HOFFMANN MINERAL
Unternehmensgruppe Hoffmann

Effects of fillers on the thermal conductivity of elastomers

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Summary

Sillitin Z 86 results in high heat conductivity with minimal anisotropy.

While higher values can be achieved with talc and soft clay, this is at the price of a considerable increase in anisotropy. All other fillers tested did not achieve the same levels as Sillitin.

Any comparison must also examine the mechanical properties, as the requirements placed on elastomers overall must take several factors into account in practice. Without going into detail, section 4 below shows that using Sillitin Z 86 produces good basic values. This is characterized by a combination of moderate tensile strength, high tear resistance, moderate compression sets and excellent surface features on extrusion.

C O N T E N T

1 Introduction

Like sound, heat conductivity can be seen as the expansion of heat waves in the direction of the temperature gradient, where heat is transferred from molecule to molecule[1].

Heat conductivity is an important aspect for elastomers as it influences vulcanization behavior. Low heat conductivity means a long heat-up period. This can sometimes result in extreme over-vulcanization of the surface of the vulcanizate. At the same time the inside of the material may be under-vulcanized. In other words, heat conductivity has a direct effect on productivity and quality.

Fillers are an important factor in this equation, as they possess relatively high conductivity, as well as accounting for a relatively high percentage in filled rubber compounds.

Unfortunately, fillers are always comprised of a fine powder making it difficult to determine heat conductivity directly. In addition to this, the dispersion effect must also be taken into account. This means that measurement can only be achieved using the compound as a whole.

[1] Definition from: Schnetger, Jochen: Lexikon der Kautschuktechnik, 2nd revised and expanded edition, Heidelberg 1991, p. 740

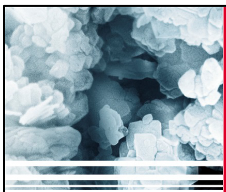
2 Study Plan

2.1 Objective of the Study

The objective of the study is to show what effect fillers have on the heat conductivity of a rubber compound. This was achieved by testing typical fillers used in the rubber industry. The filler dosage was selected to give a comparable Shore A hardness of between 50 to 60 in the vulcanizate.

In addition, two low dosages using Sillitin were selected giving the same volume amount of fillers as precipitated silica or carbon black compound, thereby enabling direct comparison.

2.2 Tested Fillers and Dosage



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Tested Fillers and Dosage

Filler	Density g/cm³	Particle size distribution µm		Particle shape model*	Surface BET m²/g	DBP-absorption ml/100 g
		d_{50}	d_{97}			
Sillitin Z 86	2.6	1.8	6,7	kk/ll	11	-
American Talkum	2.7	2.2	10	ll	11	-
English soft clay	2.6	3.7	20	ll	7	-
Precipitated silica	2.0	-	-	kk	170	-
Carbon black N-550	1.8	-	-	kk	44	121
Engl. calcined clay	2.6	2.0	15.4	kk	7	-
Whiting	2.7	2.2	8.0	kk	5	-

*: c = corpuscular; l = lamellar

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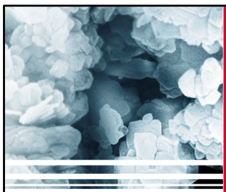

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Tested Fillers and Dosage

Filler	Dosage phr	Dosage Vol.-%
Without filler	-	-
Sillitin Z 86	65.5	12.5
Sillitin Z 86	145.5	23.9
Sillitin Z 86	200.0	30.0
American talc	200.0	28.8
English soft clay	200.0	30.0
Precipitated silica	50.0	12.3
Carbon black N-550	100.0	24.0
Engl. Calcined clay	200.0	30.0
Whiting	200.0	29.2

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2.3 Base Formulation

The main criterion used when making up the base recipe was to ensure the highest possible amount of filler at which a defect-free specimen could be produced. The polymer must also show no signs of crystallization, as this could affect the heat conductivity.

		phr
Keltan 512 x 50 (current name: Keltan 4465)	EPDM, oil content 50 phr, ML 1+4 48 ME at 125 °C, 56 % ethylene content	150
Stearic acid	Stearic acid	1
Zinkoxyd activ	Zinkoxide	5
Filler		var.
TAC 50 gr	Triallylcyanurat, 50 %	2
Perkadox 14/40	Bis(tert-butylperoxyisopopyl)benzene, 40 %	8
		166

