Calcined Neuburg Siliceous Earth

in thermoplastics:

Polyamide 6 and 66

Author: Petra Zehnder
Hubert Oggermüller

VM-1/0810/10.2014

Contents

1 Introduction

Polyamides are used in a multitude of application areas, above all in the automotive and electrical industries.

Important properties are - apart from easy processing – high surface quality, high stiffness and toughness, low warpage as well as good dimensional stability at elevated temperatures.

Mineral fillers, also combined with glass fibers, are often added in order to achieve certain properties.

For parts with low warpage, calcined clays or wollastonite with a blocky grain shape are preferred as typical fillers.

In the following study, Neuburg Siliceous Earth will be presented as a filler for thermo-plastics, above all polyamides.

The objective was to improve the property profile by using Aktifit AM in place of conventional competitive fillers with particular respect to flow properties and mechanical properties in polyamide.

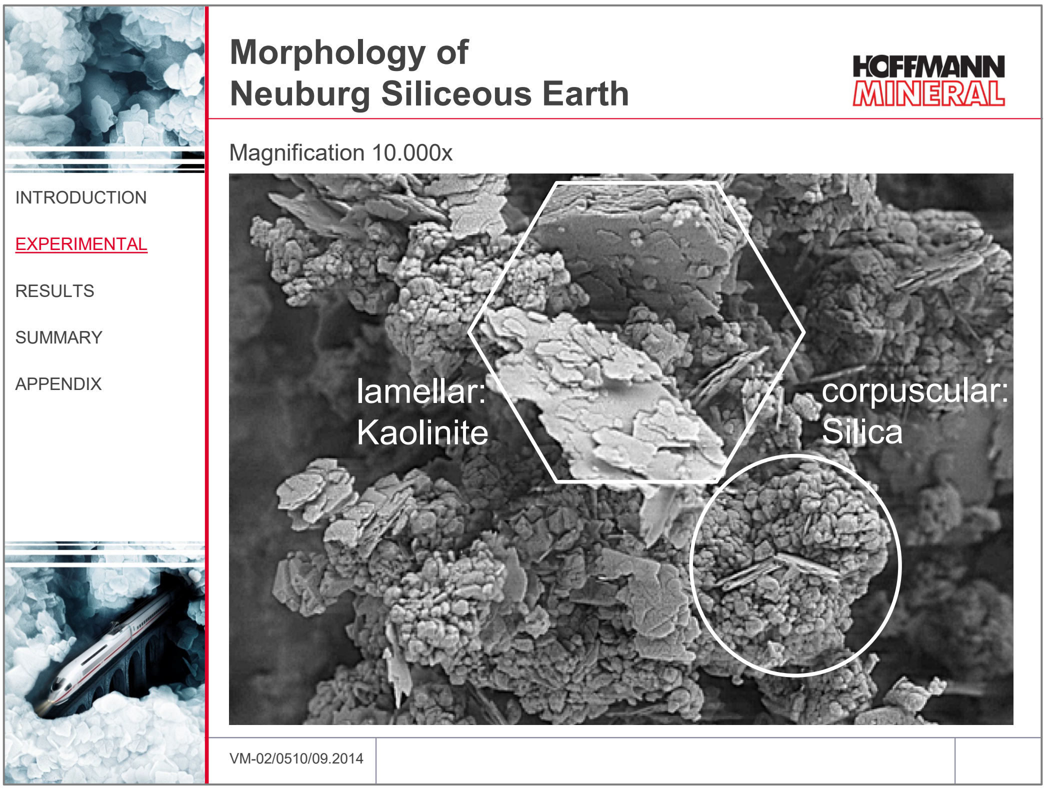
Silfit 91 was included as a less costly version of a filler without surface treatment.

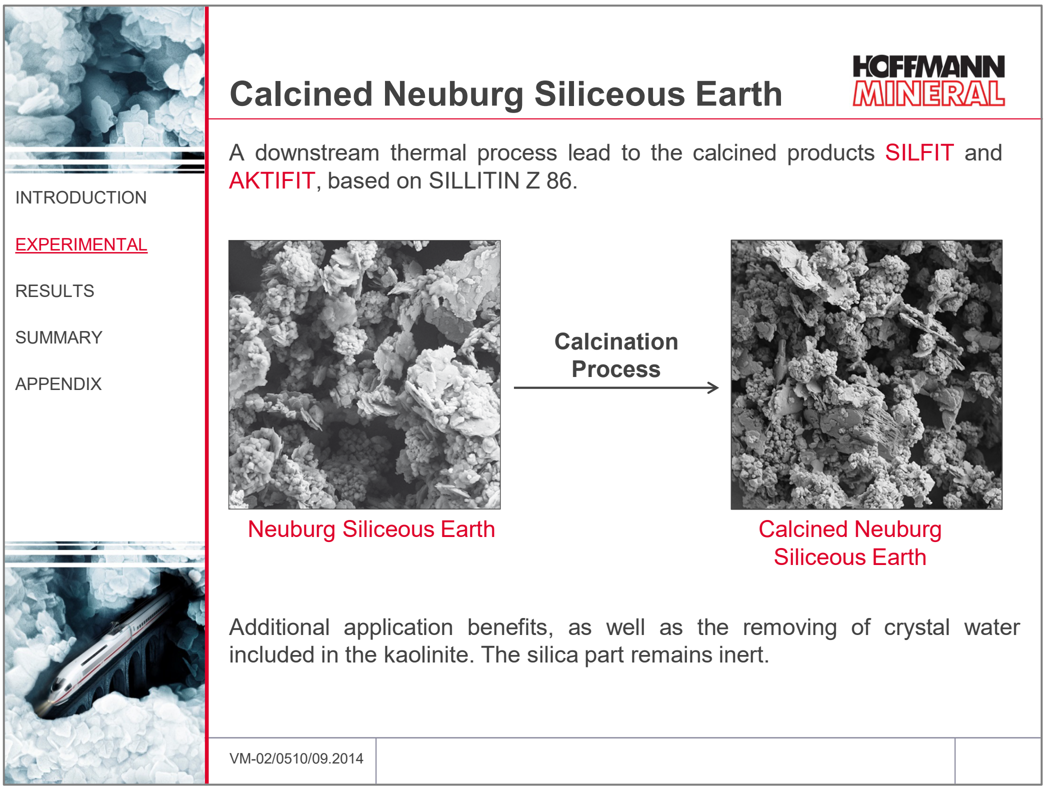
2 Experimental

2.1 Neuburg Siliceous Earth

Neuburg Siliceous Earth, extracted in the surrounding of Neuburg (Danube), is a natural combination of corpuscular Neuburg silica and lamellar kaolinite: a loose mixture impossible to separate by physical methods. As a result of natural formation, the silica portion exhibits a round grain shape and consists of aggregated, crypto-crystalline primary particles of about 200 nm diameter.

The special morphological composition of Neuburg Siliceous Earth, which represents a class of minerals on its own, is illustrated here by a SEM photograph.



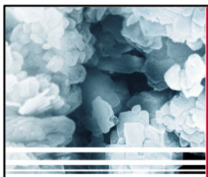


Silfit Z 91 is a Neuburg Siliceous Earth which has been subjected to a heat treatment. The components and the thermal process lead to a product that offers special performance benefits as a functional filler.

Aktifit AM is an activated Silfit Z 91, produced by modifying the surface with a special amino functional group. During compounding, the amino groups of Aktifit AM ensure good wetting and excellent dispersion in the matrix polymer. In addition, in polymers with suitable functional groups the use of this filler leads to high composite strength via hydrogen bonds.

2.2 Fillers and their characteristics

The table shows a summary of the most important filler properties.



INTRODUCTION

EXPERIMENTAL

RESULTS

SUMMARY

APPENDIX

Fillers and Characteristics

HOFFMANN MINERAL

		Calcined clay		Wollastonite	Calcined Neuburg Siliceous Earth	
		Grade 1	Grade 2	block-like particle structure	Silfit Z 91	Aktifit AM
Color value L* (CIELAB)		96.3	96.0	96.7	95.1	95.1
Color value a* (CIELAB)		-0.1	-0.4	-0.2	-0.2	-0.2
Color value b* (CIELAB)		2.5	2.2	1.0	1.0	1.0
Particle size d_{50}	[µm]	3.8	3.4	3.4	1.9	1.9
Particle size d_{97}	[µm]	13	14	14	10	10
Oil absorption	[g/100g]	68	61	33	60	61
Specific surface area BET	[m²/g]	5.8	9.1	3.6	7.4	6.6
Sieve residue > 40 µm	[mg/kg]	180	44	28	8	21
Functionalization		Amino		Amino	none	Amino

VM-02/0510/09.2014

Among the Neuburg Siliceous Earth grades, Silfit Z 91 and Aktifit AM were used.

For comparison purposes, two different calcined clays and a wollastonite were included. Both clays are frequently used standard grades with a somewhat coarser particle size distribution than the Calcined Neuburg Siliceous Earth.

This is also true for the wollastonite. The grade used has a low aspect ratio (L/D) and, therefore, a blocky particle structure. Contrary to highly needle-like grades with a high aspect ratio, the compact particle shape is essential to produce low-warpage plastics parts.

Compared with the clays and the calcined Neuburg Siliceous Earth, both the oil absorption and the specific surface area of the wollastonite are much lower. The specific surface area shows also a difference for the two clays.

Another differing criterion is the sieve residue, where particularly clay no.1 stands out in a negative way, followed by grade no. 2. By contrast, the wollastonite as well as Silfit Z 91 and Aktifit AM come out at the lowest level.

All competitive fillers were surface treated with an aminosilane.

2.3 Compounding and molding

The polymers used were a polyamide 6 grade and two polyamide 66 grades:

- Durethan® B 31 SK, an easy-flowing and easily demolded polyamide standard injection molding grade from LANXESS, black-colored version (9005/0)
- Ultramid® A3K, an easy-flow and easily processable polyamide 66 injection molding grade from BASF, natural-colored version
- Schulamid® 66 MV 2, a medium viscosity polyamide 66 standard injection molding grade from A. Schulman Inc., natural-colored version

In order to evaluate the filler properties without the influence of additives, the composition of the compounds was just 60 weight percent polymer and 40 weight percent filler.

The compounding was made in a Coperion twin-screw extruder ZSK 30 (screw diameter 30 mm, L/D ratio 45).

The matrix polymer was pre-dried for at least 8 hours in dry air at 80 °C. The fillers, however, were not pre-dried, and used as received. In the compounding operation, the polyamide was introduced into the main stream, and the filler was added to the melt via side feeder. The extruded strands were pelletized by cold-face cutting and the pellets were subsequently homogenized in a tumble mixer.

The preparation of the test specimens was made on a screw injection molding unit FX 75 (Ferromatik Milacron) resp. 320A 600-170 (Arburg) using a specimen tool according to ISO 294 with exchangeable inserts for the individual test specimens.

Prior to processing, the pellets were pre-dried (dry air, 8 h/80 °C) and then injected in an injection molding unit according to ISO 1874 with a melt temperature of 260 °C for polyamide 6 or 305 °C for polyamide 66, a mold temperature of 80 °C and a flow front rate of 200 mm/s. The extruded samples were stored in airtight containers until testing.

The compounding and injection molding was carried out at the Deutsches Kunststoff-Institut (DKI) at Darmstadt. The tests were run at Hoffmann Mineral.

