Partial replacement of carbon black with Neuburg Siliceouth Earth in cellular EPDM profile compounds

Author: Nicole Holzmayr
Hubert Oggermüller

VM-2/1220/12.2023

HOFFMANN MINERAL GmbH · Muenchener Strasse 75 · D-86633 Neuburg (Donau) · Phone +49 (0) 8431 53-0
www.hoffmann-mineral.com • e-mail: info@hoffmann-mineral.com

Contents

1 Introduction

Cellular profiles are often used in the automotive industry due to the possibility of weight reduction. In most cases, it is necessary for these profiles to have an electrically insulating character to prevent electrochemical corrosion.

Its good property profile often makes carbon black the filler of choice for extrusion applications. However, it can only be used pure if the vulcanizate is allowed to be electrically conductive. Furthermore, it is highly dependent on the price of crude oil, which repeatedly leads to major price fluctuations.

In contrast, Neuburg Siliceous Earth is hardly dependent on changes in the crude oil market. It also makes it possible to develop electrically insulating components, making it ideal for use in e.g. electrically non-conductive extrusion profiles.

The aim of this investigation is to partially replace the carbon black in a cellular EPDM profile formulation with Neuburg Siliceous Earth (NSE). In addition to the electrical and mechanical properties, the cell structure and its influence on the water absorption are discussed and the effects on the compound costs are highlighted.

2 Experimental

2.1 Formulation, mixing and curing

Filler Combinations

INTRODUCTION
EXPERIMENTAL
RESULTS
SUMMARY

in phr	**conventional** filled with CB	**conventional** replacement of CB	**non-conductive**
N 550 [vol.%]	18.8	15.3	11.9
N 550	85	70	55
NSE	-	30	60

VM-2/1220/12.2023

Fig. 1

Base Formulation

INTRODUCTION
EXPERIMENTAL
RESULTS
SUMMARY

Material	phr
Keltan 8550C	100
N 550	as indicated
Neuburg Siliceous Earth (NSE)	as indicated
Process Oil P 460	70
Zinkoxyd aktiv	8
Stearic acid	1
Kezadol GR	2.25
PEG 4000	2
Rhenogran DPG-80	1.1
Rhenogran MBT-80	2
Rhenogran ZBEC-70	2
Rhenogran TP-50	4
Sulfur	1.52
Rhenogran CLD-80	1
TRACEL K 3/95	2.5
TRACEL OBSH 75 EPR-1	1.9

VM-2/1220/12.2023

Fig. 2

The carbon black-filled compound with 85 phr N 550 serves as a basis for comparison with 18.8 vol.% carbon black (Fig. 1). In the following, this variant is referred to as "conventional", equivalent to "electrically conductive".
In the conventional version, 30 phr Neuburg Siliceous Earth replace 15 phr of the carbon black and reduce its loading to 70 phr. This results in vulcanizates that are in a comparable hardness range. The volume fraction of the carbon black is 15.3 %.

To obtain non-conductive vulcanizates, the carbon black content must be reduced to approx. 12 vol.%, as known from previous investigations. For a comparable hardness level this results in a combination of 55 phr N 550 with 60 phr Neuburg Siliceous Earth.

Fig. 2 shows the basic formulation in which the above filler combinations are tested.

The raw materials used are described in more detail below:

Keltan 8550C	EPDM, ML 1+4, 125 °C: 80 MU, ethylene content: 63 %, ENB content: 5.5 %
Process Oil P 460	paraffinic plasticizer
Zinkoxyd aktiv	crosslinking activator
Stearic acid	crosslinking activator / processing aid
Kezadol GR	CaO, desiccant
PEG 4000	PEG, processing aid
Rhenogran DPG-80	diphenylguanidine (80 %), accelerator
Rhenogran MBT-80	mercaptobenzothiazole (80 %), accelerator
Rhenogran ZBEC-70	zinc dibenzyldithiocarbamate (70 %), accelerator
Rhenogran TP-50	zinc dialkyldithiophosphate (50 %), accelerator
Sulfur	crosslinker
Rhenogran CLD-70	caprolactam disulfide (70 %), accelerator
TRACEL K 3/95	azodicarbonamide, foaming agent
TRACEL OBSH 75 EPR-1	oxydibenzenesulfonyl hydrazide (75 %), foaming agent

Fillers and Characteristics

INTRODUCTION

EXPERIMENTAL

RESULTS

SUMMARY

Filler	Description	Functionalisation
N 550	carbon black, FEF	-
Sillikolloid P 87	Neuburg Siliceous Earth, d_{50}: 1.5 µm	-
Sillitin Z 86	Neuburg Siliceous Earth, d_{50}: 1.9 µm	-
Sillitin N 75*	Neuburg Siliceous Earth, d_{50}: 3.0 µm	-
Aktisil PF 216	Neuburg Siliceous Earth, d_{50}: 2.2 µm Basic material: Sillitin Z 86	tetrasulfane, hydrophobic
Aktifit PF 115	Calcined Neuburg Siliceous Earth, d_{50}: 2.0 µm Basic material: Silfit Z 91	amino, hydrophobic

*The tests were carried out with Sillitin N 82. This product is no longer available. Recommended: Sillitin N 75.

VM-2/1220/12.2023 6

Fig. 3

The three untreated grades Sillikolloid P 87, Sillitin Z 86 and Sillitin N 75 are compared with the two functionalized Siliceous Earth grades Aktisil PF 216 and Aktifit PF 115. (Fig. 3).

Compound Preparation, Extrusion and Curing

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Mixing	
Open mill	Ø 150 x 300 mm
Batch weight	ca. 800 g
Mill Temperature	50 °C
Mixing time	approx. 15 min.

Extrusion, Band 30 x 2 mm	
Speed	3 m/min.
Temp. Zone 1+2 / Head	70 / 70 / 110 °C

Curing	
Salt bath	3 min. / 200 °C

VM-2/1220/12.2023

Fig.4

The compounding was carried out on a laboratory open mill (Schwabenthan Polymix 150 L). The polymer was added to the mill at 50 °C, then all other ingredients were mixed at constant mill temperature. The typical mixing time was 15 minutes.
The laboratory extruder was used to extrude strips, which were cut into 15 cm long sections and then cured in a salt bath.

