Non-black fillers in peroxide cured EPDM cable insulation compounds

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Introduction

- Cable insulation compounds are subject to many different requirements, as for instance listed in DIN VDE 0207 Part 20 EI4.

- Appropriate EPDM compounds are made up with fillers which can markedly affect the processing and final performance properties.

- The profile required includes good mechanical properties, excellent extrusion characteristics as well as high electrical resistivity also after water immersion.

Design of Experiments

- Insulation compounds for wire and cables based on EPDM, peroxide cured, according to DIN VDE 0207 Part 20 EI4.
- Required properties – taken from parts of this standard:

	Tensile strength	Elongation at break	Volume resistivity1)
Before Aging	> 5.0 MPa	> 200 %	> 10^{12} W x cm
After hot air aging 168 h / 100 °C	> 4.2 MPa < +/- 25 % Change	> 200 % < +/- 25 % Change	

1) Only valid for national constructions

- As to resistivity testing, an additional water immersion test was carried out as an important criterion for differentiating between the fillers.
- The test program included potentially suitable fillers for this application, as summarized in the following table.
- Also blends with whiting, as common in the industry, were considered in appropriate variations.

Fillers Selected

Characteristics

	Particle size [µm]		Oil Absorption [g/100g]	Specific Surface area BET [m²/g]	Functiona-lization
	d_{50}	d_{97}			
American hard clay	3.7	31	50	25	none
English calcined clay	3.6	19	60	6.5	none
Sillitin Z 86	1.9	8	55	11	none
Surface treated American calcined clay	3.0	18	61	7.5	Vinyl silane
Aktisil VM 56	2.2	10	45	7.0	Vinyl
Whiting	2.4	13	28	4.9	none

Base Formulation

EPDM – 70 Shore A

	phr	
Buna AP 258 (Buna EP G 3963)	130.0	130.0
Stearic acid	1.0	1.0
Zinkoxyd aktiv	5.0	5.0
Paraffin 54/56	4.0	4.0
Filler	225.0	125.0
Whiting	-	100.0
Sunpar 2280	15.0	15.0
Vulkanox HS/LG	1.0	1.0
Vulkanox MB/MG	0.5	0.5
TAC GR 50 %	2.0	2.0
Perkadox 14/40 pd	8.0	8.0
Total	391.5	391.5

Preparation and Curing of the Compound

- **Preparation**

  Open mill Ø 150 x 300 mm

  Batch volume: approx. 500 cm³

  Temperature: 60 °C

  Mixing cycle: approx. 25 min.

- **Curing**

  Press, 180 °C, t_{90} + 10 %

Extrusion

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According to ASTM D 2230

- Schwabenthan - Extruder Polytest 30R

  D = 30 mm, L/D-Ratio = 15

- Temperature:

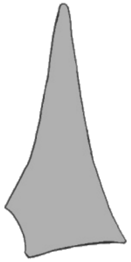
  70 / 70 / 110 °C

- Variations:
  - Constant screw speed 50 rpm
  - Constant output rate 1 m/min

- Garvey extrusion rating:

  First digit: Die swell
  Third digit: Surface appearance

- Assessment
  1 = poor to 4 = very good



Volume Resistivity

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DIN IEC 93

Test outline:

- Dimension of plates: 10 x 10 cm
- Thickness of plates: about 2 mm
- Electrical relaxation: 2 h / 70 °C
- Electrode set-up: circular plate electrode with protective ring
- Test method: Voltage/Amperage method
- Test voltage: > 10^{12} Ωxcm: 500 V; < 10^{12} Ωxcm: 100 V
- Recording time: 1 min. after application of voltage
- Test temperature: 23 °C
- Water immersion: 7 / 14 / 28 days at 70 °C in deionized water
- Evaluation:

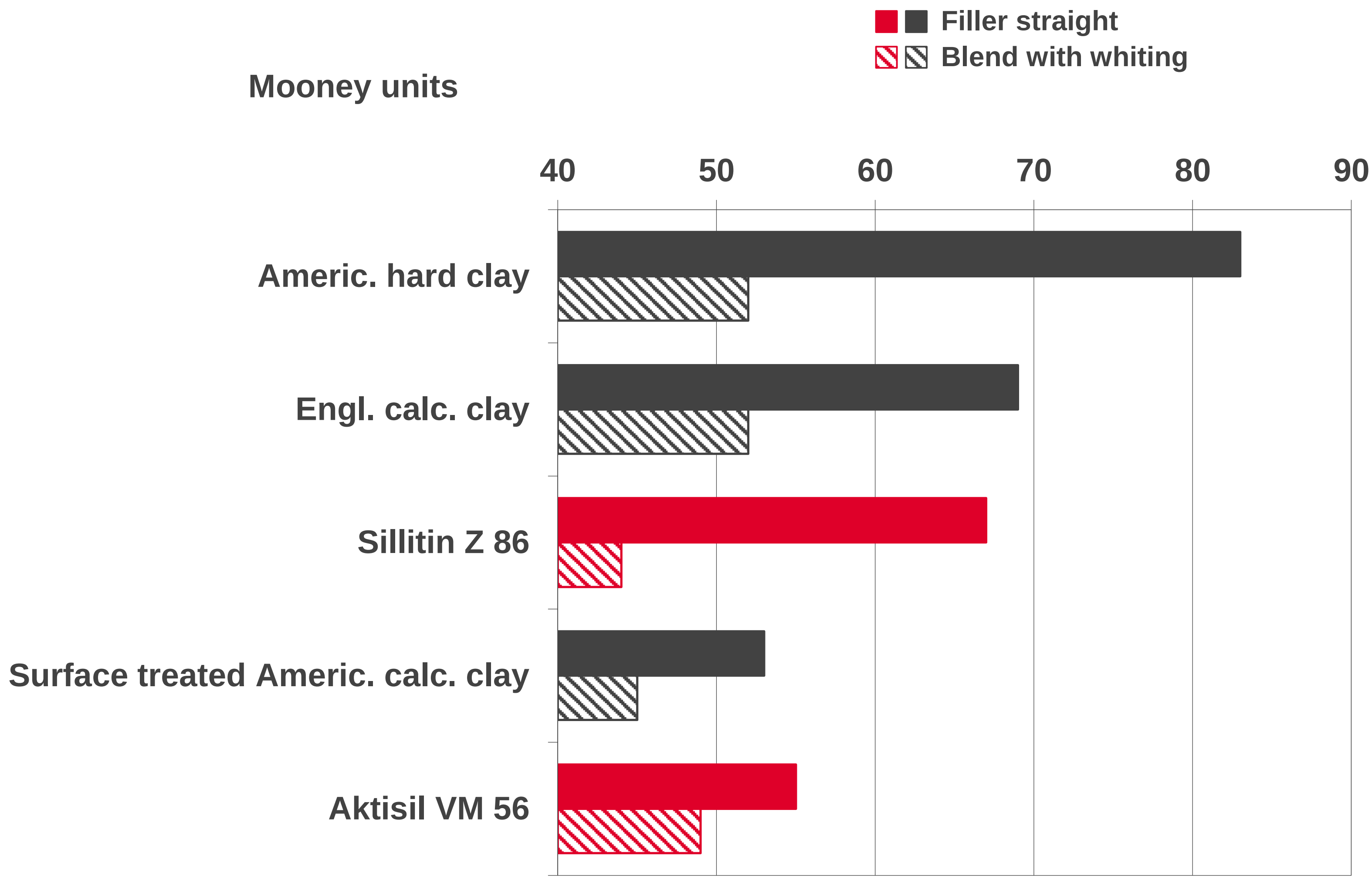
$$\rho = R_X * A / h$$

with

ρ	resistivity in Ωxcm
R_X	volume resistance in Ω
A	effective surface area of the protected electrode (24 cm²)
h	median thickness of the test plate in cm