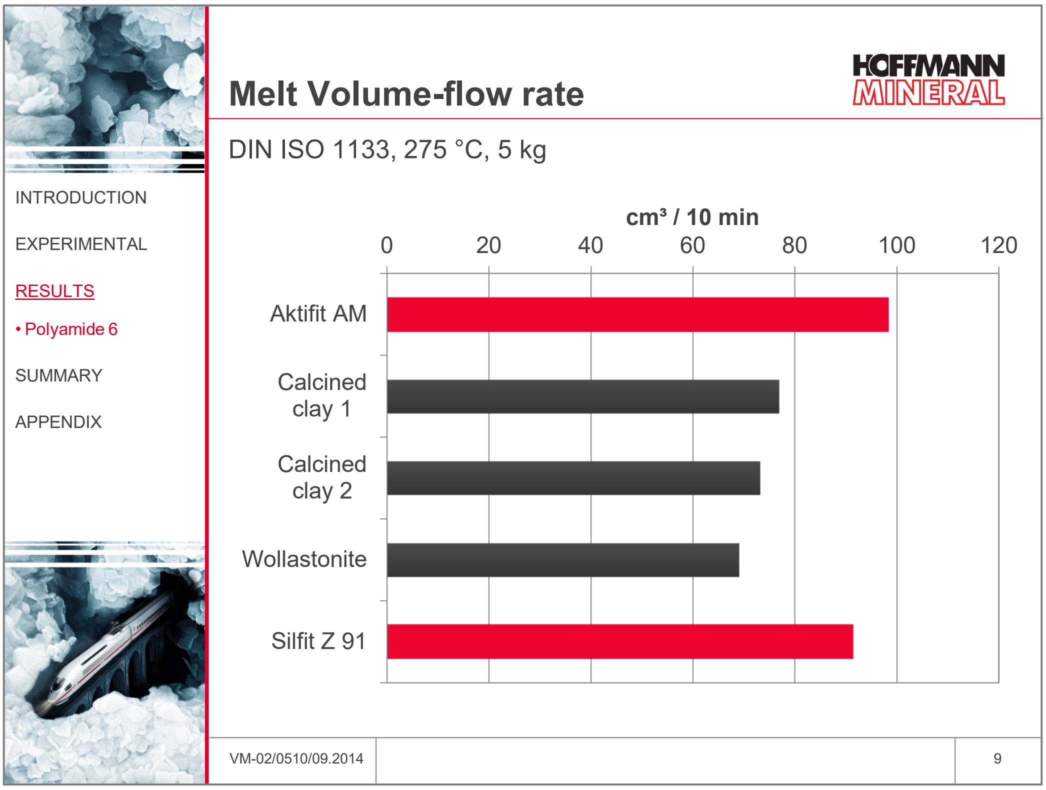
3 Results polyamide 6

For the tests with Polyamide 6, Durethan® B 31 SK was used in the black color version 9005/0. The tests included samples dry-as-molded as well as after conditioning. The moisture content of the dry-as-molded samples was about 0.2 %. They were conditioned at 23 °C and 50 % relative humidity until constant weight.

The diagrams show the results dry-as-molded. Tables with the individual results of dry-as-molded respectively conditioned samples can be found in the appendix.

3.1 Melt volume-flow rate

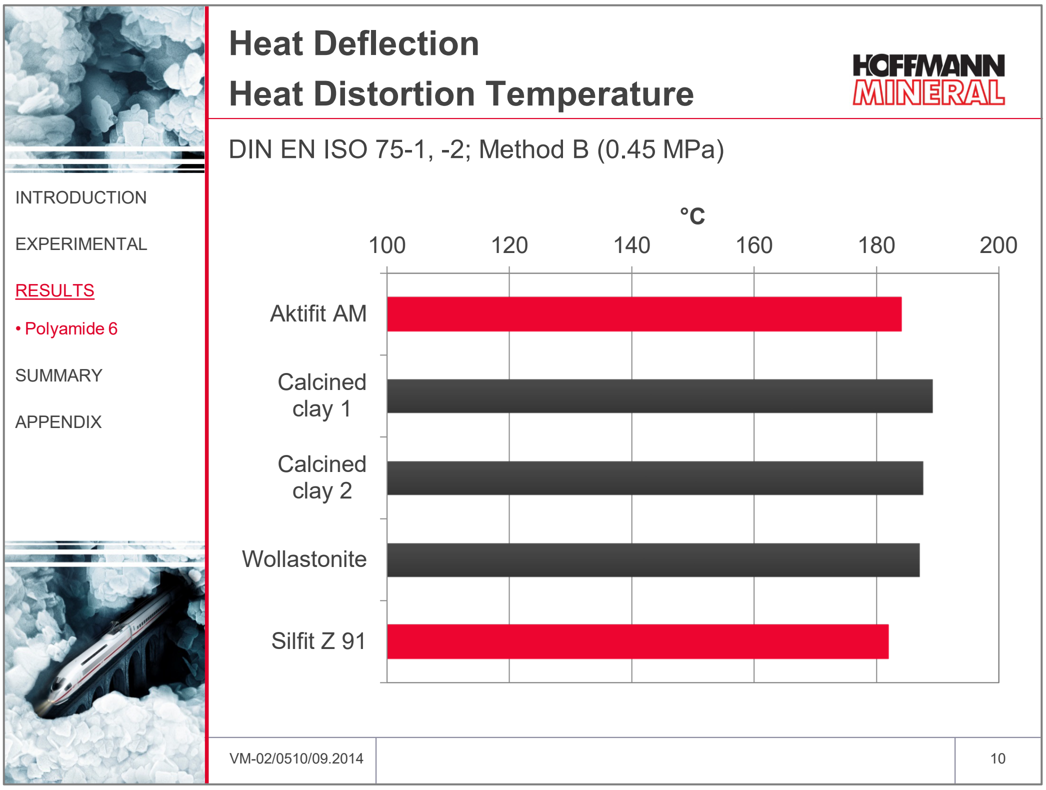
Samples for this test were taken from the homogenized and pre-dried pellets ready for injection molding.



The calcined Neuburg Siliceous Earth grades Aktifit AM and Silfit Z 91 lead to considerably better flow properties than the competitive fillers.

3.2 Heat deflection

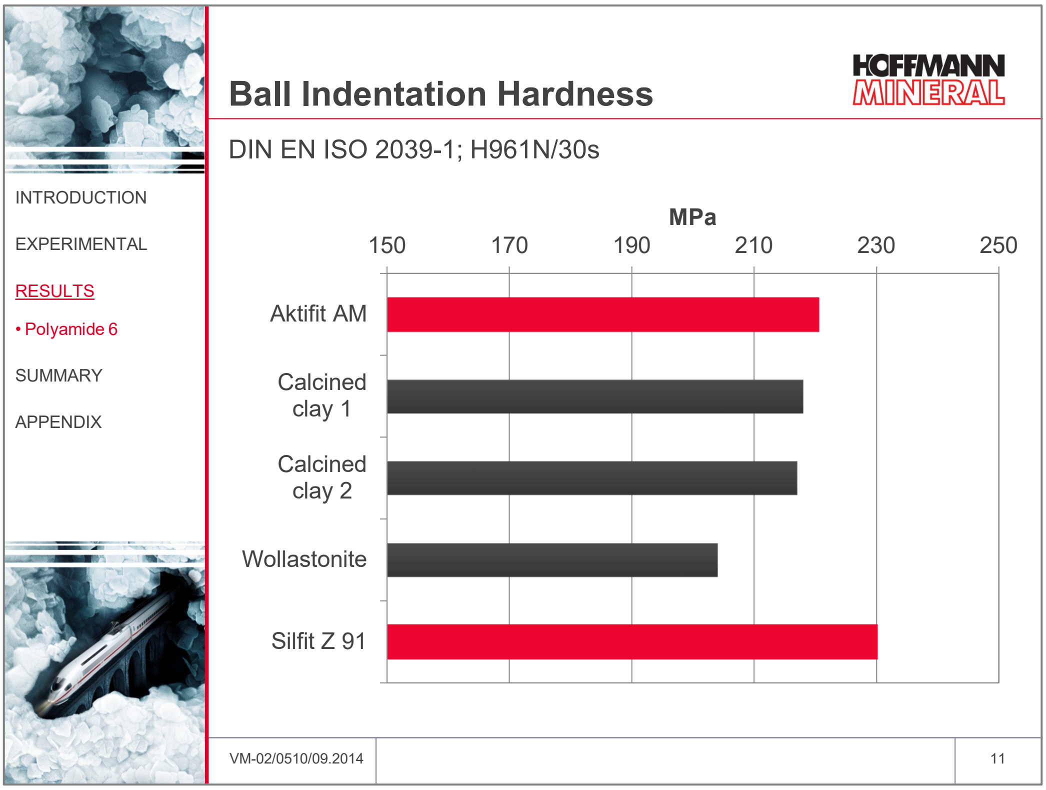
For the determination of the Heat Distortion Temperature (HDT), the sample was bent according to the 3-Point bending principle, charged with a constant load and heated with a rate of 120 K/h. The required load as a function of the sample thickness is calculated in order to arrive at an outer fiber stress of 0.45 MPa (Method B). The HDT then is the temperature that leads to a defined standard bending corresponding to 0.2 % outer fiber strain.



With the competitive fillers the heat deflection was marginally higher than with Aktifit AM, which can probably be explained by slight differences in the E- moduli.

3.3 Ball indentation hardness

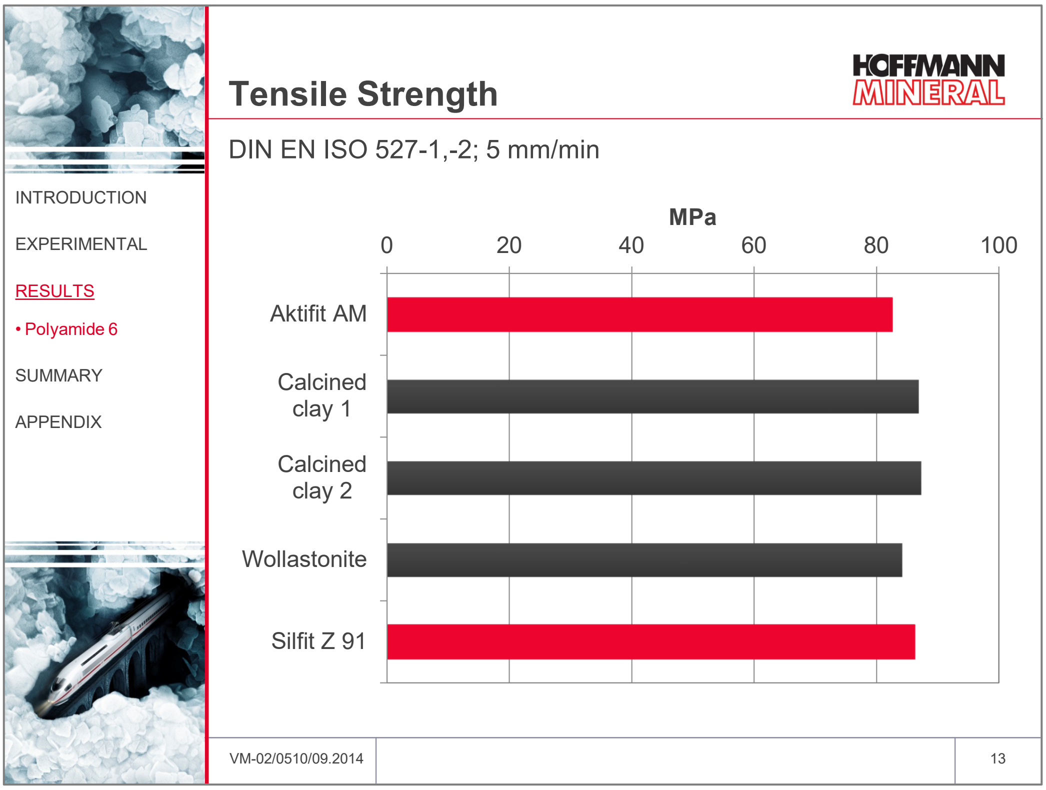
This test method determines the depth of indentation of a steel ball (Ø 5 mm) under load after a defined period of time. The load and the resulting depth of indentation resp. the indentation area allow to calculate the ball indentation hardness. The polyamide samples were tested with a load of 961 N for a time period of 30 s.