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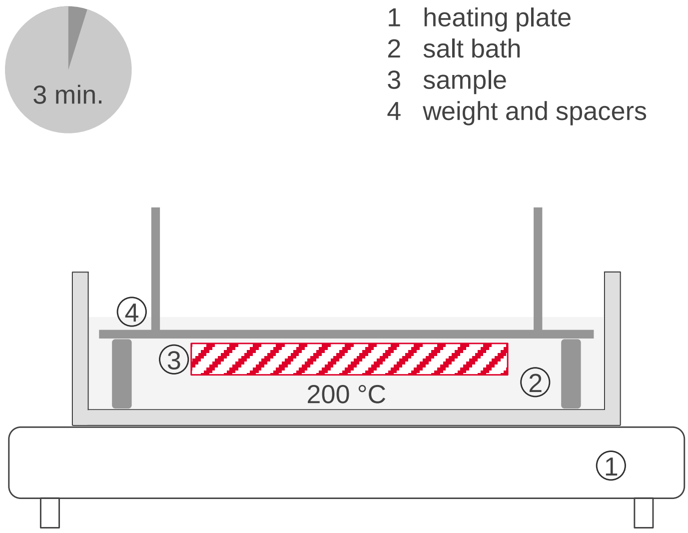
Salt Bath, Schematic

INTRODUCTION

EXPERIMENTAL

RESULTS

SUMMARY



VM-2/1220/12.2023

Fig. 5

Fig. 5 shows a schematic illustration of the salt bath vulcanization.

The temperature of the salt bath was set to 200 °C. The sample to be cured was placed between the two spacers on which the weight was placed. This prevented the foamed vulcanizate from floating up, so that the curing time of 3 minutes for all samples could be easily maintained.

After curing in the salt bath, all vulcanizates showed a comparable volume increase of approx. 140 %.

2.2 Tests

Test Standards

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INTRODUCTION

EXPERIMENTAL

RESULTS

SUMMARY

Test	Standard
Hardness	DIN ISO 7619-1
Tensile strength	DIN 53 504, S2
Modulus 100 %	DIN 53 504, S2
Elongation at break	DIN 53 504, S2
Tear resistance	DIN ISO 34-1, A
Compression set [1]	DIN ISO 815-1, B
Volume resistivity	DIN IEC 93
Water absorption	ASTM D 1056

Thickness of the sheet from which specimens have been cut out: 4-5 mm

[1] 2 piled-up specimens used

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Fig. 6

In addition to the hardness measurement and the tensile tests, the compression set, the volume resistivity and the water absorption were tested.
The thickness of the test specimens deviated slightly from the specifications of the test standards. However, preliminary tests showed that this had virtually no influence on the measurement result, but that a more reliable combination of foaming and crosslinking was possible.

3 Results

3.1 Electrical properties

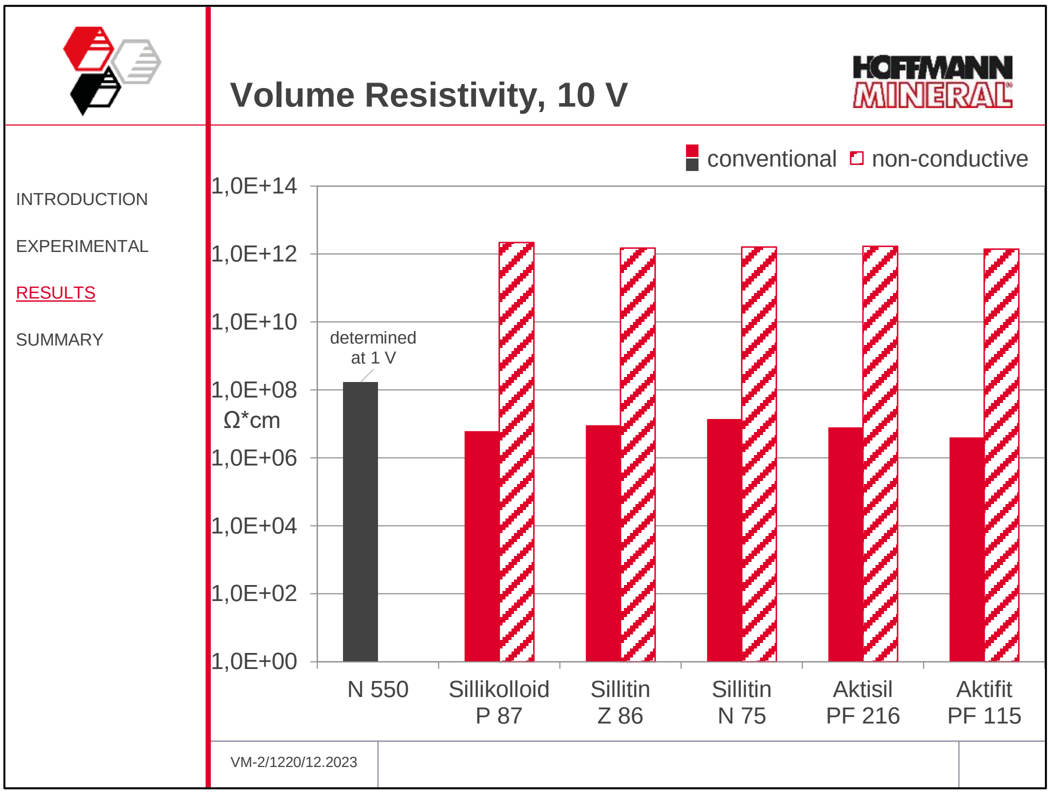


Fig. 7

The volume resistivity of the sample filled only with carbon black could only be measured at 1 V due to the high conductivity. The remaining measurements could all be carried out at 10 V.

As can be seen in Fig. 7, there are practically no differences between the NSE grades after the carbon black has been replaced. By reducing the volume fraction of the carbon black to 12 %, the volume resistivity increases as expected, so that these compound variants are electrically non-conductive.