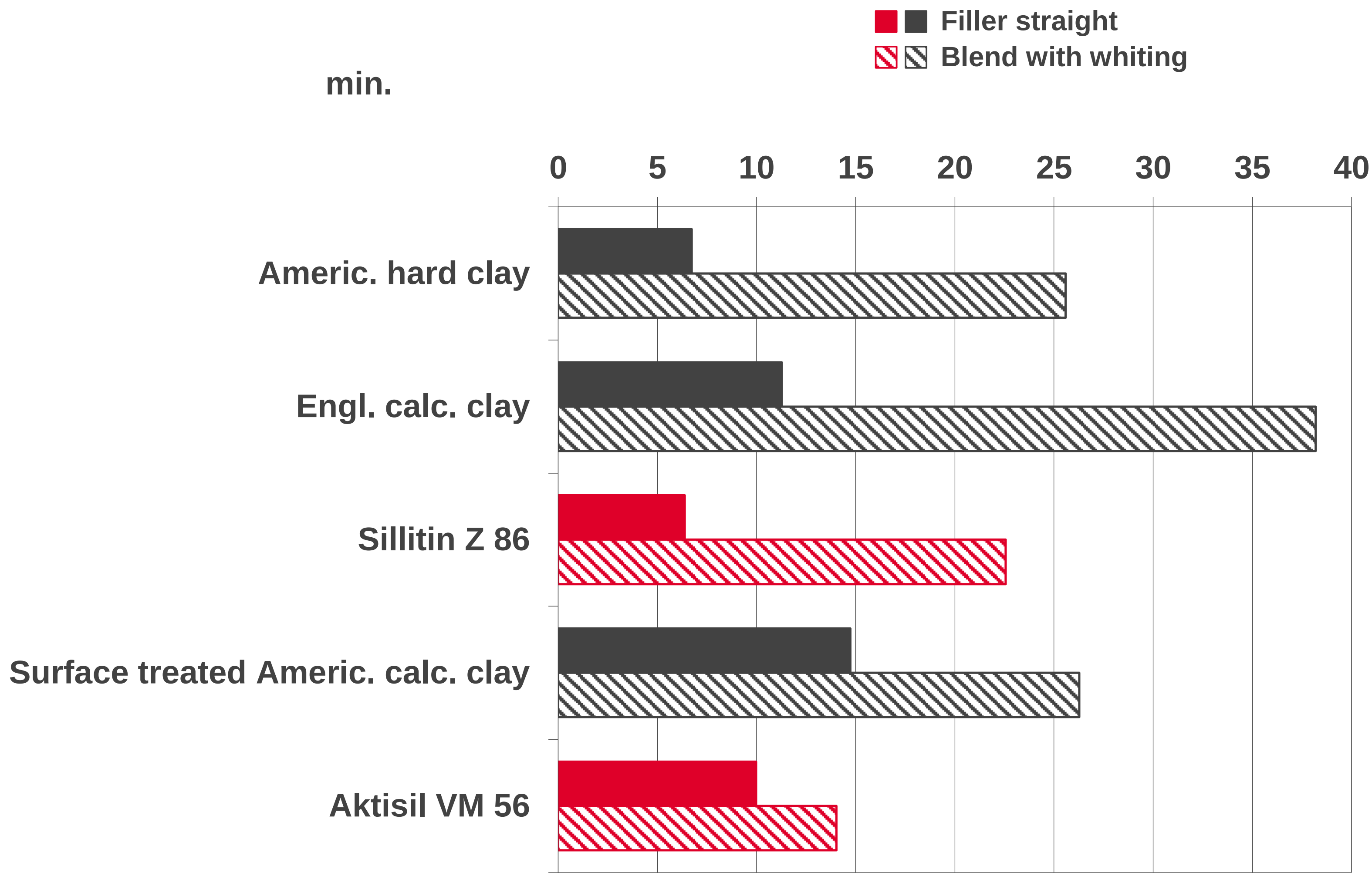
Mooney Viscosity

DIN 53 523 Part 3, ML 1+4 120 °C