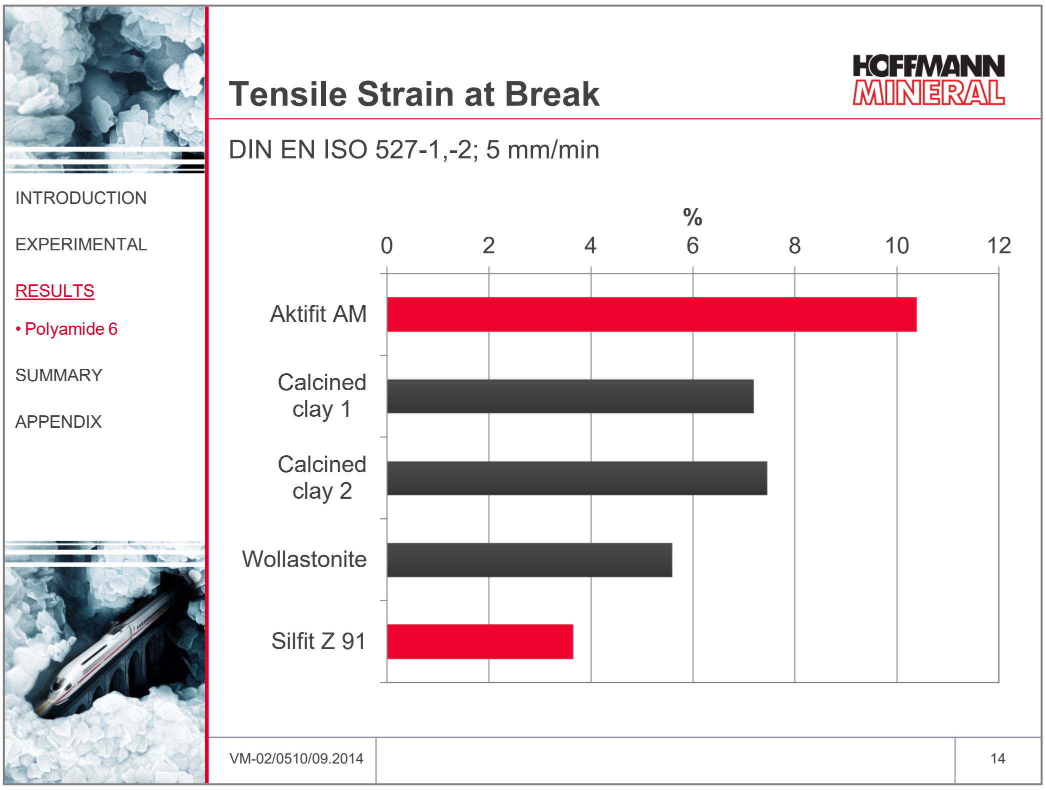
Calcined Neuburg Siliceous Earth gave rise to a higher hardness compared with the competitors, especially wollastonite.

3.4 Tensile strength and tensile strain at break

The test was run with specimens type 1A at an extension rate of 5 mm/min up to break.



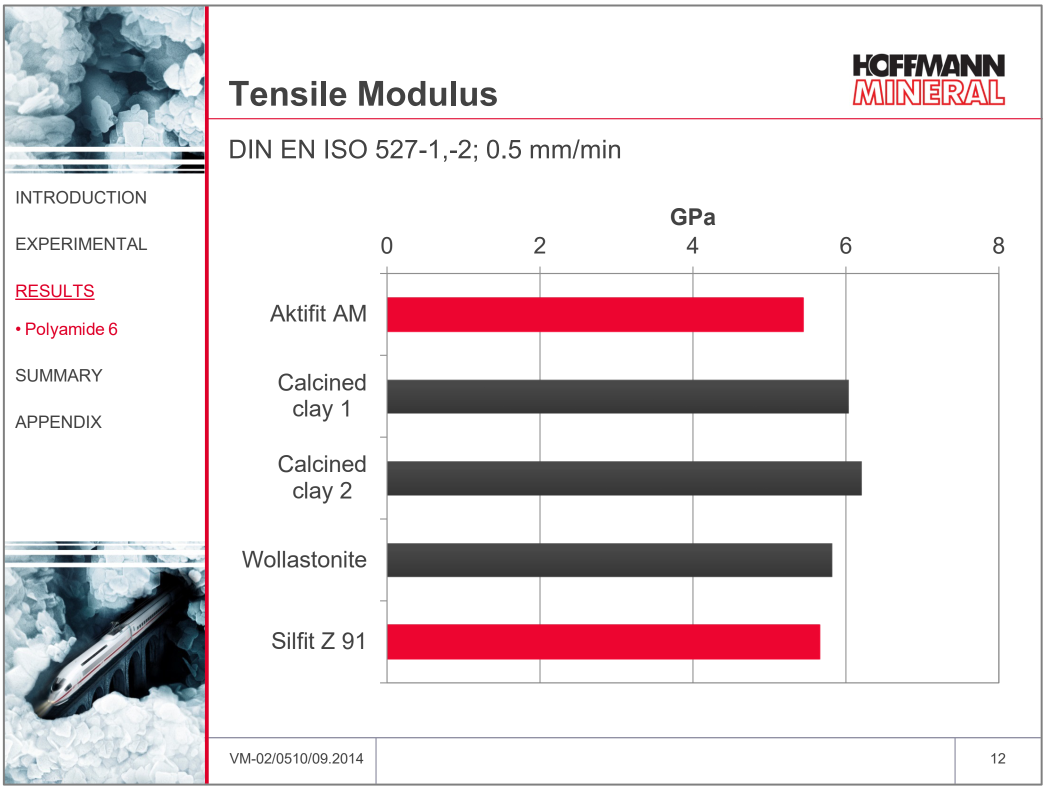
The tensile test did not show any noticeable differences in tensile strength. Both clays had a tendency towards slightly higher results.



Compared with the competitive fillers, the samples with Aktifit AM suffered breakage only at a markedly higher elongation. The results corresponded to an improvement of 40 % vs. the clays, and 85 % vs. wollastonite. This effect should prove useful in applications where the components during assembly have to withstand defined deformations, such as snap-fit connections.

3.5 Tensile modulus

In place of the stiffness of the material, the tensile modulus was determined in a tensile test at an extension rate of 0.5 mm/min.

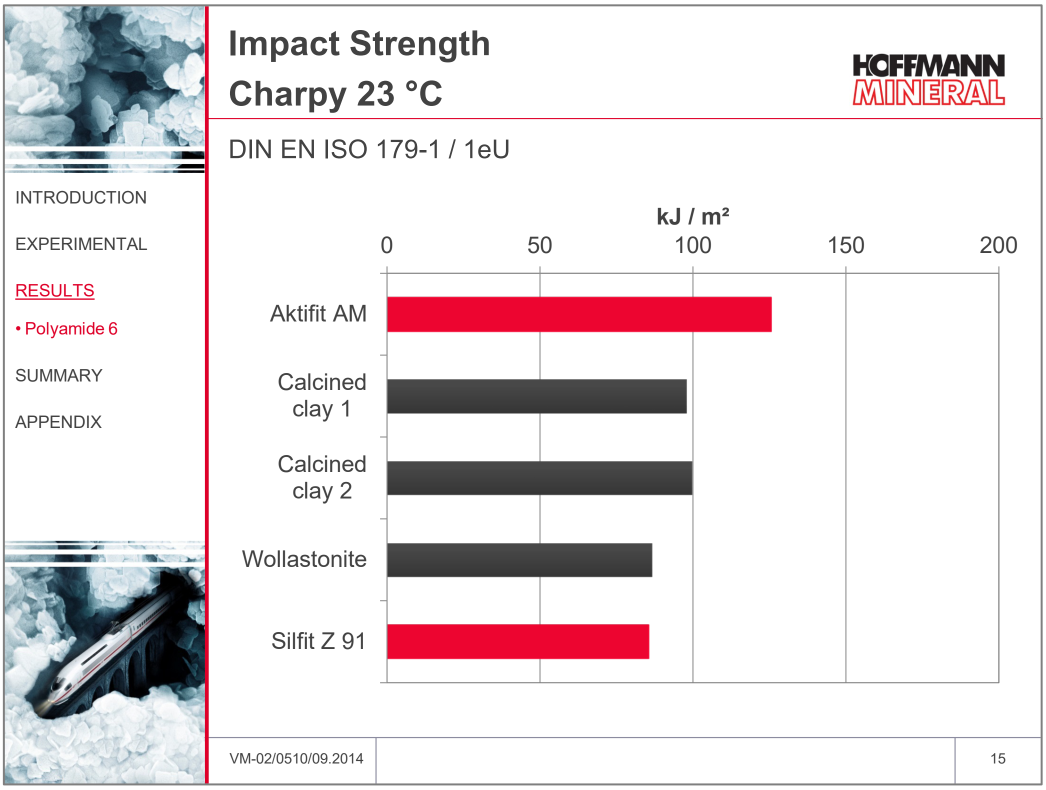


With the two clays, especially clay no. 2, the stiffness was somewhat higher. Aktifit AM arrived at a level almost similar to wollastonite.