3.2 Density and mechanical properties

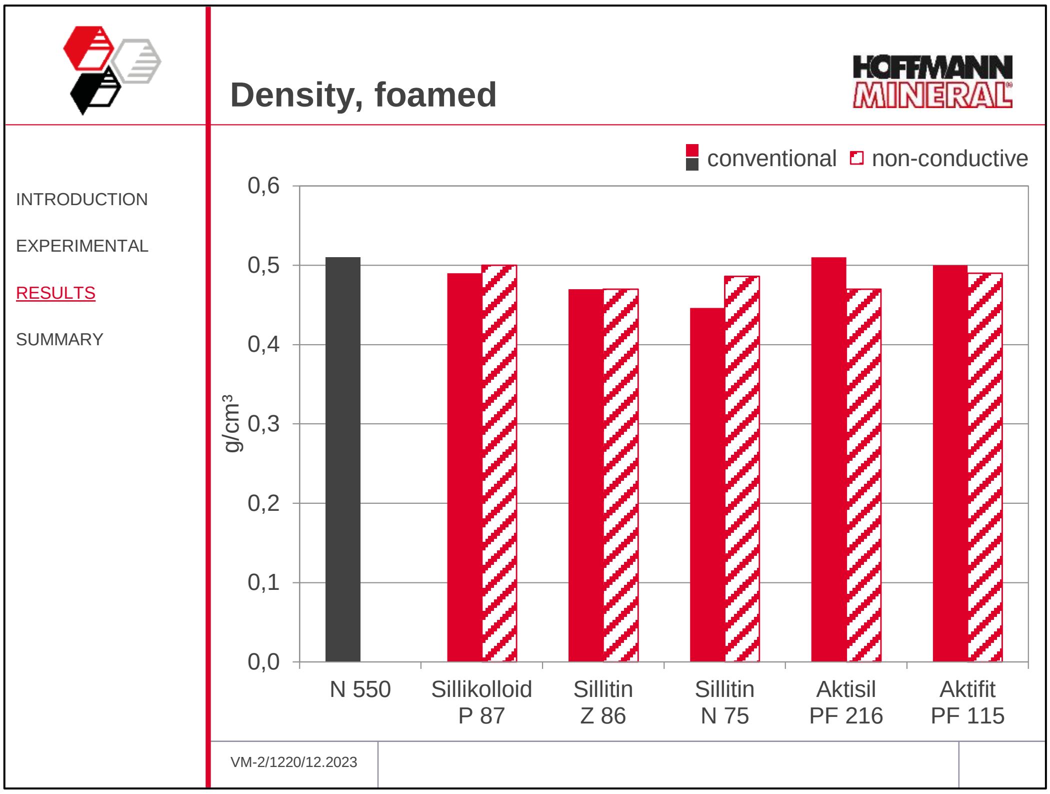


Fig. 8

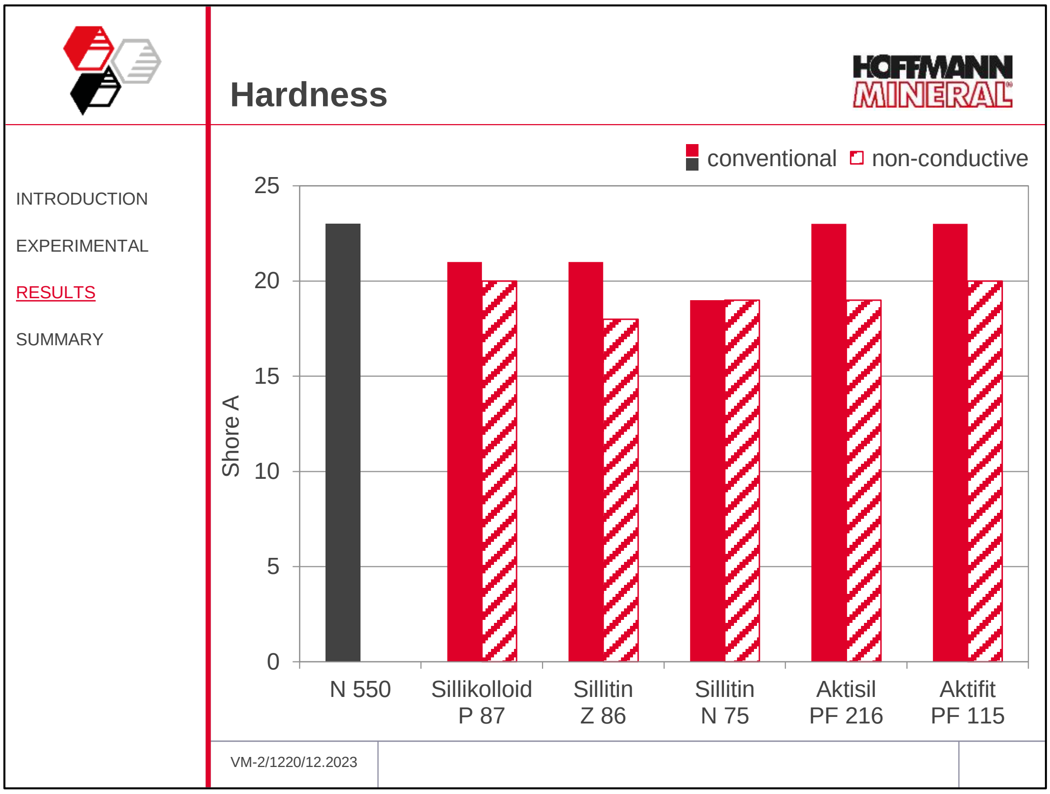
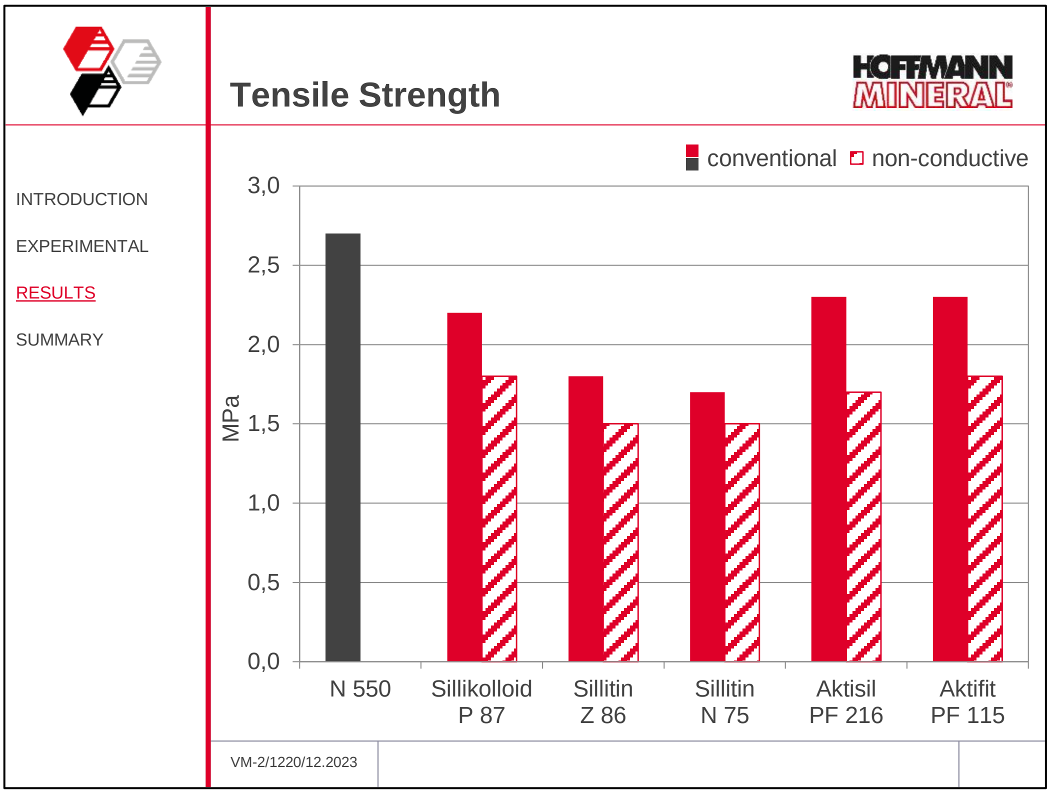