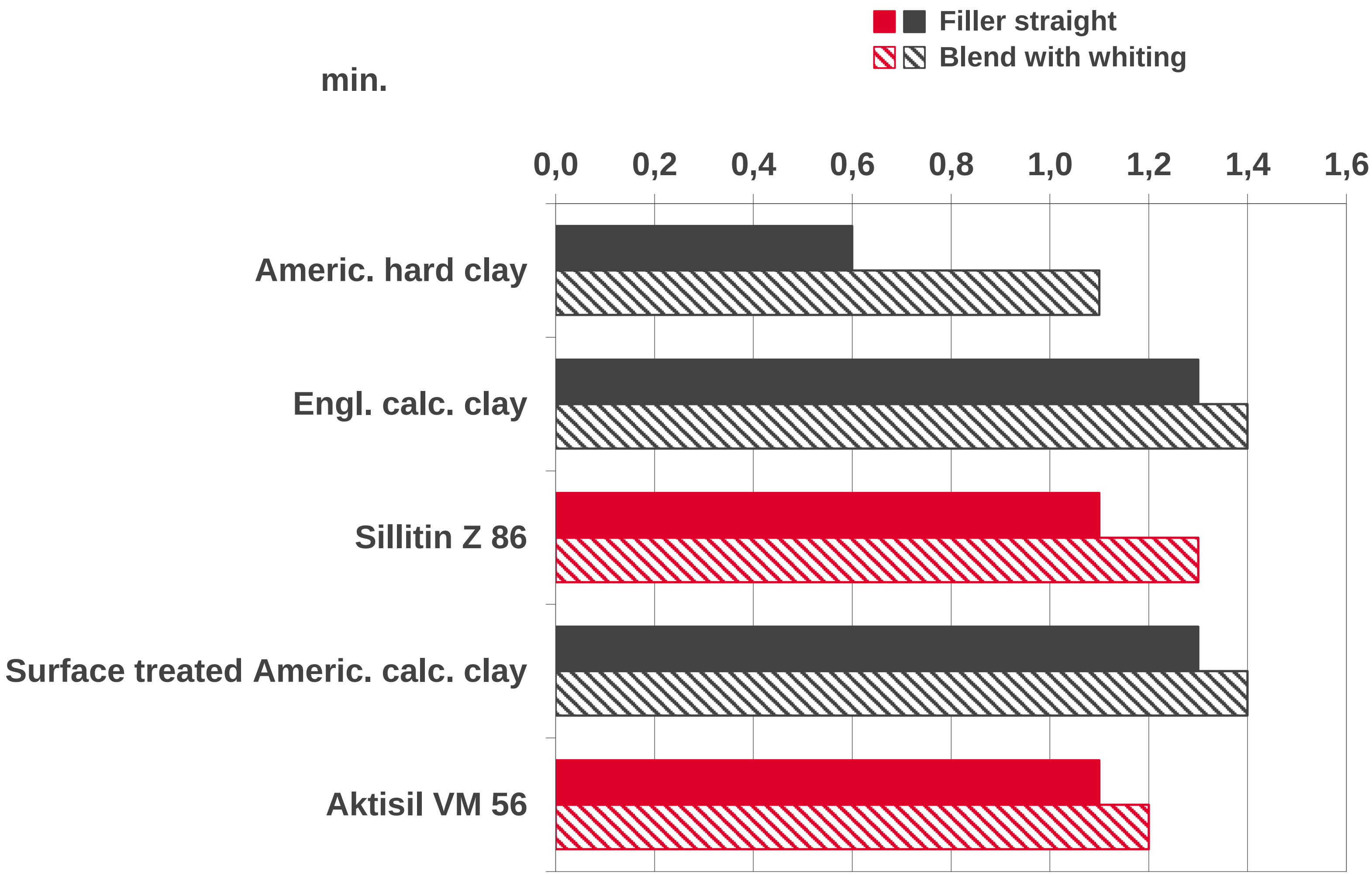
Mooney Scorch

DIN 53 523 Part 3, ML +5 120 °C