3.6 Impact strength (unnotched)

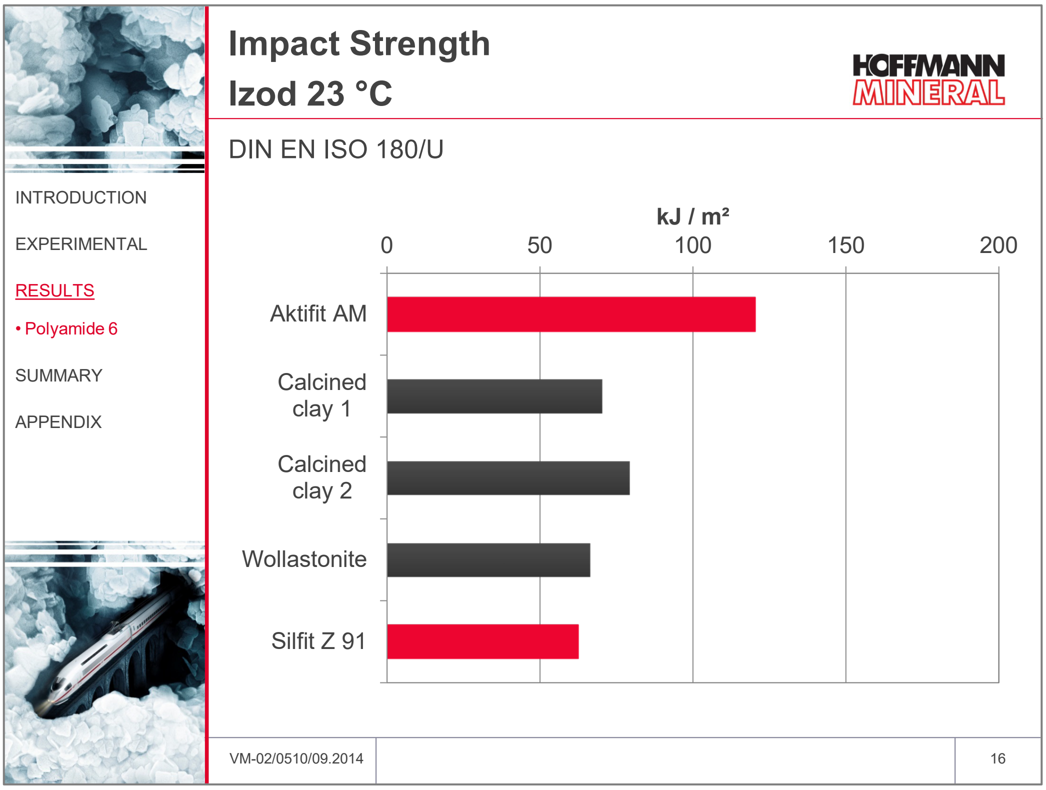
According to the Charpy method, the sample is supported unclamped at both ends and hit in the middle with a pendulum hammer. The test was run on unnotched standard samples 80 x 10 x 4 mm with the impact hitting the narrow side, i.e. the pendulum hits the 4 mm side of the sample.

In order to assure the breakage of all samples, the unnotched Charpy samples were tested throughout with an impact pendulum of an energy capacity of 15 J. When working with the frequently used 4 J pendulum, in view of the lower energy capacity only impact strength levels up to 100 J/m² max. can be differentiated. For higher levels - this way also for Aktifit AM - the result would be registered as „No Break“, and no statement about a quantification of the improvement could be given.



Aktifit AM was able to distinguish itself for impact strength vs. competitive fillers by improvements up to 40 %.

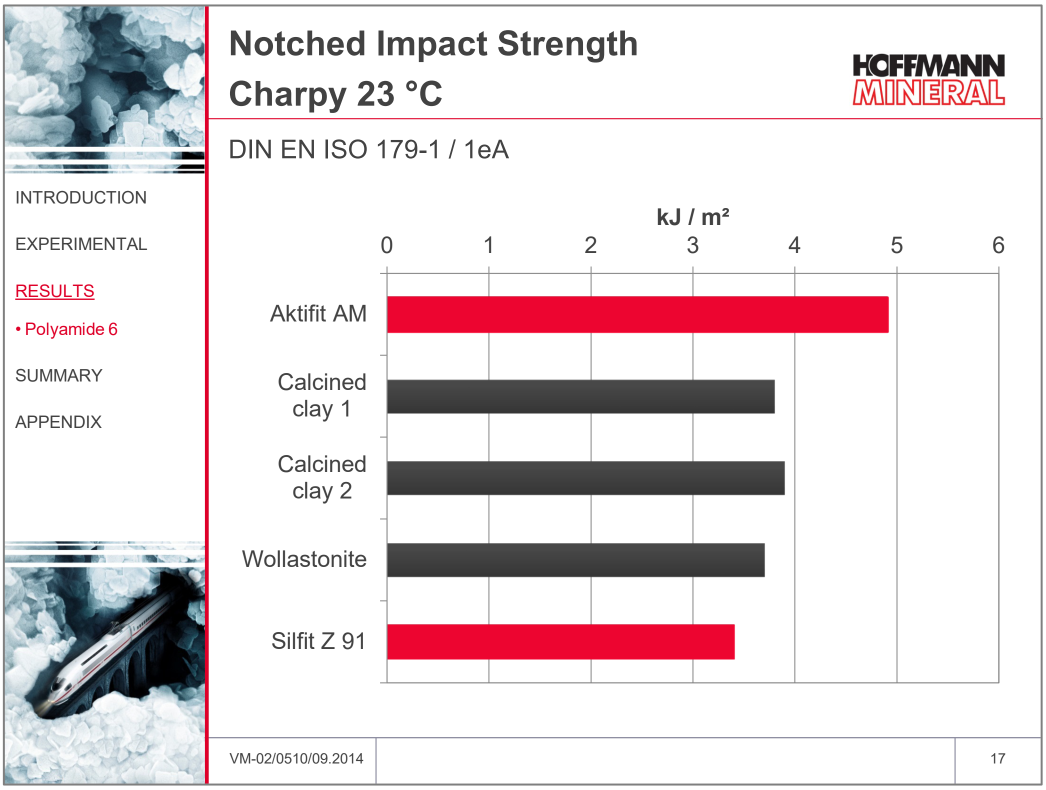
In the Izod test method, the sample is clamped on one side. The impact is given on the free end of the sample, again on the 4 mm side. The test was run with an 11 J pendulum on unnotched samples.



With this method, throughout somewhat lower results were obtained. On principle, the same ranking of the fillers came out, with Aktifit AM even still more superior to the competitive fillers.

3.7 Impact strength (notched)

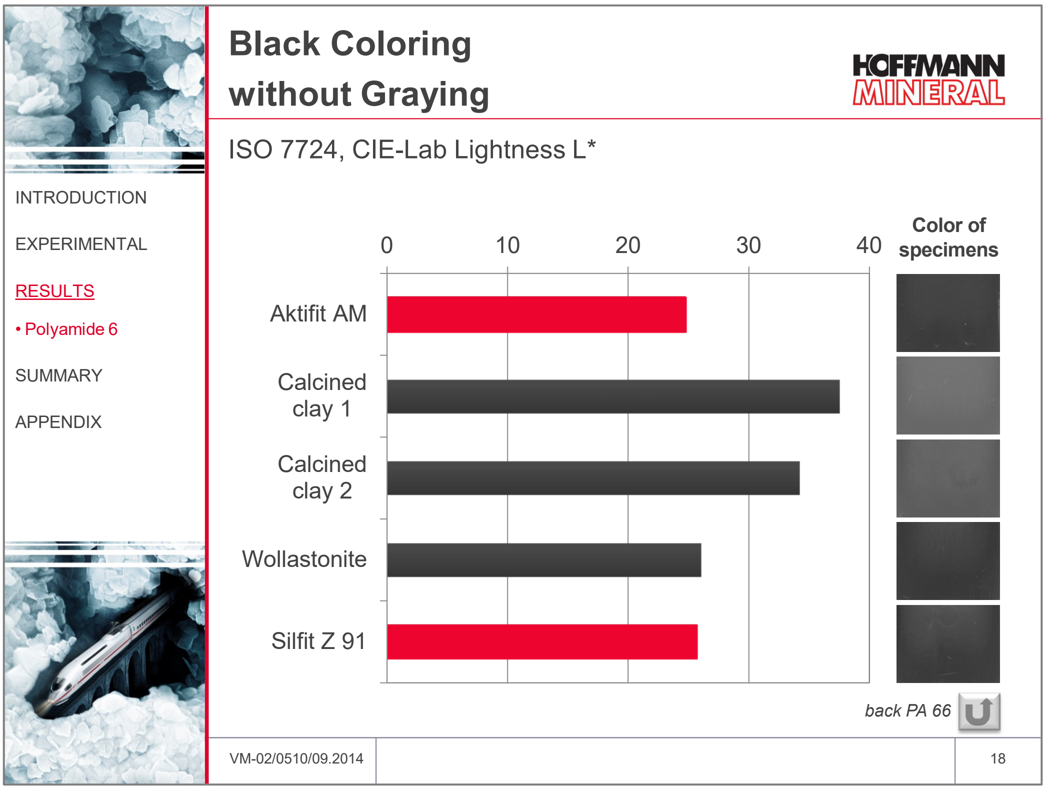
For this test, the standard samples are provided in the middle with a single notch of the preferred kind A (notch root radius 0.25 mm, rest ground width 8.0 mm). The impact strength was determined according to the standard test with an impact on the narrow side opposite the notch (edgewise), hit with a 0.5 J pendulum.



Here too, Aktifit AM showed an advantage with distinctly better results than the competitors.

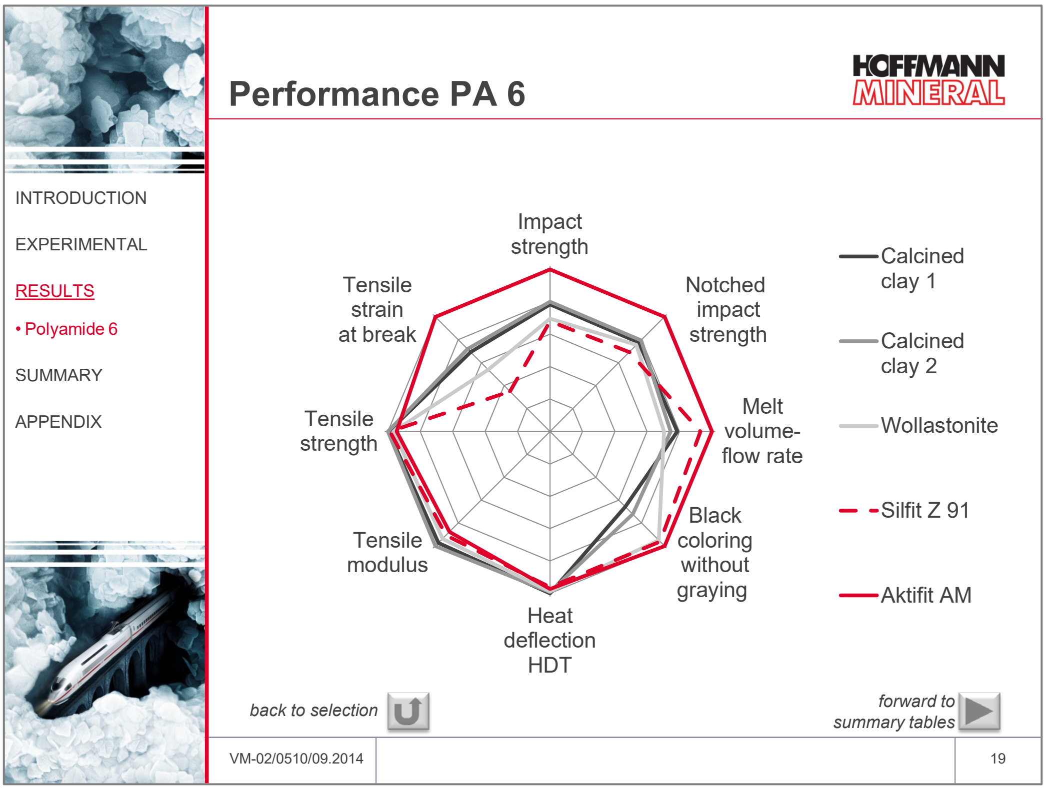
3.8 Black coloring without graying

The CIE-Lab lightness L* was determined with the configuration parameters light D65, test geometry d/8, standard observation angle 10°.
The small pictures on the right side of the graph show the shoulder area of the tensile specimens, photographed under the same light conditions.