Fig. 9

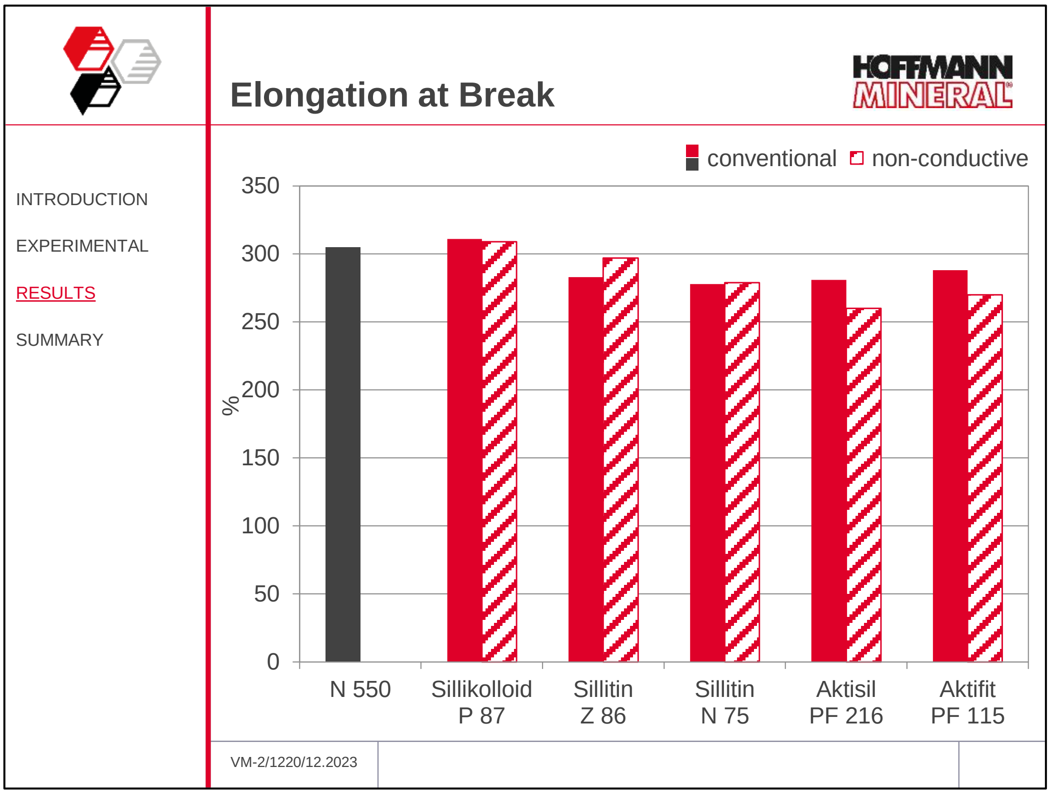
The density (Fig. 8) was determined from the dimensions and weight of foamed test specimens for tear resistance.
The values lie at approx. 0.5 g/cm³. Between the NSE grades no significant differences can be found.

The hardness (Fig. 9) remains roughly comparable in the conventional compound variant when the carbon black is replaced by Neuburg Siliceous Earth. The value level decreases slightly with the non-conductive version.
Neither in the conventional nor in the non-conductive version do the types of Neuburg Siliceous Earth differ.



Tensile Strength
HOFFMANN MINERAL
INTRODUCTION
EXPERIMENTAL
RESULTS
SUMMARY
conventional
non-conductive
MPa
3,0
2,5
2,0
1,5
1,0
0,5
0,0
N 550
Sillikolloid P 87
Sillitin Z 86
Sillitin N 75
Aktisil PF 216
Aktifit PF 115
VM-2/1220/12.2023

Fig. 10



Elongation at Break
HOFFMANN MINERAL
INTRODUCTION
EXPERIMENTAL
RESULTS
SUMMARY
conventional
non-conductive
%
350
300
250
200
150
100
50
0
N 550
Sillikolloid P 87
Sillitin Z 86
Sillitin N 75
Aktisil PF 216
Aktifit PF 115
VM-2/1220/12.2023