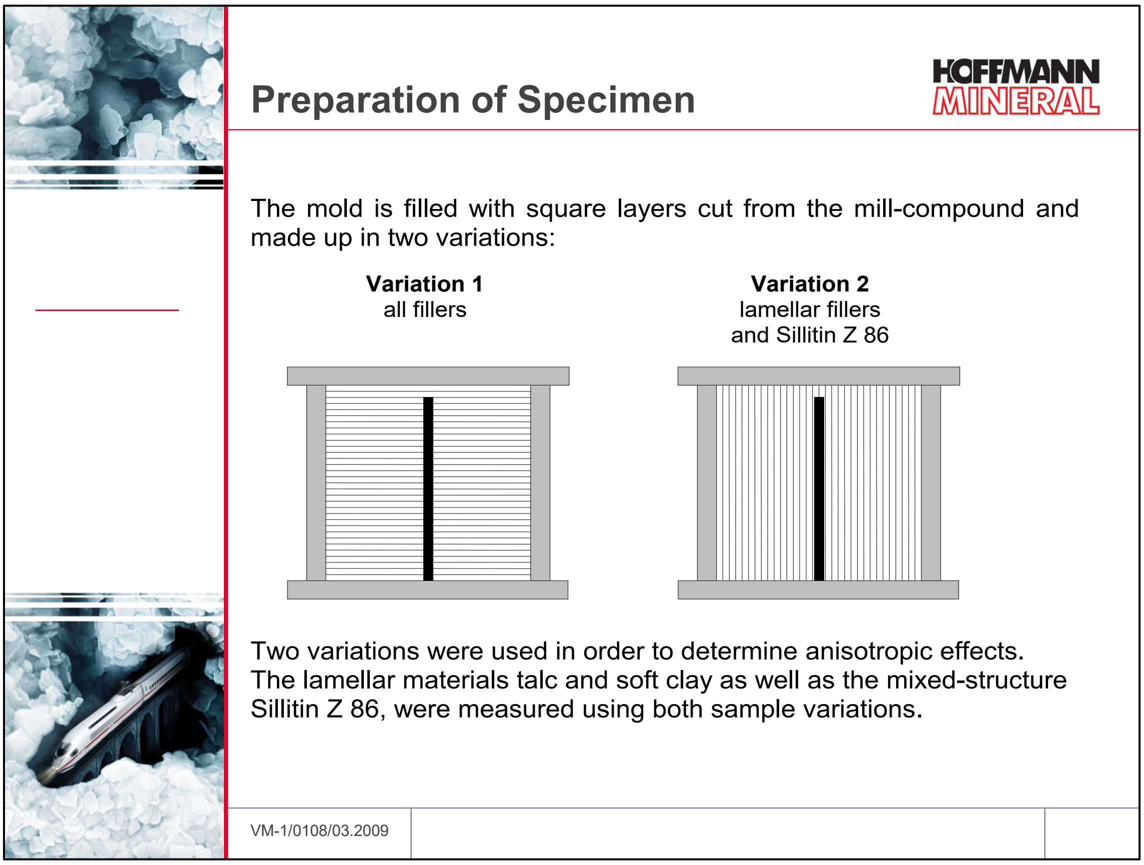
2.4 Preparation of Specimen

Preparation of the Compound

The compound was made up using a laboratory roller (Schwabenthan Polymax 150 L). The rubber was applied to the roller at 50 °C, followed by mixing in all the remaining ingredients in the order shown in the recipe while keeping temperature constant. The roller gap was adjusted as the mixing volume increased. Before the compound layer was removed, the gap was set so that no bulges occurred. The layer was then removed from the roller.

Specimen

The specimen is cube-shaped with an edge of 55 mm. A borehole 49 mm deep, with a diameter of 2.9 mm, was drilled centrally on one surface.



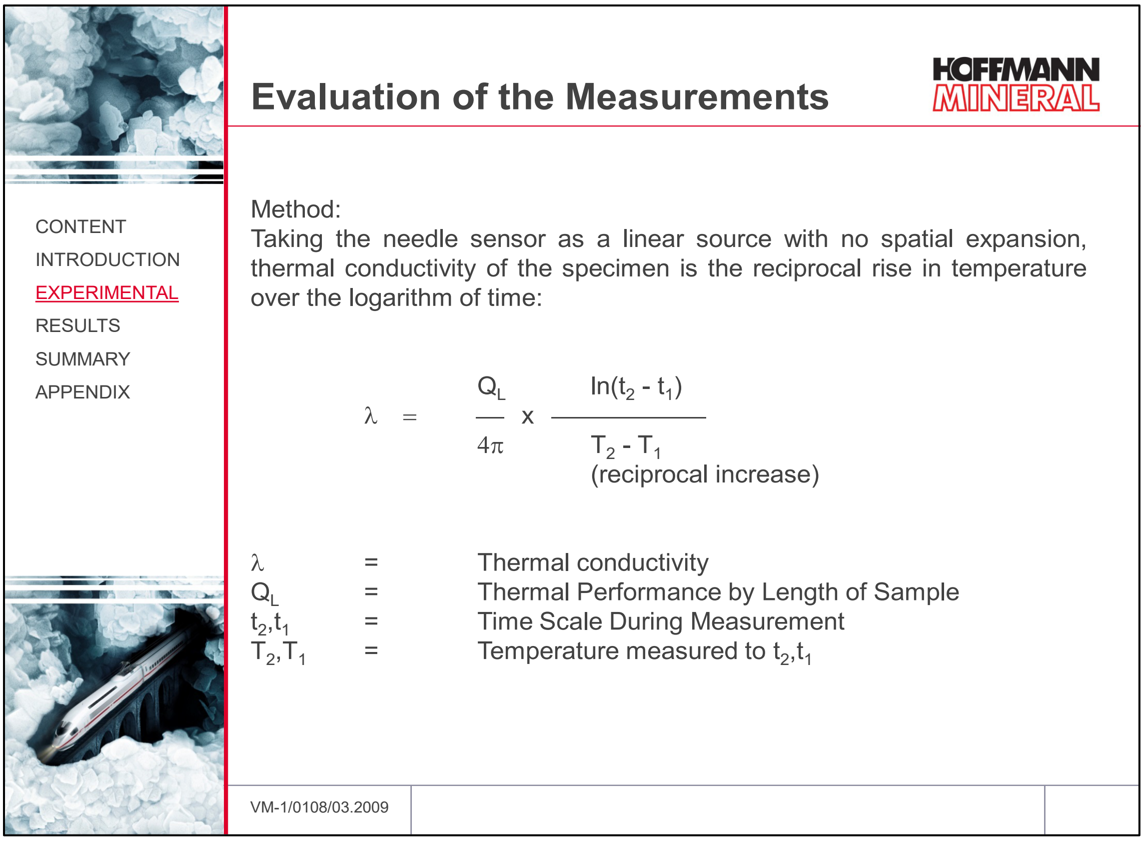
The compound was vulcanized using an electrically heated press. Starting at 100 °C in the pre-heated die, temperature was kept at 100 °C for 15 min, followed by 15 min at 140 °C and then 30 min at 180 °C. Measurements were taken from the point in time of each change in temperature. The die was sprayed with a release agent after each vulcanization cycle.