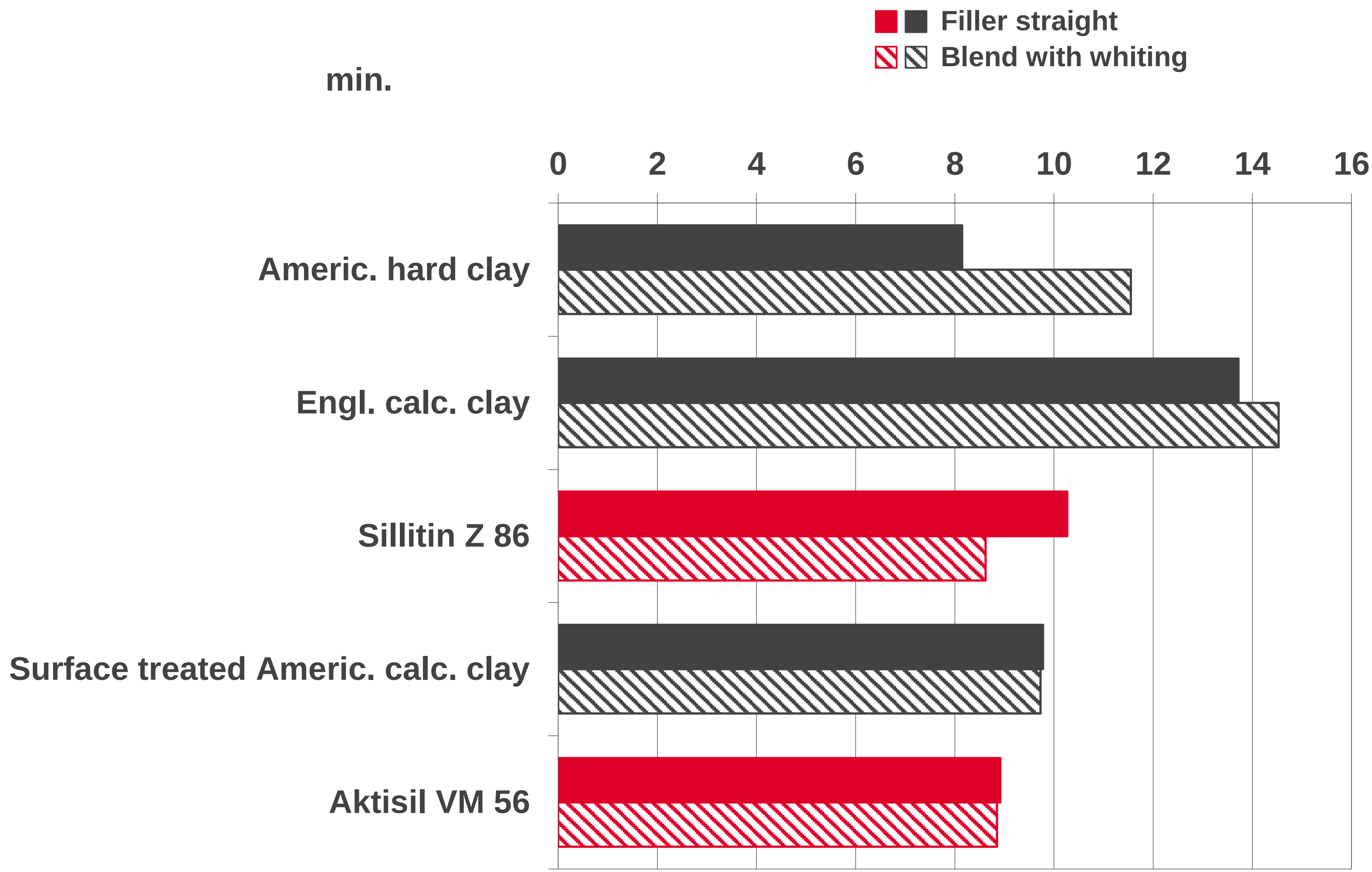
Conversion Time t_5

DIN 53 529-A3, Frank Linear