Fig. 11

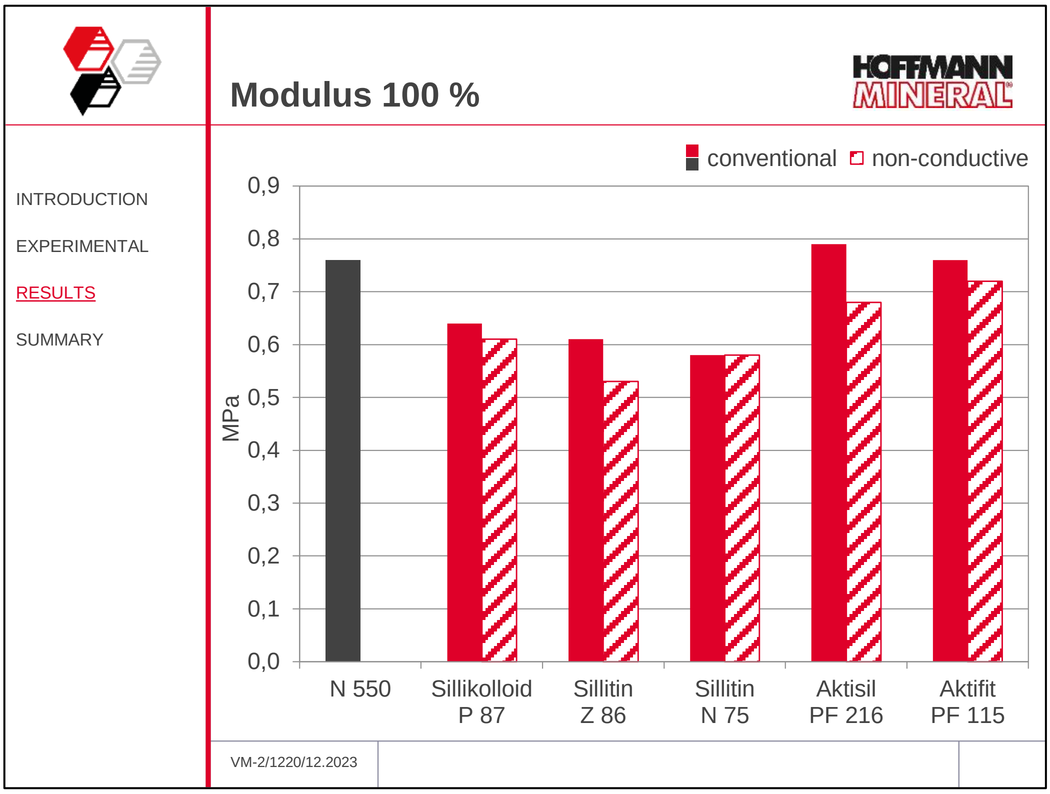


Fig. 12

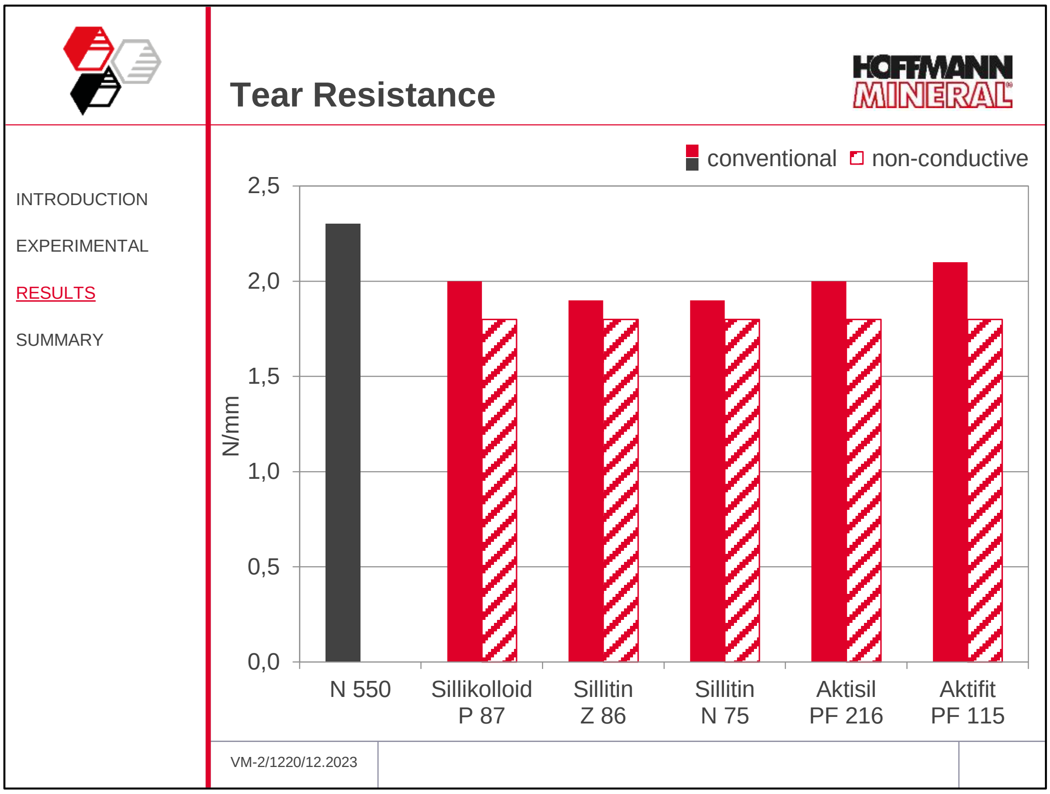


Fig. 13

Fig. 10 shows the tensile strength, which after partial carbon black replacement is generally somewhat lower in the non-conductive variant than in the conventional one. In this version, Sillikolloid P 87, Aktisil PF 216 and Aktifit PF 115 can come close to the pure carbon black at a high level.
Sillikolloid P 87 in both loadings leads to an elongation at break comparable to straight carbon black (Fig. 11). With the other NSE grades, the elongation drops somewhat compared to carbon black, but the value levels are still sufficiently high.

Similar to the tensile strength, the moduli at 100% elongation (Fig. 12) in the non-conductive compound version are also slightly lower than in the conventional version after carbon black replacement by NSE. The two functionalized fillers Aktisil PF 216 and Aktifit PF 115 reach, especially in the conventional compound design, an absolutely comparable level with the carbon black.
The partial replacement of carbon black by NSE leads to a general slight reduction of the tear resistance (Fig. 13). In the conventional version, Aktifit PF 115 can come close to matching the carbon black.

However, due to the generally low value level, the differences in the tensile tests are not very pronounced.