2.5 Measurement of Heat Conductivity

Heat conductivity of the specimen was determined using a specially developed measuring apparatus. Measurement is based on the dynamic volumetric heat transfer method.

The temperature sensor comprises a steel needle with a diameter of around 3 mm and a length of 5 cm enclosing a thermocouple capable of measuring changes of temperature. A heating element is applied to the outside jacket of the specimen. Measurement is performed by introducing the sensor into the bore in the cube. A thermal conducting paste is applied to exclude any space between the bore hole and sensor.

Measurement is performed by heating the jacket surrounding the sensor to a constant temperature for around 300 seconds, at the same time recording temperature several times per second. The heat conductivity of all samples was tested several times at different temperatures (3.54 / 9.05 / 13.27 and 36.65 W/m). Depending on the heat level applied and the heat conductivity of the samples, temperatures ranged from 23 °C up to 39 °C.



However, the start of the curve is not fully linear, as the sensor itself undergoes a certain amount of radial expansion, thereby changing the measurement value. Several unsolvable differential equations would have been necessary in order to allow for this deviation analytically. Heat conductivity analysis would then have only been possible using very expensive repetitive procedures. For this reason, only the linear part of the curve was used in the evaluation, with conductivity values calculated from this point onwards.

Due to the method used, only the surface vertical to the axis of the sensor is measured. Heat conductivity therefore represents the average value for an approximately circular area along this surface. Where anisotropic bodies are tested, heat conductivity will depend greatly on the spatial arrangement of the anisotropes. Heat conductivity is measured parallel to the layer (Variation 1) and traverse to the layer (Variation 2). Repeat measurements in the sample specimens resulted in a measuring uncertainty of around 1 %.

3. Results

Sillitin Z 86 is the reference filler used when comparing compounds in these results.

In principle, fillers have a definite effect on the heat conductivity of the compound. The greater the filler value, the higher the heat conductivity. This is best shown in Figs. 1 and 2 by Sillitin Z 86. Dependence of heat conductivity on the amount of filler used can be seen from the very clear linear function obtained. This applies particularly in relation to the volume of filler used (Fig. 2).