In the black compounds, the two clays give rise to a distinct brightening resp. grey coloring. With Aktifit AM, Silfit 91 and wollastonite this was not the case. As a multitude of polyamide applications is based on black-colored parts, avoiding of grey tones or a lower need for pigment batch with Aktifit AM represent an additional benefit.

3.9 Overview: performance polyamide 6



In polyamide 6, Aktifit AM was able to convince particularly with regard to impact strength and strain at break. In comparison with the calcined clays tested, the flow properties were distinctly improved. Black colored compounds could be prepared with Aktifit AM without brightening or graying. The tensile strength was maintained on the level of wollastonite. Marginal setbacks existed only with respect to the stiffness (tensile modulus).

4 Results polyamide 66

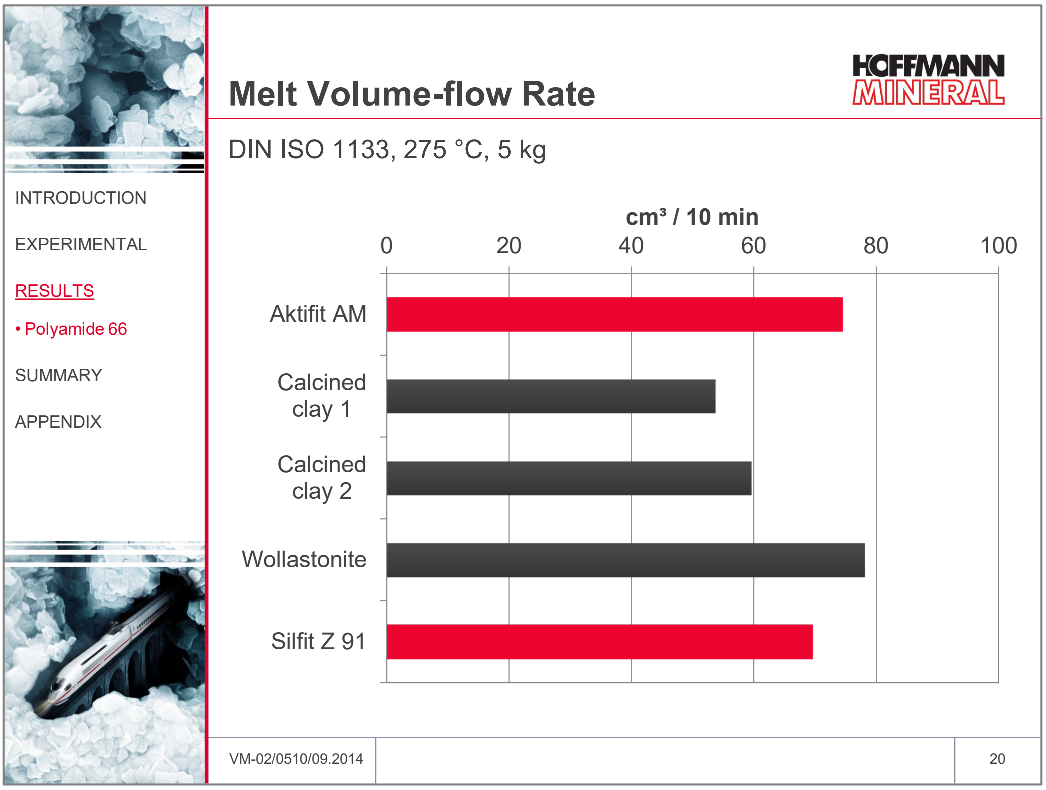
Two different polyamide 66 grades were used: Ultramid® A3K and Schulamid® 66 MV 2, both in the nature-colored version.

In view of the different base properties of the polymers, the results partly came out at varying levels. But the effects of the fillers and the ranking within each polymer were the same for both polyamide 66 grades.

The tests were run with the same samples types and conditions as with Polyamide 6. The moisture content of the dry-as-molded samples again was around 0.2 %.

The following presentations will go only into the test results for dry-as-molded samples based on Ultramid® A3K. Tables with individual results for the dry-as-molded and the conditioned samples from this polymer and those from Schulamid® 66 MV 2 are summarized in the appendix.

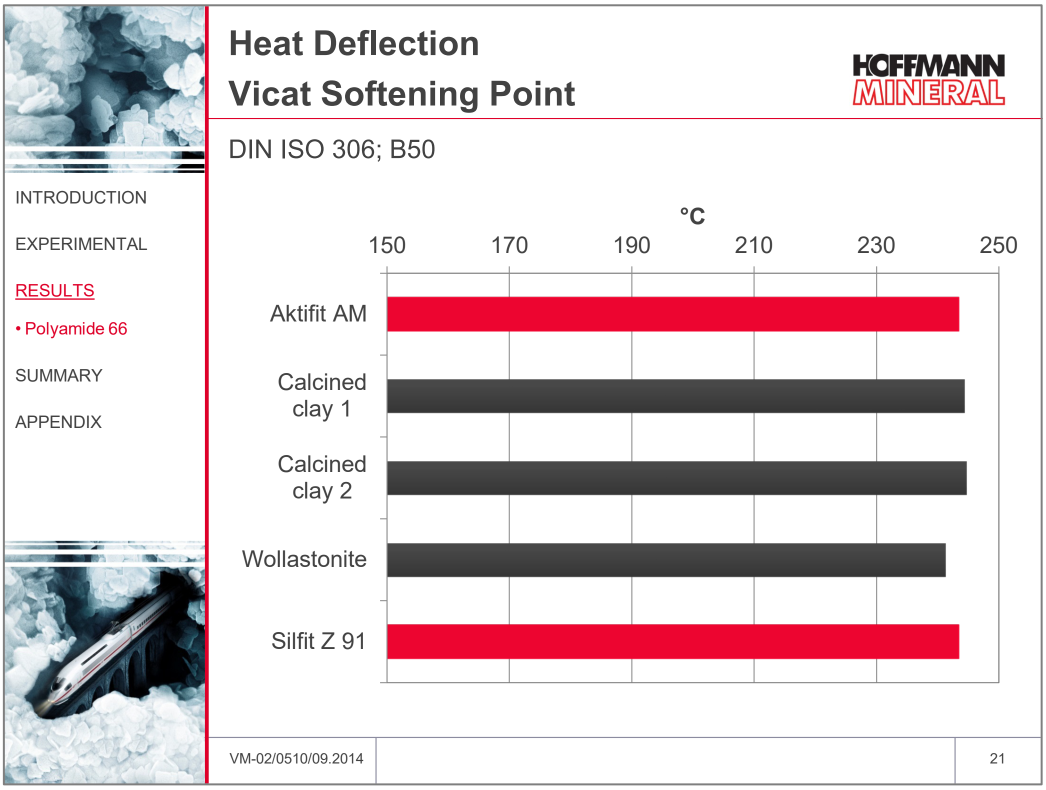
4.1 Melt volume-flow rate



Aktifit AM in polyamide 66 gave similar flow properties to wollastonite, and therefore came out markedly better then the clays tested.

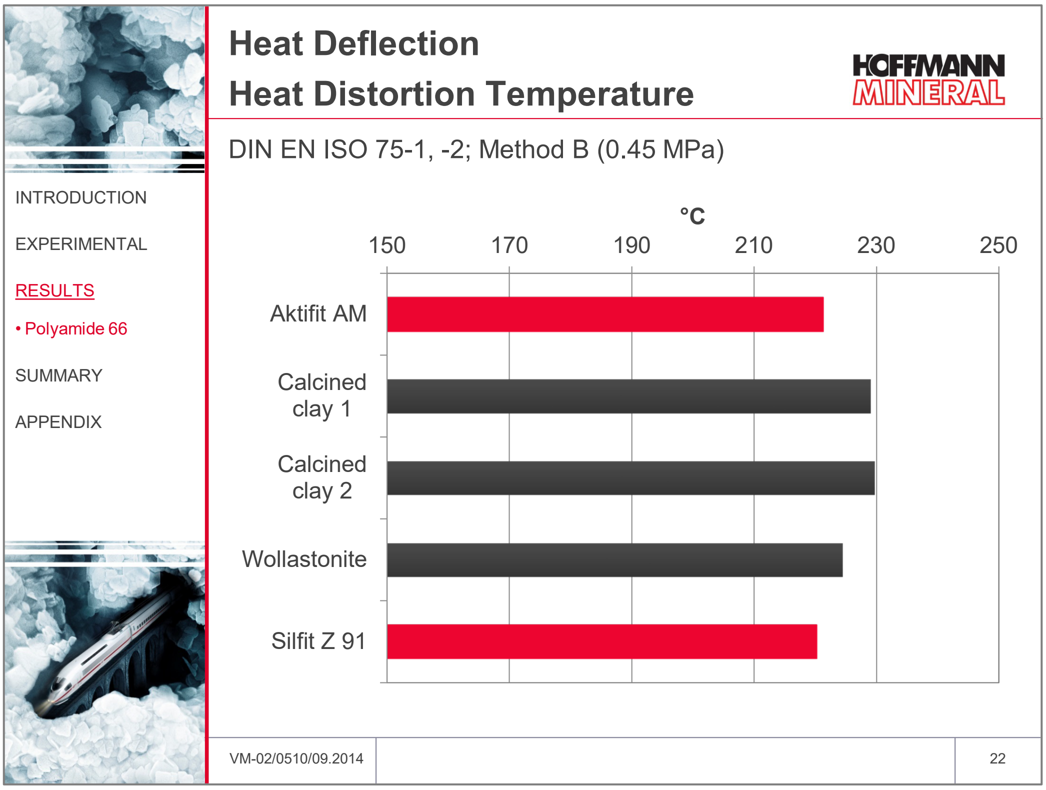
4.2 Heat deflection

The heat deflection in polyamide 66 was tested via the Vicat Softening Point as well as via the Heat Distortion Temperature (HDT).
The Vicat method determines the temperature when a defined steel pin under a defined weight load under a gradual temperature increase penetrates 1 mm into the sample. The test was carried out in an oil bath according to the method B 50, i.e. with a heating rate of 50 K/h and a weight load of 50 N.