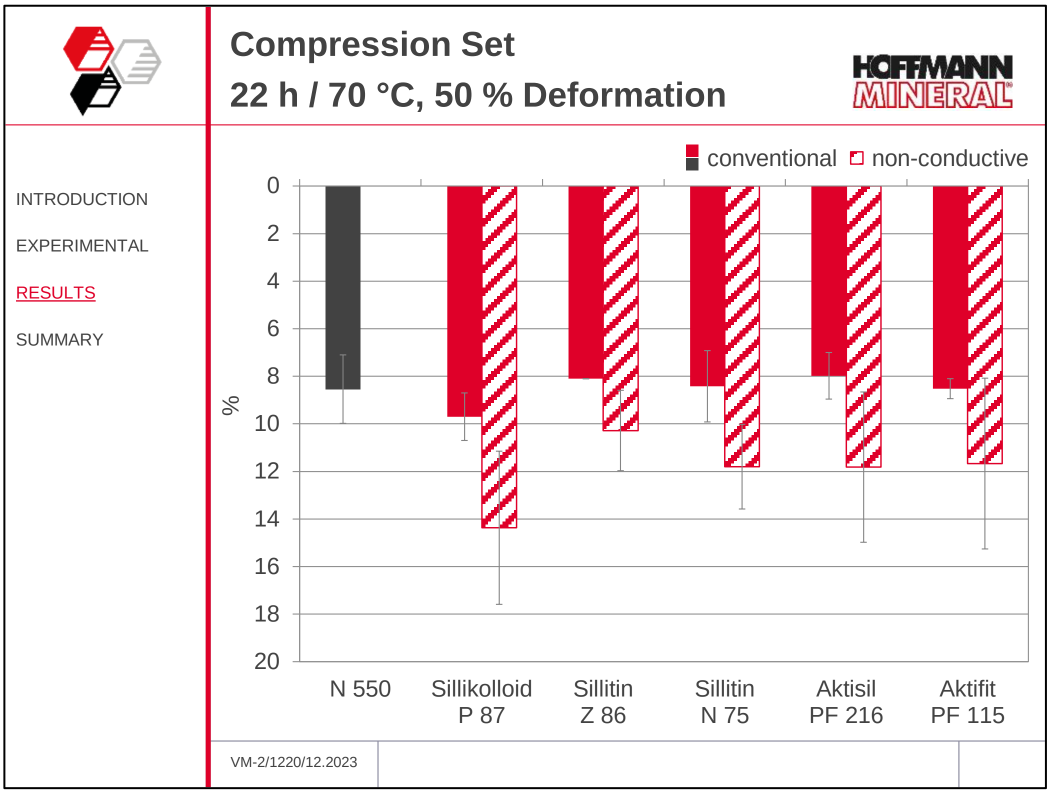


Fig. 14

The partial replacement of the carbon black has virtually no effect on the compression set if the formulation is kept in the conventional way (Fig. 14). With the non-conductive variant, the values turn out to be slightly higher than in the conventional one, but these differences are no longer very large when taking a closer look at the scaling.