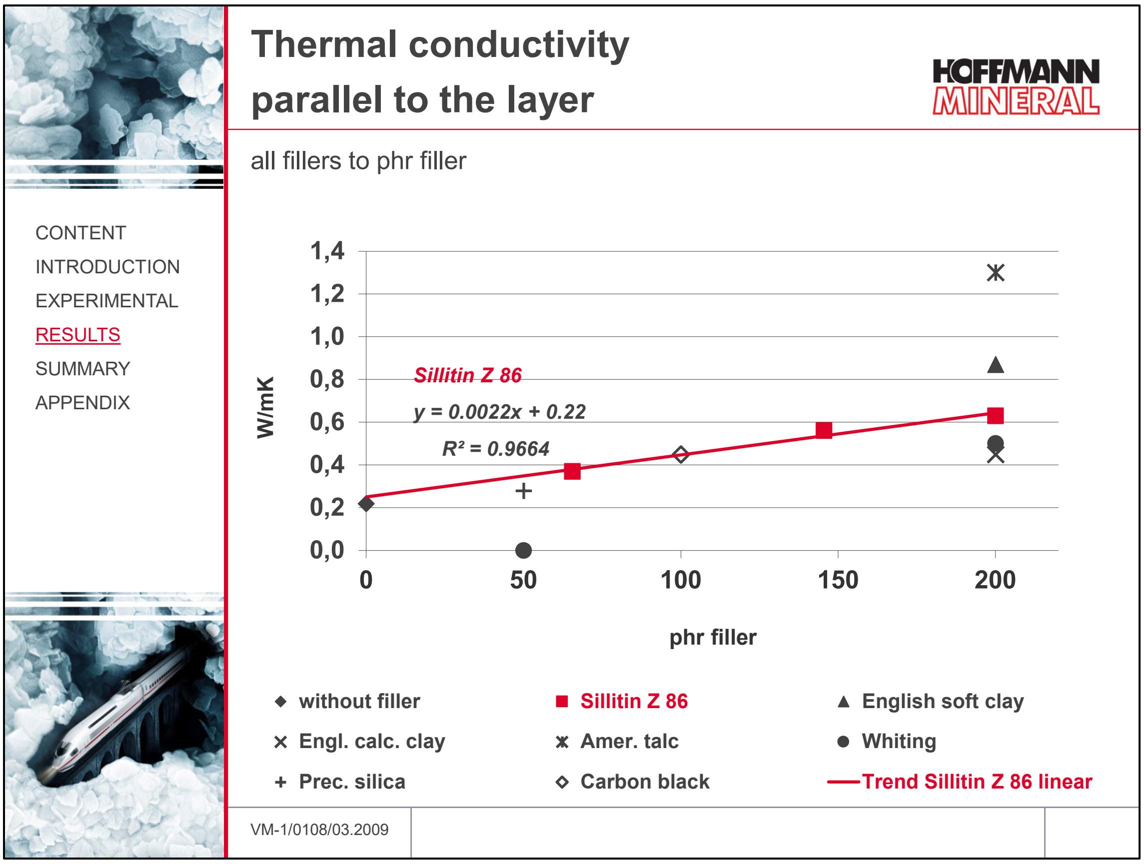


Fig. 1

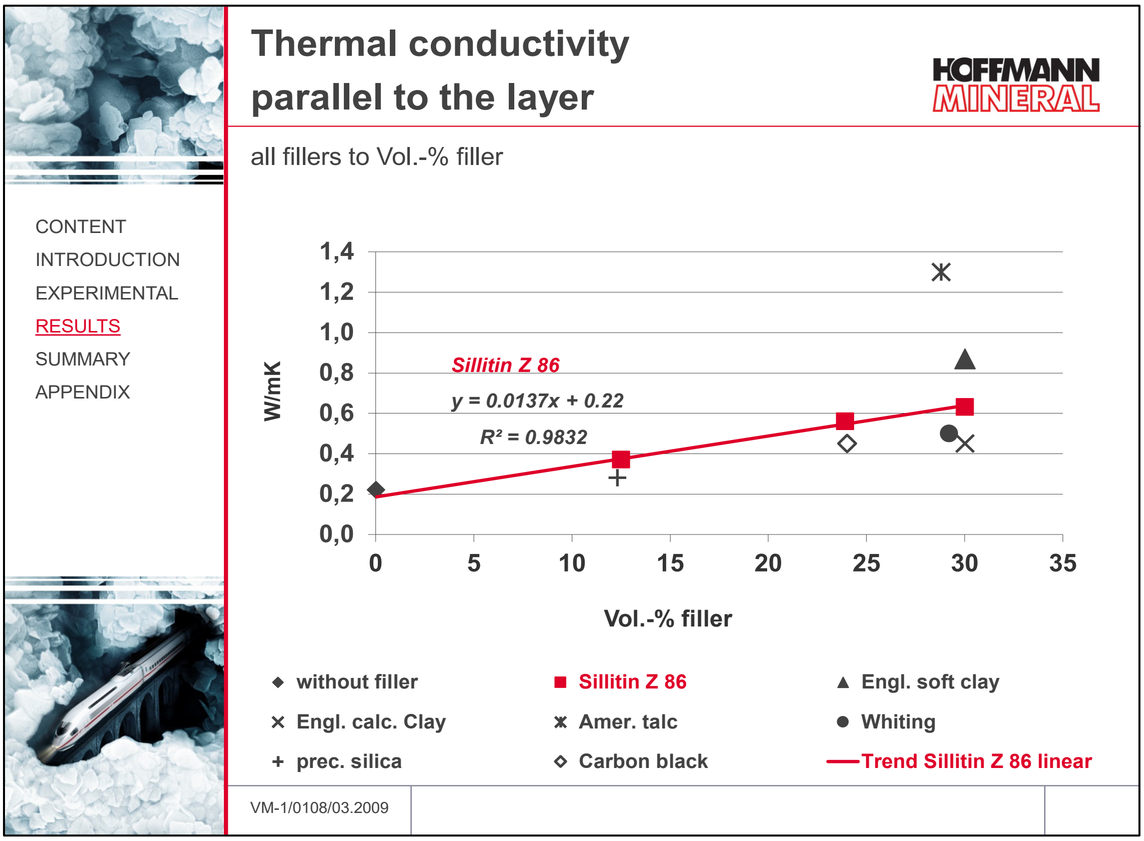


Fig. 2

Secondly, heat conductivity appears to be dependent on particle shape. The more laminar the particle shape, the higher the heat conductivity. Typical representatives for this type of laminar structure are talc and soft clay. However, a laminar structure results in greater anisotropy, as expressed by the large differences in values obtained between measurements taken parallel and traverse to the layer (Fig. 3).