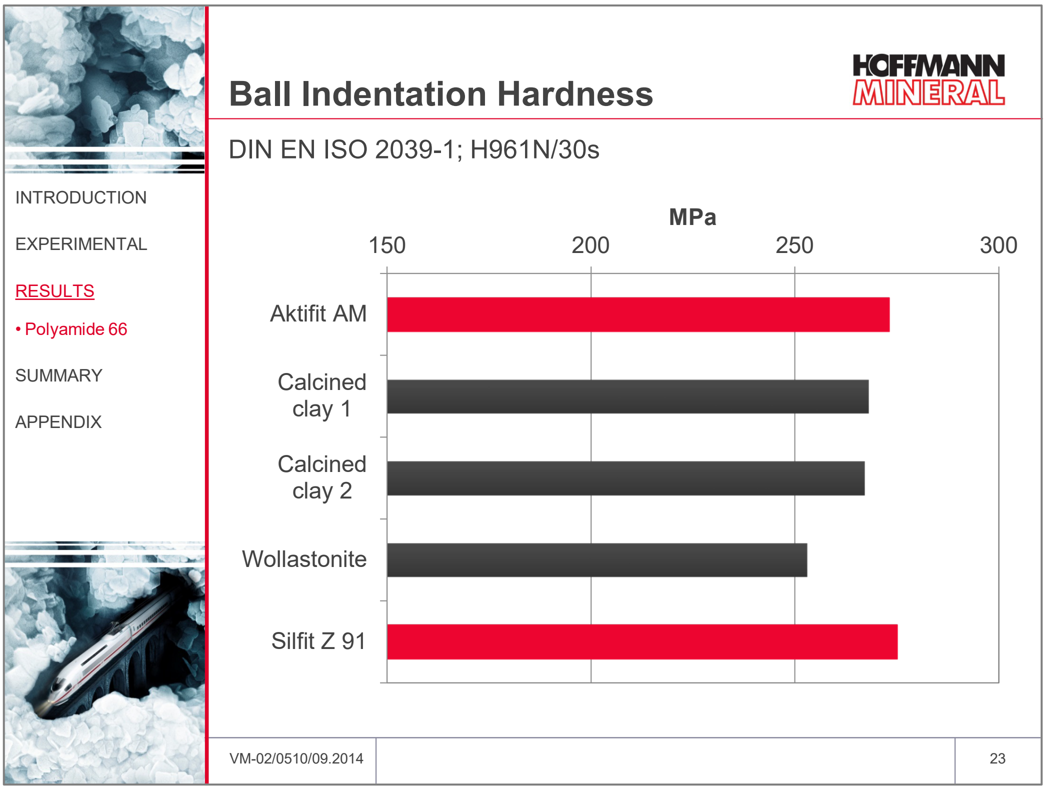
Between the fillers used no serious difference could be observed, just wollastonite did not quite come close to the overall level.

The HDT was determined, as was done for polyamide 6, according to Method B (0.45 MPa).



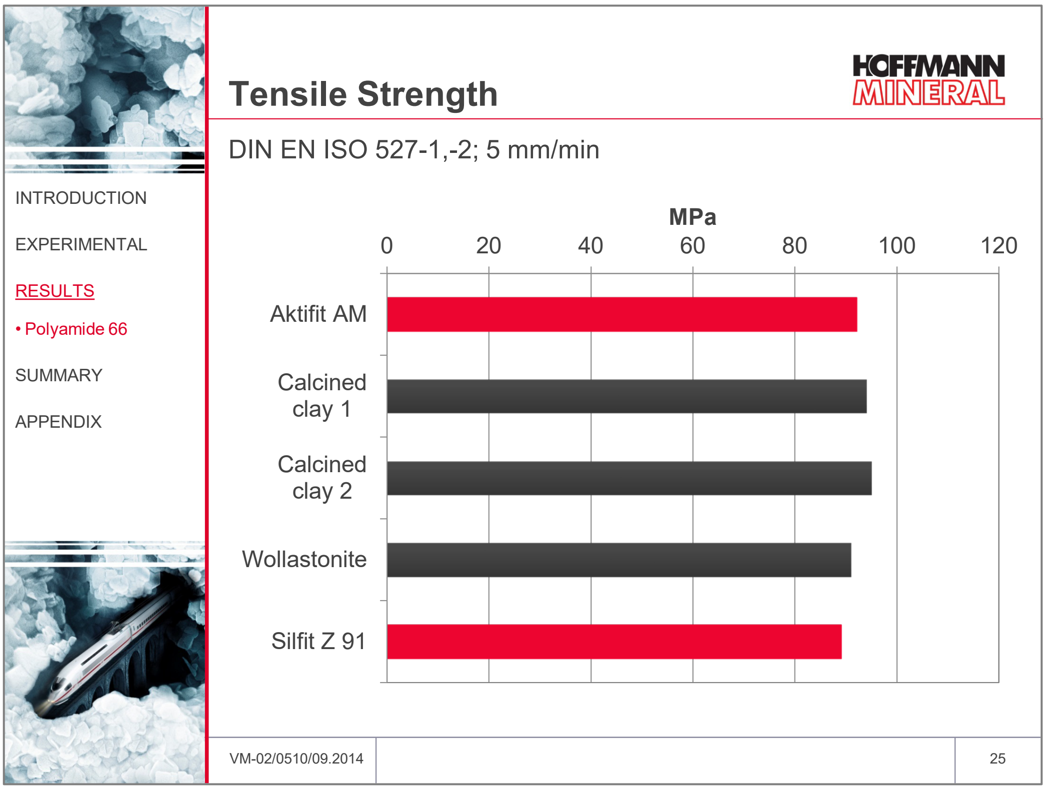
Both clays here give rise to a slightly higher HDT compared with wollastonite and Aktifit AM, which could be explained mainly by the somewhat different E-moduli.

4.3 Ball indentation hardness

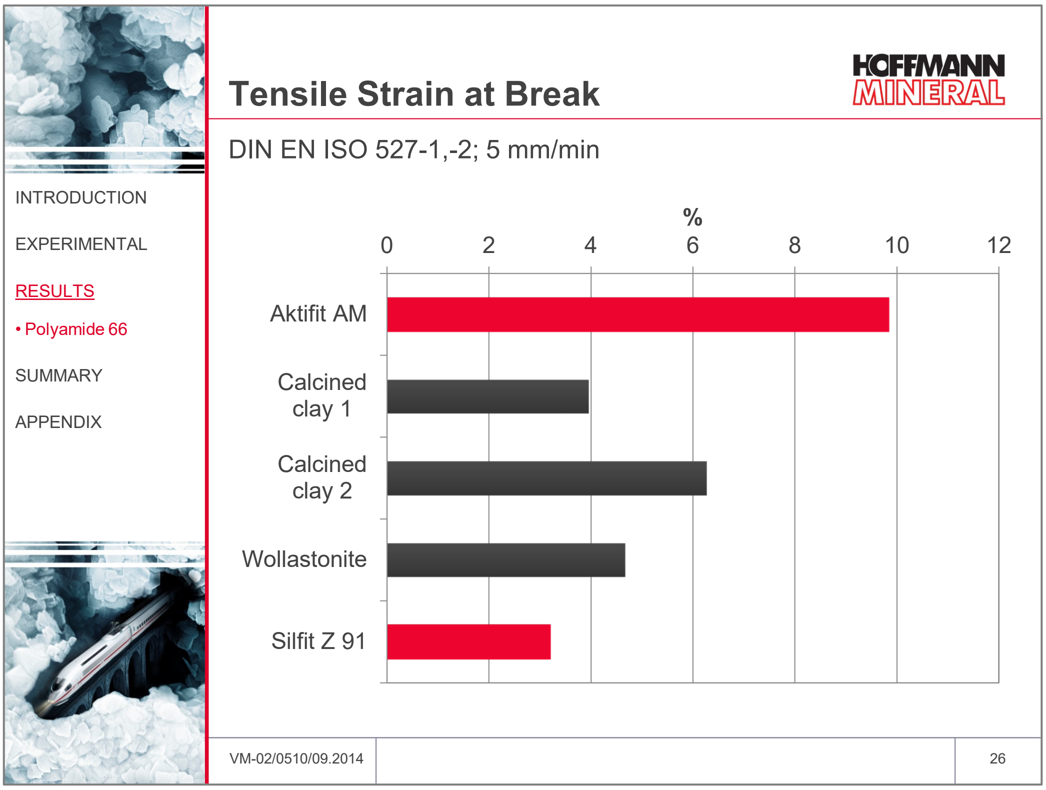


The ball indentation hardness with the calcined Neuburg Siliceous Earth grades was found at a higher level vs. the competitive fillers, especially wollastonite.

4.4 Tensile strength and tensile strain at break

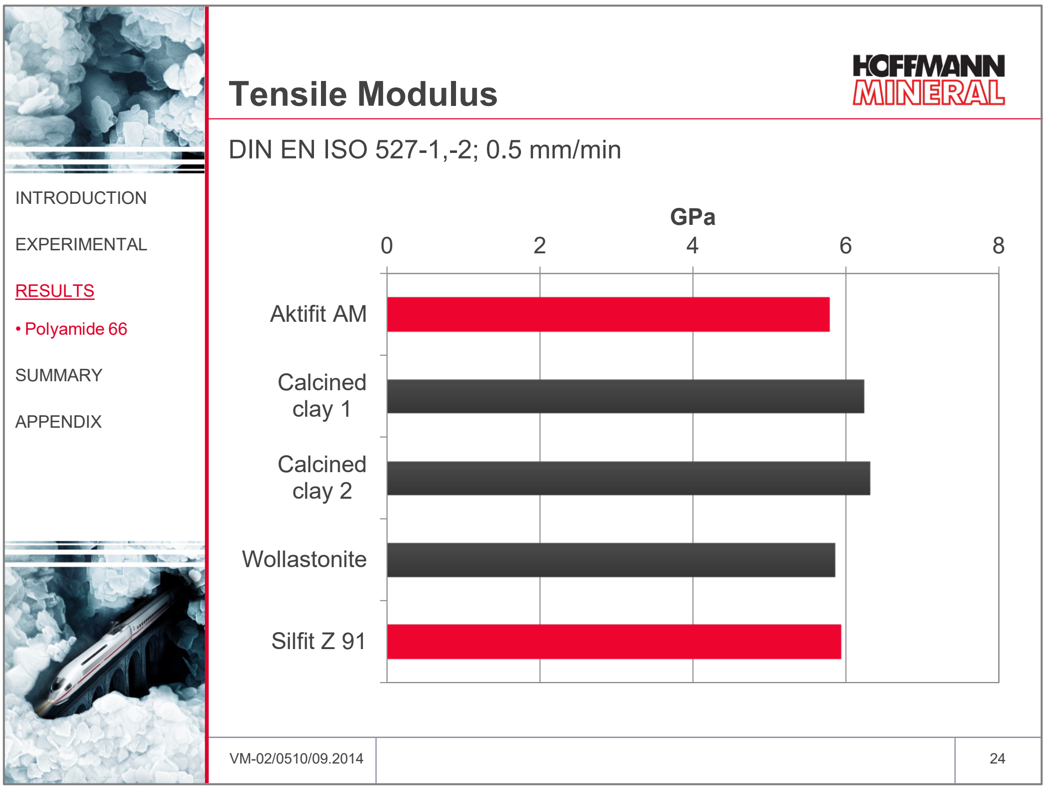


In the tensile tests, no significant differences were found for the tensile strength. The two clays tended towards marginally higher results.