3.3 Cell structure and water absorption

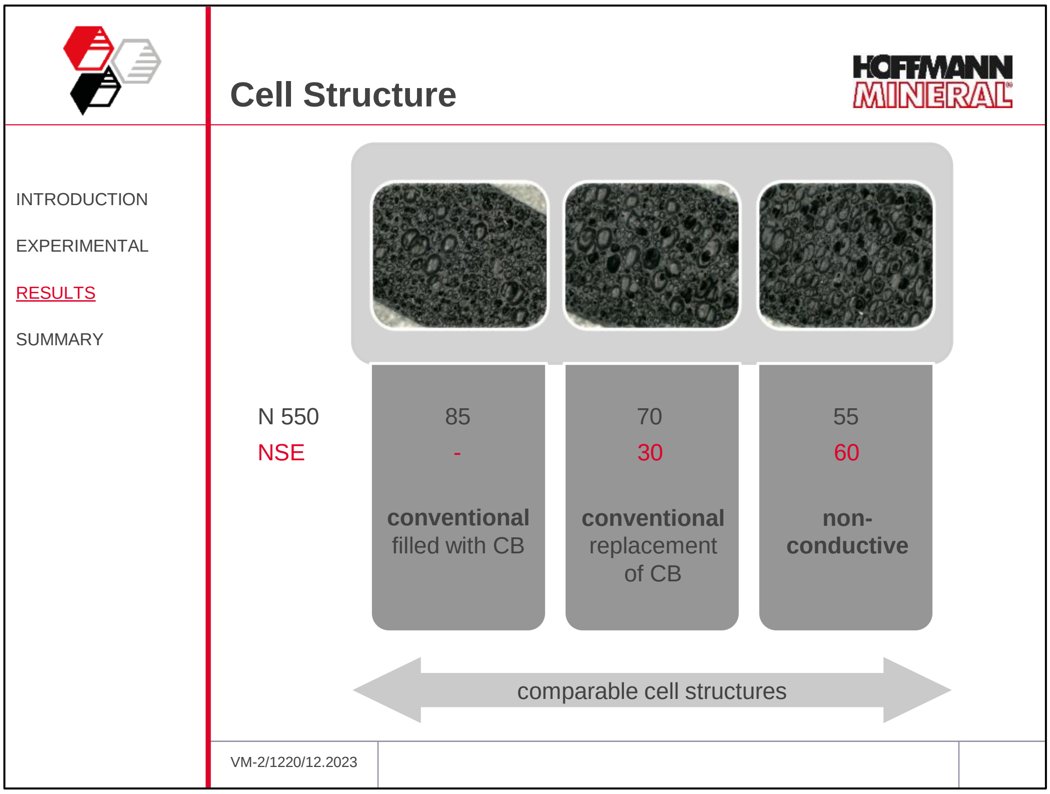


Fig. 15

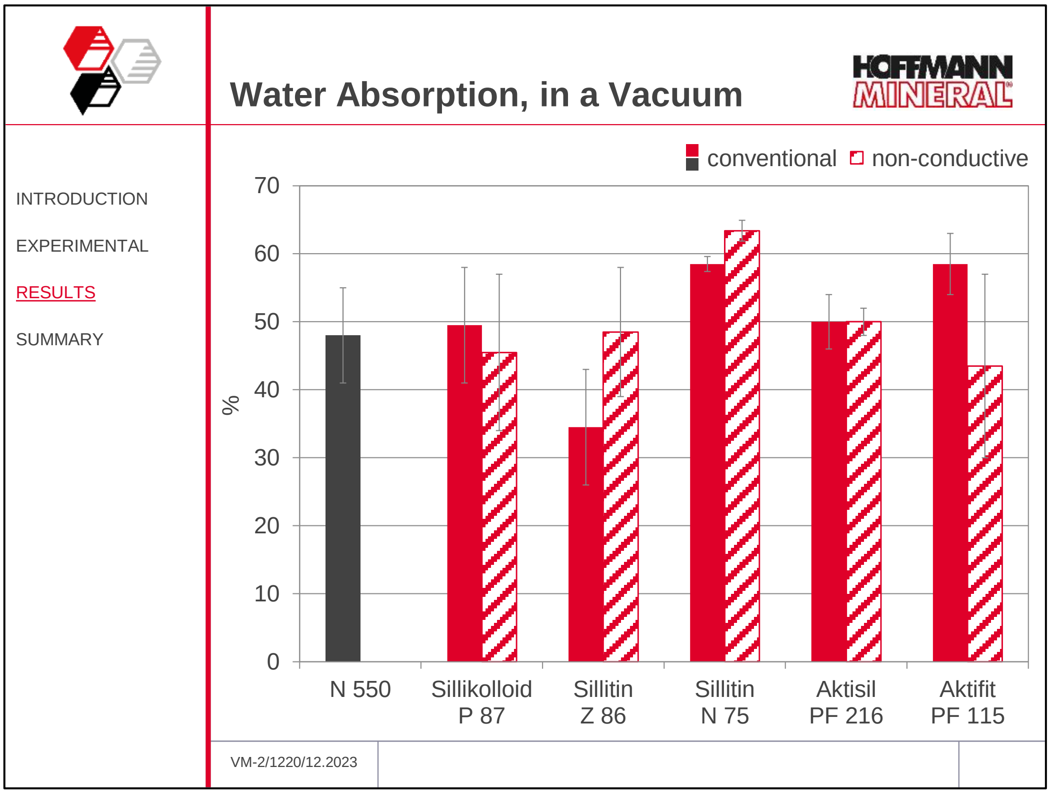


Fig. 16

Fig. 15 shows exemplary images for each compound variant. It is not considered here to illustrate each vulcanizate, since no significant differences in cell structures can be seen between the variants or between the different NSE types.

This is similarly reflected in the water absorption (Fig. 16), where the values differ somewhat but cannot be reliably differentiated and all lie in a similar range within the carbon black level. In the conventional version, Sillitin Z 86 even shows an improvement over carbon black.