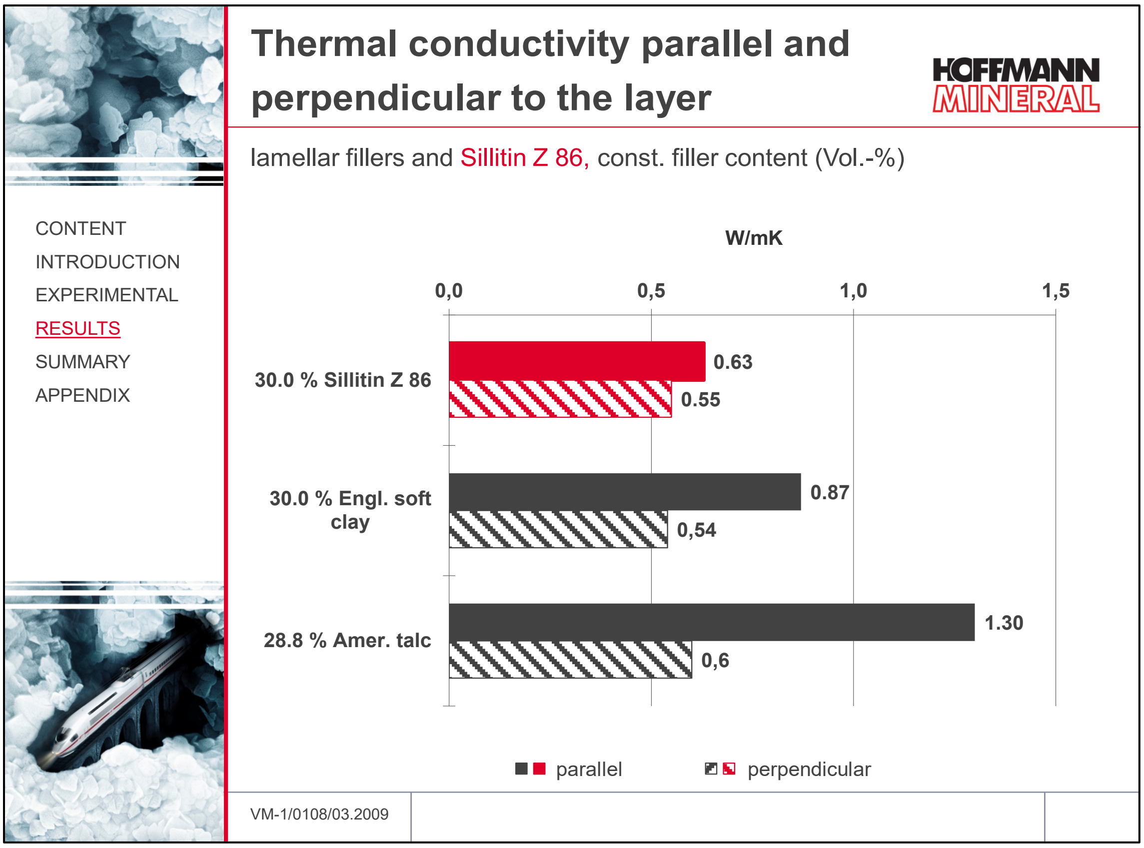


Fig. 3

The corpuscular fillers (precipitated silica, carbon black, English calcined clay and whiting) all produced low values compared to Sillitin Z 86 at corresponding dosages (Figs. 4 to 6).
The results obtained with Sillitin Z 86 show that due to its structural mix, Sillitin Z 86 can be placed between the laminar and corpuscular fillers.