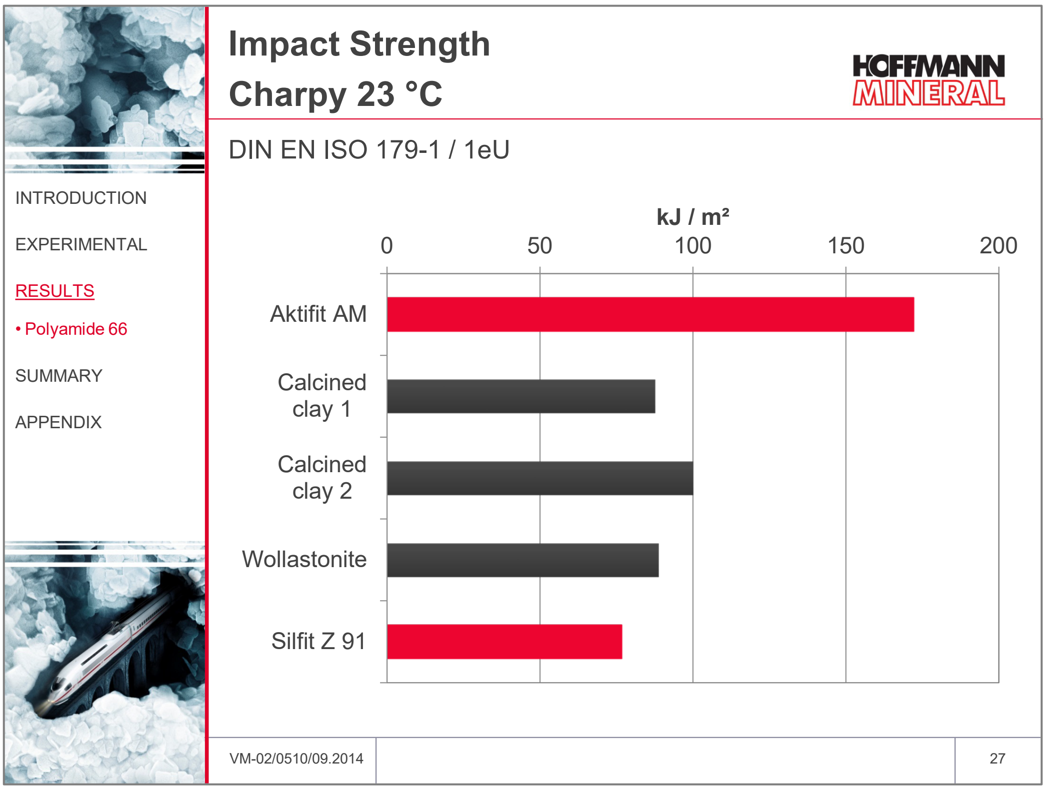
The breakage of the samples loaded with Aktifit AM occurred only at twice the strain of the competitive fillers. This represents an improvement of at least 50 % vs. the clays, and more than 100 % vs. Wollastonite. This effect should be of advantage for all applications where during assembly the components have to withstand certain deformations, such as in snap-fit connections.

4.5 Tensile modulus

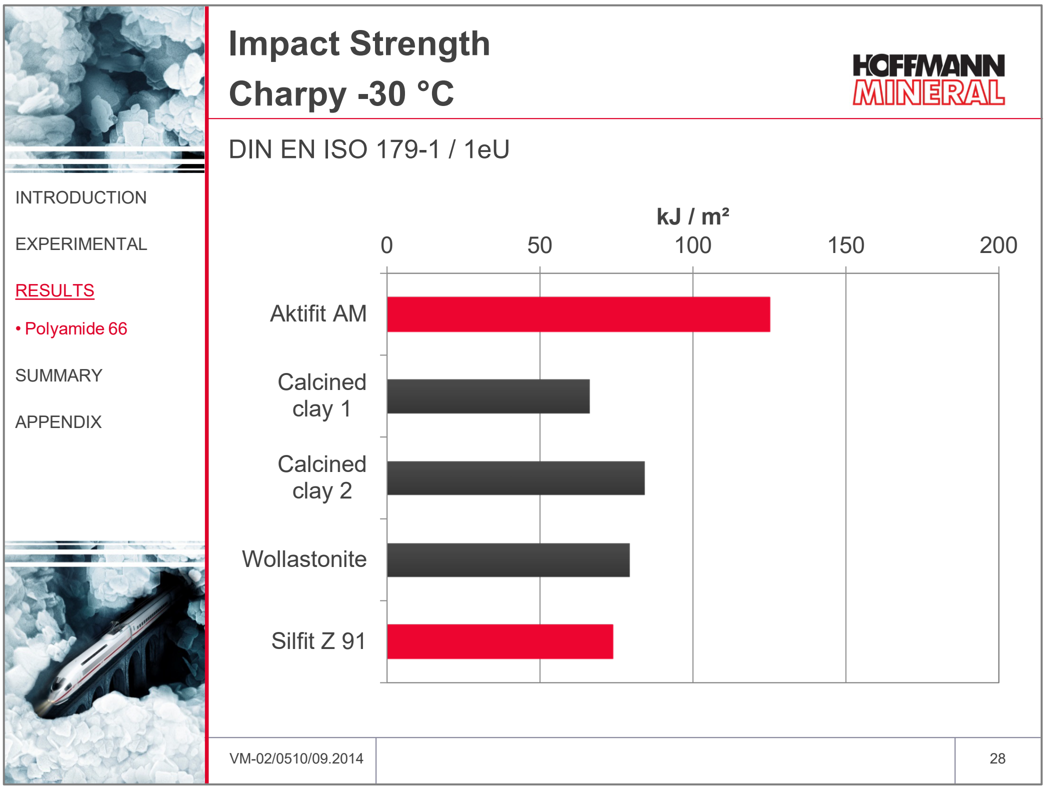


Both clays showed a somewhat higher stiffness. Aktifit AM came up to a level comparable with wollastonite.

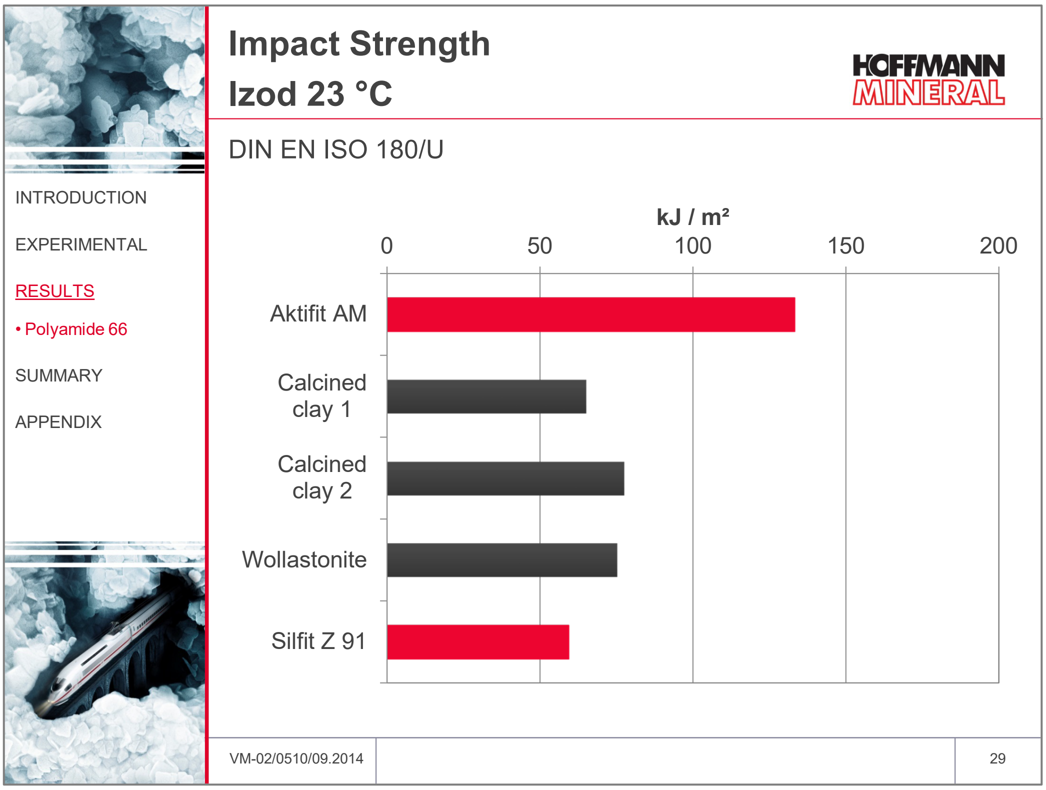
4.6 Impact strength (unnotched)



Aktifit AM, with an increase of up to 90 %, showed an impressively high Charpy impact strength, and thus marked advantages vs. the competitive fillers.

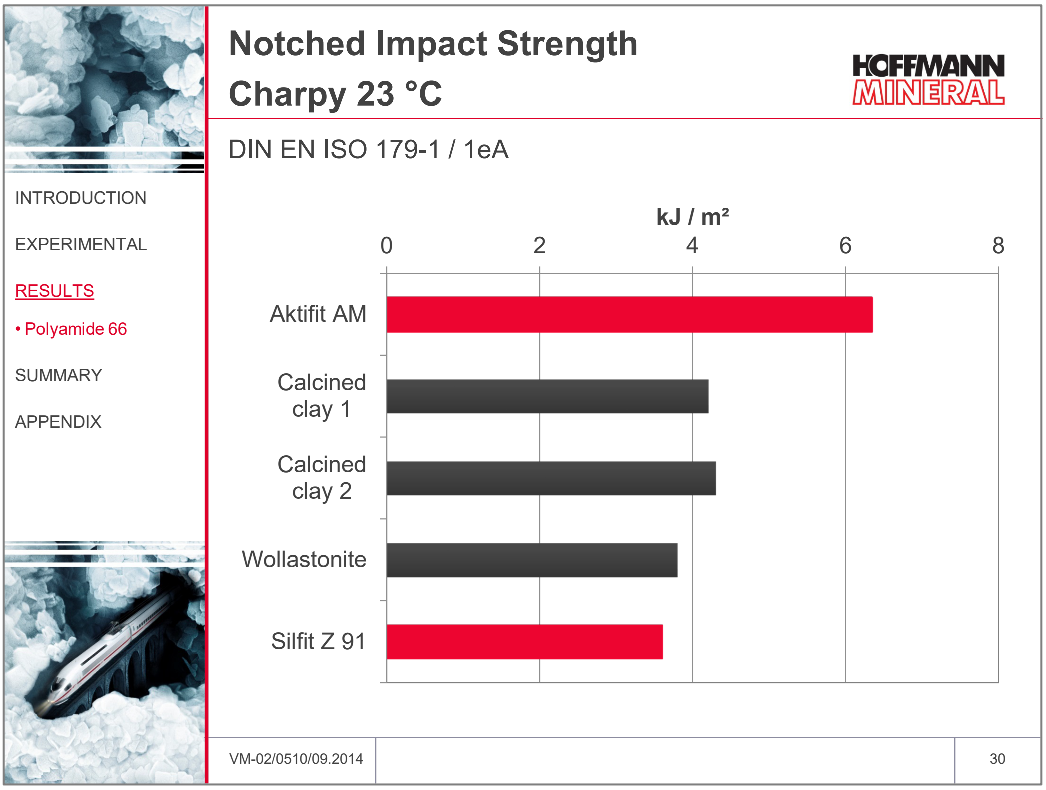


When tested at low-temperature, the overall level of the results decreased, but the ranking of the fillers and the significant advantage of Aktifit AM were maintained.
At -30 °C the impact strength of Aktifit AM was even higher than with the other fillers at room temperature.



With Polyamide 66 too the different test arrangement according to Izod resulted in overall lower impact strength results. The ranking of the fillers, however, again remained the same.

