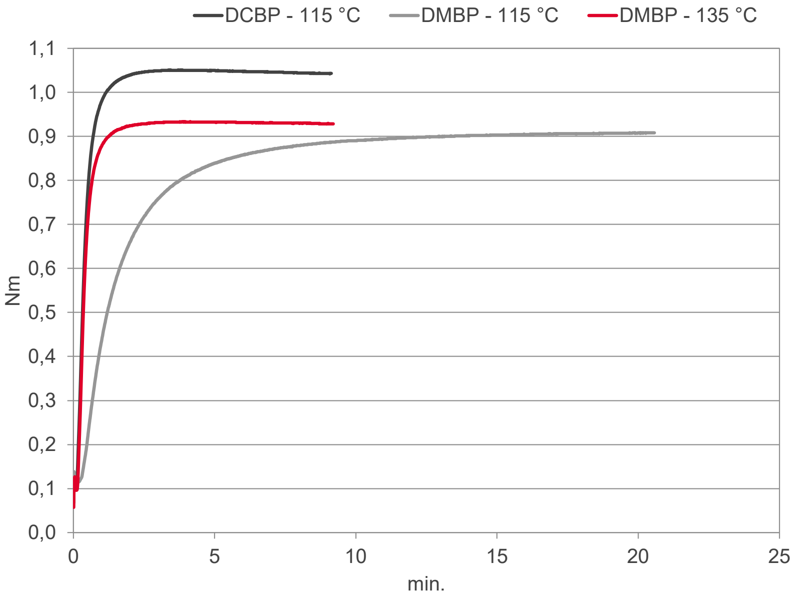

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