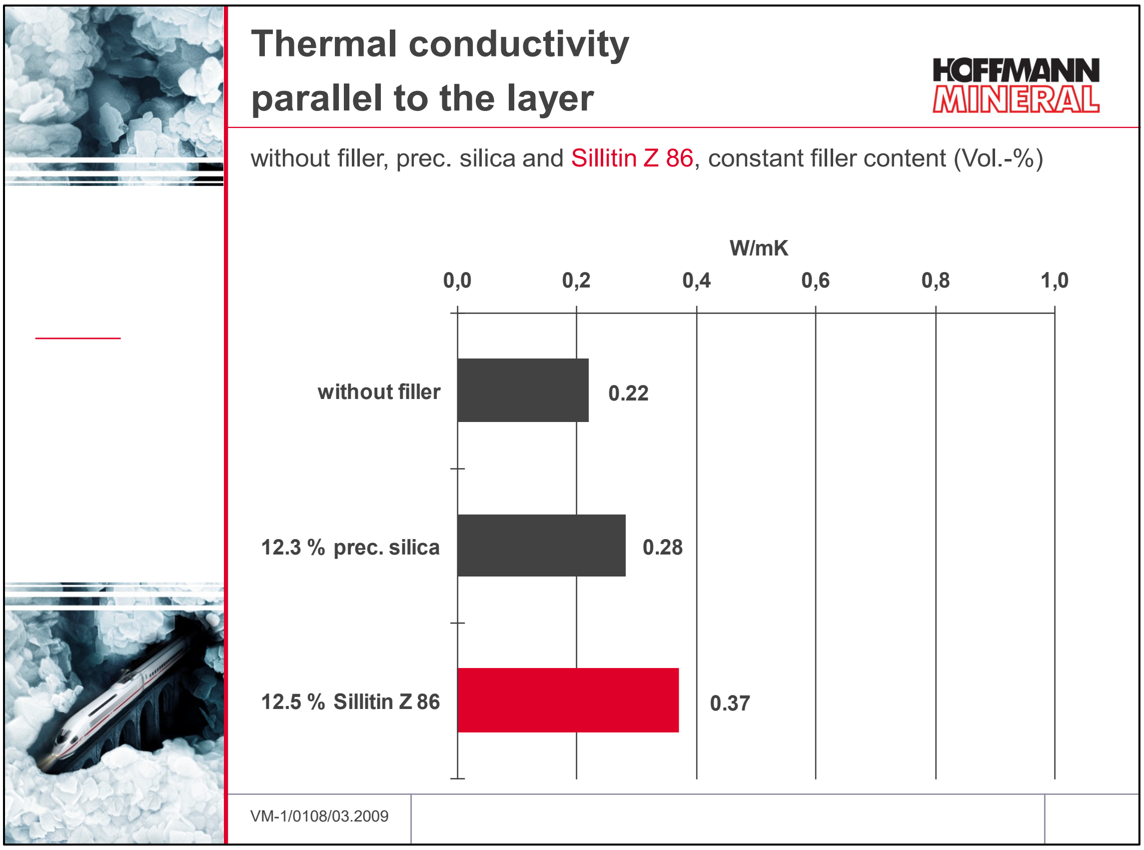


Fig. 4

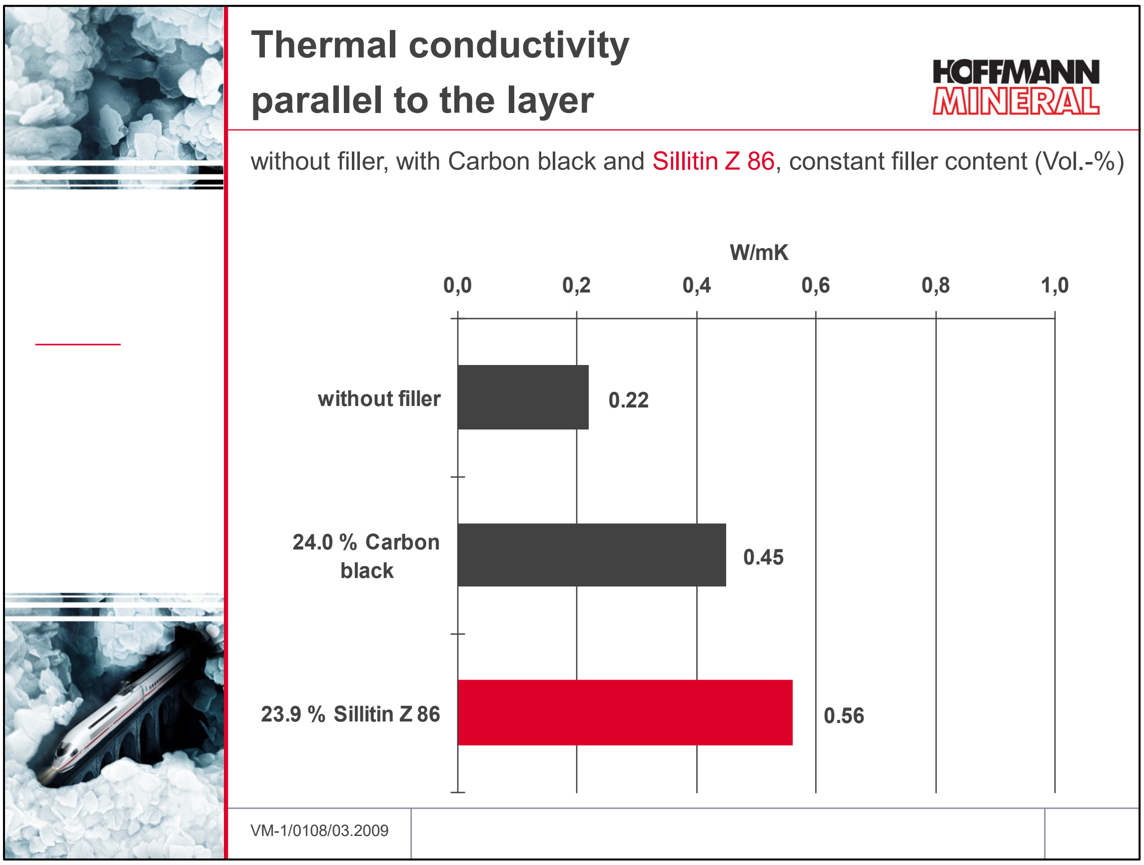


Fig. 5

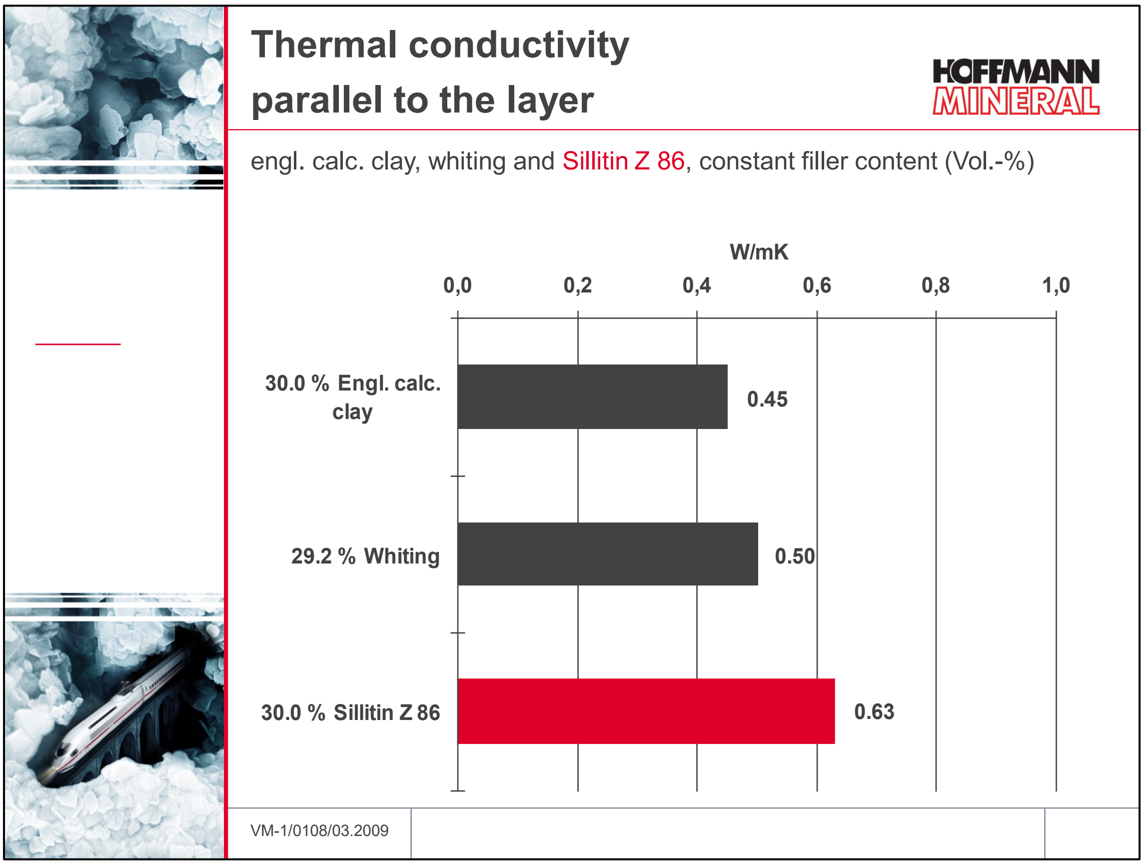


Fig. 6

The fact that Sillitin Z 86 has a high conductivity with minimal anisotropy (Fig. 7) must be of particular interest.

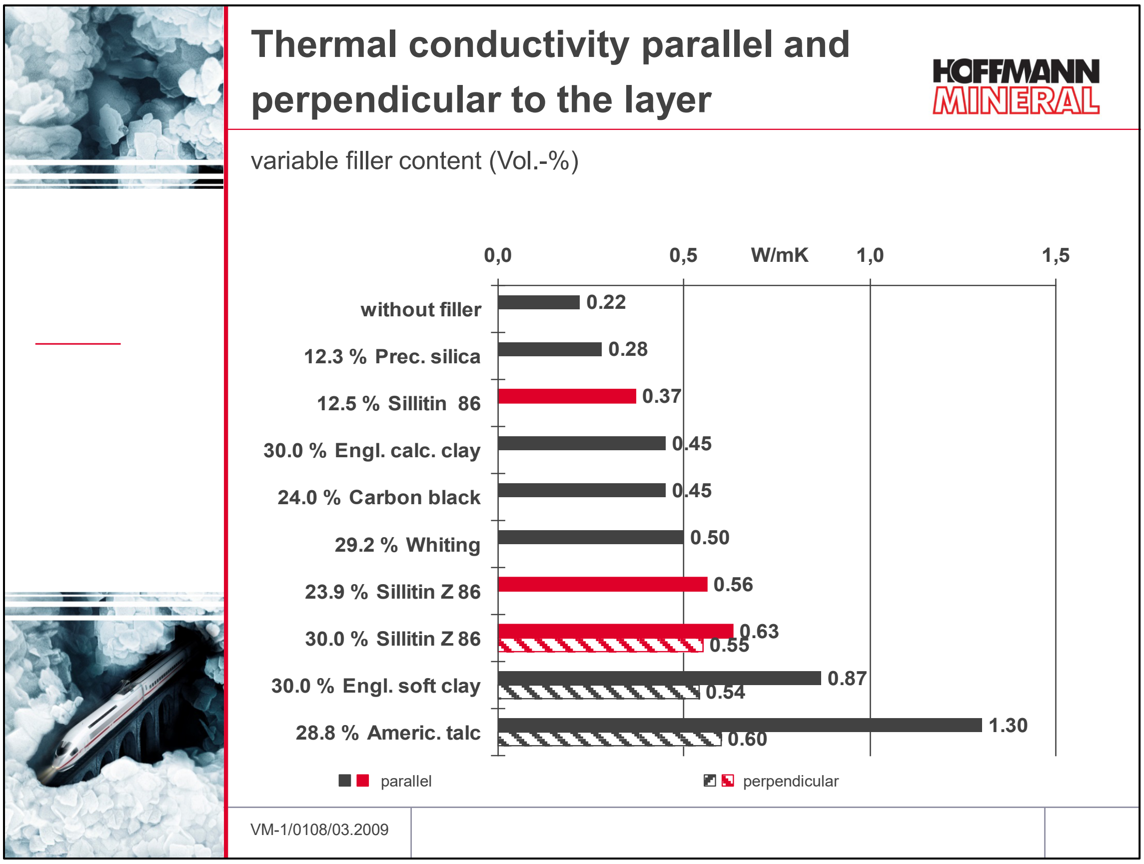


Fig. 7

4 Table of Results

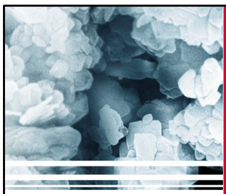


Table of Results

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Properties of uncured compound

Filler type			without filler	Sillitin Z 86	Sillitin Z 86	Sillitin Z 86	American talc
Filler content		phr	-	65.5	145.5	200	200
Filler content		Vol.-%	-	12.5	23.9	30	28.8
Mooney Viscosity (ML) 1+4, 120 °C	DIN 53523, T3	MU	35	37	55	73	47
Mooney Scorch (ML), 120 °C	DIN 53523, T4	min	> 2 h	> 2 h	> 2 h	46.23	35.03
Cure Meter Göttfert Elastograph (0.2°/ 180 °C)							
Torque Difference M_{max}-M_{min}	DIN 53529, A3	Nm	0.29	0.38	0.52	0.64	0.41
t_5	DIN 53529, A3	min	0.73	0.62	0.55	0.51	0.52
t_{90}	DIN 53529, A3	min	5.95	5.65	5.35	4.88	4.76
Cure Time t_{90} + 10 %		min	6.5	6.2	5.9	5.4	5.2