4.7 Impact strength (notched)

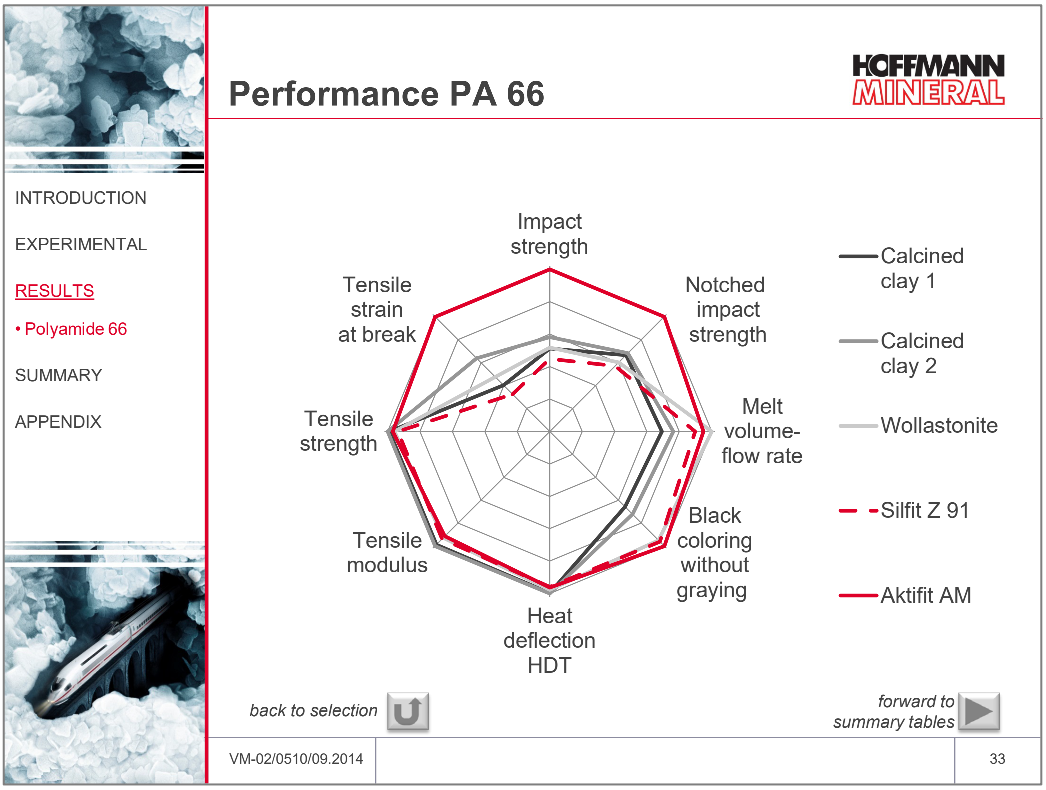


Also with notched samples Aktifit AM showed a distinct advantage vs. the competitive fillers.

4.8 Black coloring without graying

As the tests with polyamide 6 have shown (par. 3.8), the clays tested in back-colored compounds gave rise to a marked brightening or graying. With Aktifit AM and wollastonite, the compounds came out distinctly darker and with higher color depth. This has also been observed in earlier studies on black-colored polyamide 66 compounds.

4.9 Overview: performance polyamide 66



In the two polyamide 66 grades tested (Ultramid® A3K and Schulamid® 66 MV 2), Aktifit AM offered remarkable benefits with respect to impact strength and strain at break. Compared to the two calcined clays, better flow properties were evident, furthermore in black-colored compounds Aktifit AM made possible a deeper color without graying.

The other properties came out similar to the competitive fillers, just a little setback was observed for the stiffness (tensile modulus).

5 Summary

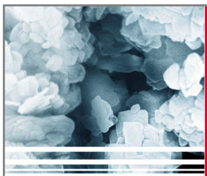
Compared to other mineral fillers suitable for low-warpage parts, Aktifit AM offers the following benefits:

- very low sieve residues
- easy feeding and metering
- good wetting and dispersion properties
- high melt flow rates
- low warpage or isotropic processing shrinkage
- excellent surface finish
- comparable heat deflection
- similar tensile strength
- no graying of black-colored compounds
- very high tensile strain at break
- excellent impact strength, even at low-temperature
- low-temperature impact strength very often higher than with competitive fillers at room temperature

In summary, Aktifit AM offers definite benefits with respect to processing and mechanical properties.

Application areas are basically where low warpage in combination with high surface quality is of importance along with easy melt flow, high strain (elongation) at break and high impact strength even in the dry-as-molded state.

6 Appendix: Summary tables



INTRODUCTION

EXPERIMENTAL

RESULTS

SUMMARY

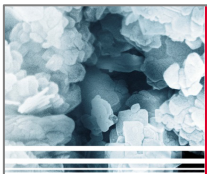
APPENDIX

Summary Table (1)
Durethan B 31 SK dry-as-molded

HOFFMANN MINERAL

		Calcined clay		Wollastonite	Calcined Neuburg Siliceous Earth	
		Grade 1	Grade 2	block-like particle structure	Silfit Z 91	Aktifit AM
Melt Volume-flow rate	cm³/10 min	77	73	69	91	98
Heat distortion temperature HDT/B	°C	189	188	187	182	184
Ball Indentation Hardness	MPa	218	217	204	230	221
Tensile Modulus	GPa	6.0	6.2	5.8	5.7	5.4
Tensile Strength	MPa	87	87	84	86	83
Tensile Strain at Break	%	7.2	7.5	5.6	3.6	10.4
Impact Strength Izod	kJ/m²	70 C	79 C	66 C	62 C	120 C
Impact Strength Charpy 23 °C -30 °C	kJ/m²	98 C 66 C	100 C 72 C	87 C 74 C	85 C 70 C	125 C 74 C
Notched Impact Strength Charpy 23 °C -30 °C	kJ/m²	3.8 C 3.3 C	3.9 C 3.2 C	3.7 C 3.1 C	3.4 C 2.6 C	4.9 C 3.6 C

VM-02/0510/09.2014 | 36



INTRODUCTION

EXPERIMENTAL

RESULTS

SUMMARY

APPENDIX

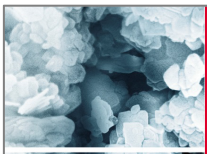
Summary Table (2)
Durethan B 31 SK conditioned

HOFFMANN MINERAL

		Calcined clay		Wollastonite	Calcined Neuburg Siliceous Earth	
		Grade 1	Grade 2	block-like particle structure	Silfit Z 91	Aktifit AM
Tensile Modulus	GPa	2.0	2.1	1.8	1.9	1.8
Tensile Strength	MPa	52	48	44	31	52
Tensile Strain at Break	%	18	10 [1]	25	19	30
Impact Strength Charpy 23 °C	kJ/m²	314 C	17 C [1]	236 C	105 C	N
Notched Impact Strength Charpy 23 °C	kJ/m²	6.0 C	3.2 C [1]	4.1 C	3.2 C	6.7 C

[1] After conditioning, the results of clay 2 were inexplicably low.

VM-02/0510/09.2014 | 37



INTRODUCTION

EXPERIMENTAL

RESULTS

SUMMARY

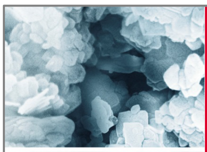
APPENDIX

Summary Table (3) Ultramid A3K dry-as-molded

HOFFMANN MINERAL

		Calcined clay		Wollastonite	Calcined Neuburg Siliceous Earth	
		Grade 1	Grade 2	block-like particle structure	Silfit Z 91	Aktifit AM
Melt Volume-flow rate	cm³/10 min	54	60	78	70	74
Vicat Softening Point	°C	244	245	241	243	243
Heat distortion temperature HDT/B	°C	229	230	224	220	221
Ball Indentation Hardness	MPa	268	267	253	275	273
Tensile Modulus	GPa	6.2	6.3	5.9	5.9	5.8
Tensile Strength	MPa	94	95	91	89	92
Tensile Strain at Break	%	4.0	6.3	4.7	3.2	9.8
Impact Strength Izod	kJ/m²	65 C	78 C	75 C	59 C	133 C
Impact Strength Charpy 23 °C / -30 °C	kJ/m²	88 C / 66 C	100 C / 84 C	89 C / 79 C	77 C / 74 C	172 C / 125 C
Notched Impact Strength Charpy 23 °C / -30 °C	kJ/m²	4.2 C / 3.7 C	4.3 C / 3.8 C	3.8 C / 3.5 C	3.6 C / 3.1 C	6.3 C / 3.9 C

VM-02/0510/09.2014 38



INTRODUCTION

EXPERIMENTAL

RESULTS

SUMMARY

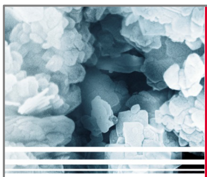
APPENDIX

Summary Table (4) Ultramid A3K conditioned

HOFFMANN MINERAL

		Calcined clay		Wollastonite	Calcined Neuburg Siliceous Earth	
		Grade 1	Grade 2	block-like particle structure	Silfit Z 91	Aktifit AM
Ball Indentation Hardness	MPa	125	119	117	119	114
Tensile Modulus	GPa	3.2	3.2	2.9	2.8	2.7
Tensile Strength	MPa	65	66	56	41	64
Tensile Strain at Break	%	13	18	15	11	25
Impact Strength Charpy 23 °C	kJ/m²	191 C	239 C	161 C	84 C	460 C
Notched Impact Strength Charpy 23 °C	kJ/m²	5.9 C	5.8 C	4.4 C	3.5 C	7.7 C

VM-02/0510/09.2014 39



INTRODUCTION

EXPERIMENTAL

RESULTS

SUMMARY

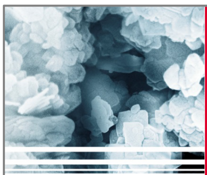
APPENDIX

Summary Table (5)
Schulamid 66 MV 2 dry-as-molded

HOFFMANN MINERAL

		Calcined clay		Wollastonite	Calcined Neuburg Siliceous Earth	
		Grade 1	Grade 2	block-like particle structure	Silfit Z 91	Aktifit AM
Melt Volume-flow rate	cm^3/10 min	47	45	57	54	59
Heat distortion temperature HDT/B	°C	221	223	215	218	214
Ball Indentation Hardness	MPa	232	218	209	237	234
Tensile Modulus	GPa	6.2	6.2	5.8	5.7	5.6
Tensile Strength	MPa	90	92	88	86	86
Tensile Strain at Break	%	4.7	7.4	4.5	3.1	8.5
Impact Strength Izod	kJ/m^2	71 C	79 C	73 C	66 C	134 C
Impact Strength Charpy 23 °C / -30 °C	kJ/m^2	97 C 69 C	103 C 84 C	84 C 74 C	88 C 81 C	159 C 108 C
Notched Impact Strength Charpy 23 °C / -30 °C	kJ/m^2	4.1 C 3.7 C	4.1 C 3.8 C	3.9 C 3.7 C	3.7 C 3.4 C	6.0 C 4.2 C

VM-02/0510/09.2014 40



INTRODUCTION

EXPERIMENTAL

RESULTS

SUMMARY

APPENDIX

Summary Table (6)
Schulamid 66 MV 2 conditioned

HOFFMANN MINERAL

		Calcined clay		Wollastonite	Calcined Neuburg Siliceous Earth	
		Grade 1	Grade 2	block-like particle structure	Silfit Z 91	Aktifit AM
Tensile Modulus	GPa	2.6	2.7	2.3	2.4	2.3
Tensile Strength	MPa	60	62	53	38	60
Tensile Strain at Break	%	18	21	16	17	28
Impact Strength Charpy 23 °C	kJ/m^2	242 C	288 C	186 C	108 C	N (455 C)
Notched Impact Strength Charpy 23 °C	kJ/m^2	6.0 C	6.2 C	5.4 C	3.6 C	9.1 C

back to selection

VM-02/0510/09.2014 41