3.4 Compound costs

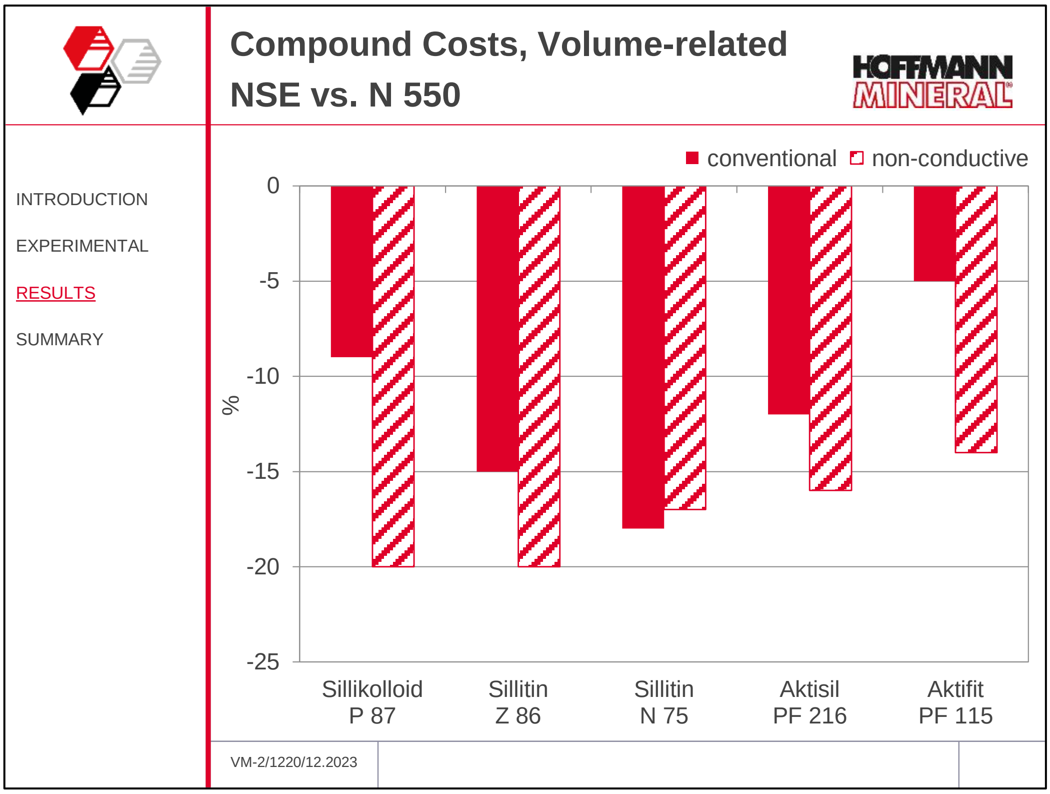


Fig. 17

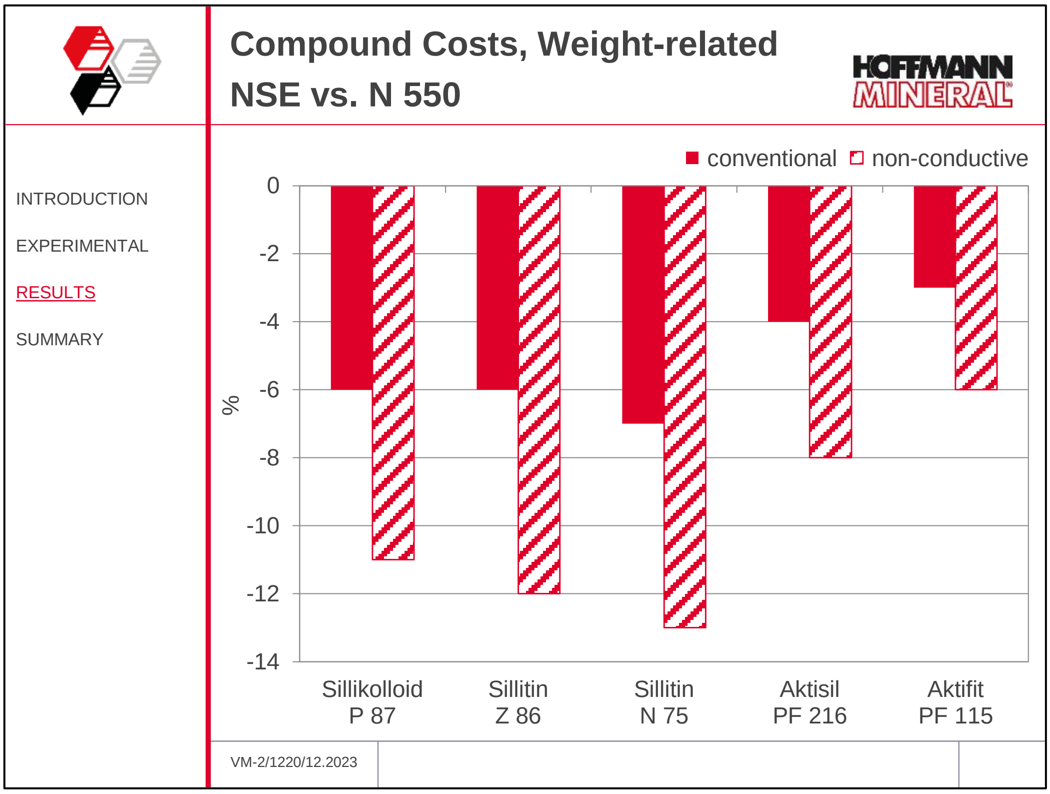


Fig. 18

The prices from 2020 were used to calculate the compound costs. Figs. 17 and 18 show the percentage changes resulting from the carbon black replacement with Neuburg Siliceous Earth compared to the compound filled with pure carbon black.

If, for example, a non-functionalized NSE grade such as Sillikolloid P 87, Sillitin Z 86 or Sillitin N 75 is used in the non-conductive version, this allows a reduction in the volume price of between -15 and -20 %. But even with the functionalized NSE products, a significant reduction in compound costs can still be realized.
sWith all NSE grades, the consideration of the weight-related costs results in lower compound prices caused by the carbon black exchange.

4 Summary

The present results show that after partial carbon black replacement with Neuburg Siliceous Earth in the conventional compound variant, a comparable property profile, such as a consistent compression set, as well as uniform cell structures are obtained.
With Aktisil PF 216 and Aktifit PF 115, it is also possible to match the high modulus level marked by the carbon black.
In addition, the compound costs can be reduced, in some cases significantly.

As expected, the reduction of the carbon black content leads to a significant increase in electrical resistance.
Also in this non-conductive variant, comparable cell structures are obtained after the partial replacement of the carbon black.
The modulus levels achieved here with Aktisil PF 216 and Aktifit PF 115 are very similar to those of the straight carbon black used.
The reduction in compound cost is somewhat higher in the non-conductive compound version than in the conventional one, due to the higher content of mineral filler. This means that the functionalized NSE grades also lead to a significant reduction in compound costs.

Neuburg Siliceous Earth thus makes it possible to replace the carbon black in a cellular EPDM profile formulation while keeping the property profile as far as possible the same or in some cases even slightly improving it.
Besides the reduction of compound costs, Neuburg Siliceous Earth helps to solve the problem of electrochemical corrosion, as the vulcanizates can be made electrically insulating, making them ideal for use in this type of application.

INTRODUCTION

EXPERIMENTAL

RESULTS

SUMMARY

APPENDIX

Table of Results

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		conventional					
		N 550	Sillikolloid P 87	Sillitin Z 86	Sillitin N 75	Aktisil PF 216	Aktifit PF 115
Rheology							
Mooney viscosity, ML 1+2, 120 °C	MU	40	41	43	43	45	43
Mooney scorch ML +5, 120 °C	min.	5.0	4.6	4.5	4.5	4.4	4.6
Rotorless curemeter M_{max}-M_{min} 200°C	Nm	0.60	0.63	0.64	0.59	0.67	0.65
Rotorless curemeter V_{max} 200 °C	Nm/min.	1.27	1.25	1.33	1.32	1.31	1.31
Rotorless curemeter t_{90} 200 °C	min.	1.1	1.1	1.1	1.1	1.2	1.1
Curing in salt bath, 3 min. / 200 °C							
Density	g/cm³	0.51	0.49	0.47	0.45	0.51	0.50
Hardness	Sh. A	23	21	21	19	23	23
Tensile strength	MPa	2.7	2.2	1.8	1.7	2.3	2.3
Modulus 10 %	MPa	0.12	0.11	0.10	0.09	0.12	0.11
Modulus 100 %	MPa	0.8	0.6	0.6	0.6	0.8	0.8
Elongation at break	%	305	311	283	278	281	288
Tear resistance	N/mm	2.3	2.0	1.9	1.9	2.0	2.1
CS, 22 h / 70 °C, 50 % def.	%	8,6	9.7	8.1	8.4	8.0	8.5
Water absorption	%	48	50	35	59	50	59
Volume resistivity 10 V (N 550 at 1 V)	Ω*cm	1.7 x 10^{8}	6.1 x 10^{6}	9.2 x 10^{6}	1.4 x 10^{7}	8.0 x 10^{6}	4.0 x 10^{6}

VM-2/1220/12.2023

INTRODUCTION

EXPERIMENTAL

RESULTS

SUMMARY

APPENDIX

Table of Results

HOFFMANN MINERAL

		non-conductive				
		Sillikolloid P 87	Sillitin Z 86	Sillitin N 75	Aktisil PF 216	Aktifit PF 115
Rheology						
Mooney viscosity, ML 1+2, 120 °C	MU	39	42	43	42	41
Mooney scorch ML +5, 120 °C	min.	4.9	4.5	4.5	4.5	4.7
Rotorless curemeter M_{max}-M_{min} 200°C	Nm	0.57	0.60	0.61	0.59	0.58
Rotorless curemeter V_{max} 200 °C	Nm/min.	1.29	1.28	1.28	1.25	1.28
Rotorless curemeter t_{90} 200 °C	min.	1.3	1.2	1.1	1.2	1.1
Curing in salt bath, 3 min. / 200 °C						
Density	g/cm³	0.50	0.47	0.49	0.47	0.49
Hardness	Sh. A	20	18	19	19	20
Tensile strength	MPa	1.8	1.5	1.5	1.7	1.8
Modulus 10 %	MPa	0.11	0.09	0.10	0.10	0.10
Modulus 100 %	MPa	0.6	0.5	0.6	07	0.7
Elongation at break	%	309	297	279	260	270
Tear resistance	N/mm	1.8	1.8	1.8	1.8	1.8
CS, 22 h / 70 °C, 50 % def.	%	14	10	12	12	12
Water absorption	%	46	49	63	50	44
Volume resistivity 10 V	Ω*cm	2.2 x 10^{12}	1.5 x 10^{12}	1.6 x 10^{12}	1.7 x 10^{12}	1.4 x 10^{12}

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