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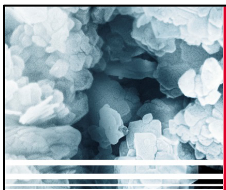

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Properties of uncured compound

Filler type			English soft clay	Precipitated silica	Carbon black N-550	Engl. calcined clay	Whiting
Filler content		phr	200	50	100	200	200
Filler content		Vol.-%	30	12.3	24	30	29.2
Mooney Viscosity (ML) 1+4, 120 °C	DIN 53523, T3	MU	48	84	70	81	56
Mooney Scorch (ML), 120 °C	DIN 53523, T4	min	19.98	18.38	12.18	67.67	35.00
Cure Meter Göttfert Elastograph (0.2°/ 180 °C)							
Torque Difference Mmax-Mmin	DIN 53529, A3	Nm	0.37	0.61	0.50	0.62	0.42
t5	DIN 53529, A3	min	0.54	0.57	0.47	0.54	0.52
t90	DIN 53529, A3	min	4.25	5.42	4.79	4.82	4.40
Cure Time t90 + 10 %		min	4.7	5.9	5.3	5.3	4.8

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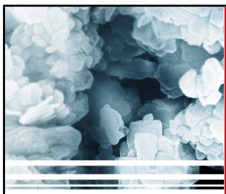

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Properties of Vulcanizate

Filler type			without filler	Sillitin Z 86	Sillitin Z 86	Sillitin Z 86	American talc
Filler content		phr	-	65.5	145.5	200	200
Filler content		Vol.-%	-	12.5	23.9	30	28.8
Tensile Strength	DIN 53504, S2	MPa	1.4	4.7	9.1	8.4	6.2
Elongation at Break	DIN 53504, S2	%	290	640	720	750	690
Modulus 100 %	DIN 53504, S2	MPa	0.6	0.9	1.6	2.0	2.8
Modulus 300 %	DIN 53504, S2	MPa	-	2.1	3.4	3.9	3.6
Hardness	DIN 53505	Shore A	27	37	51	58	59
Rebound Elasticity	DIN 53512	%	68	64	56	50	50
Tear Resistance	DIN ISO 34-1	N/mm	1.5	3.9	9.4	14.5	15.6
Compression Set (24 h/100 °C 25 % Deformation)	DIN ISO 815	%	7	8	12	17	32

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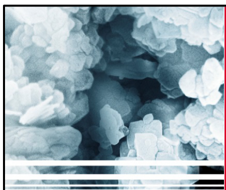

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Properties of Vulcanizate

Filler type			English soft clay	Precipitated silica	Carbon black N-550	Engl. calcined clay	Whiting
Filler content		phr	200	50	100	200	200
Filler content		Vol.-%	30	12.3	24	30	29.2
Tensile Strength	DIN 53504, S2	MPa	3.6	16.0	12.9	6.0	5.1
Elongation at Break	DIN 53504, S2	%	750	660	240	560	770
Modulus 100 %	DIN 53504, S2	MPa	2.2	1.3	3.1	2.7	1.2
Modulus 300 %	DIN 53504, S2	MPa	2.6	3.4	-	4.4	1.6
Hardness	DIN 53505	Shore A	54	50	59	59	47
Rebound Elasticity	DIN 53512	%	54	57	49	51	58
Tear Resistance	DIN ISO 34-1	N/mm	13.3	8.7	5.3	13.7	7.0
Compression Set (24 h/100 °C 25 % Deformation)	DIN ISO 815	%	25	16	6	18	11

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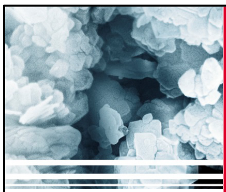

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Properties of Extrusion and thermal conductivity

Filler type		without filler	Sillitin Z 86	Sillitin Z 86	Sillitin Z 86	American talc
Filler content	phr	-	65.5	145.5	200	200
Filler content	Vol.-%	-	12.5	23.9	30	28.8
Extrusion (Garvey, 1m/min.)	ASTM 2230 A	1111	1121	2141	3142	4121
Thermal Conductivity parallel to layer	W/mK	0.22	0.37	0.56	0.63	1.30
Thermal Conductivity perpendicular	W/mK	-	-	-	0.55	0.60

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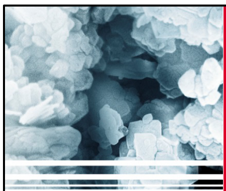

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Properties of Extrusion and thermal conductivity

Filler type		English soft clay	Precipitated silica	Carbon black N-550	Engl. calcined clay	Whiting
Filler content	phr	200	50	100	200	200
Filler content	Vol.-%	30	12.3	24	30	29.2
Extrusion (Garvey, 1m/min.)	ASTM 2230 A	3131	2131	2131	3141	2141
Thermal Conductivity parallel to layer	W/mK	0.87	0.28	0.45	0.45	0.50
Thermal Conductivity perpendicular	W/mK	0.54	-	-	-	-

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