Shear Vulcameter, 180 °C

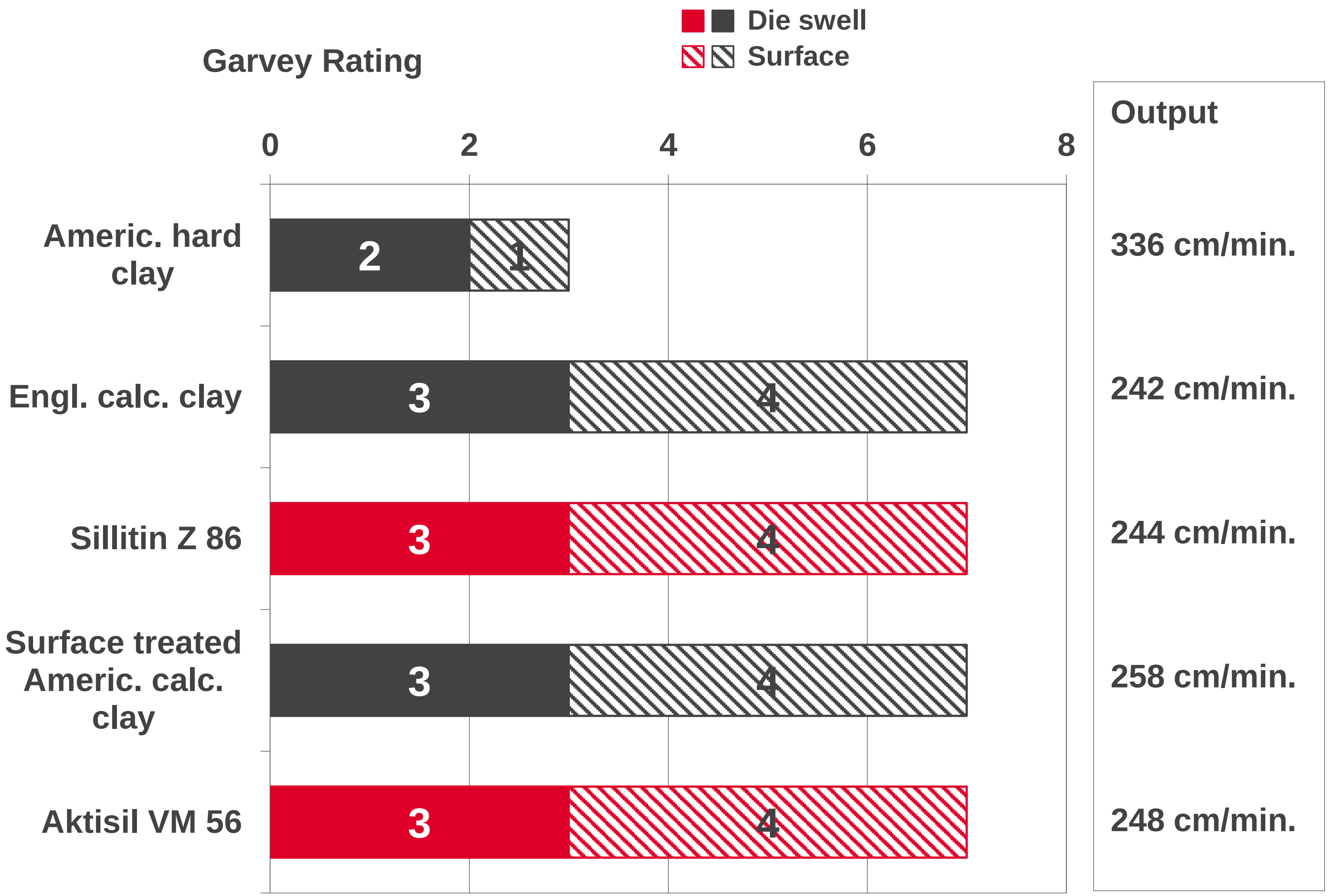


Conversion Time t_{90}

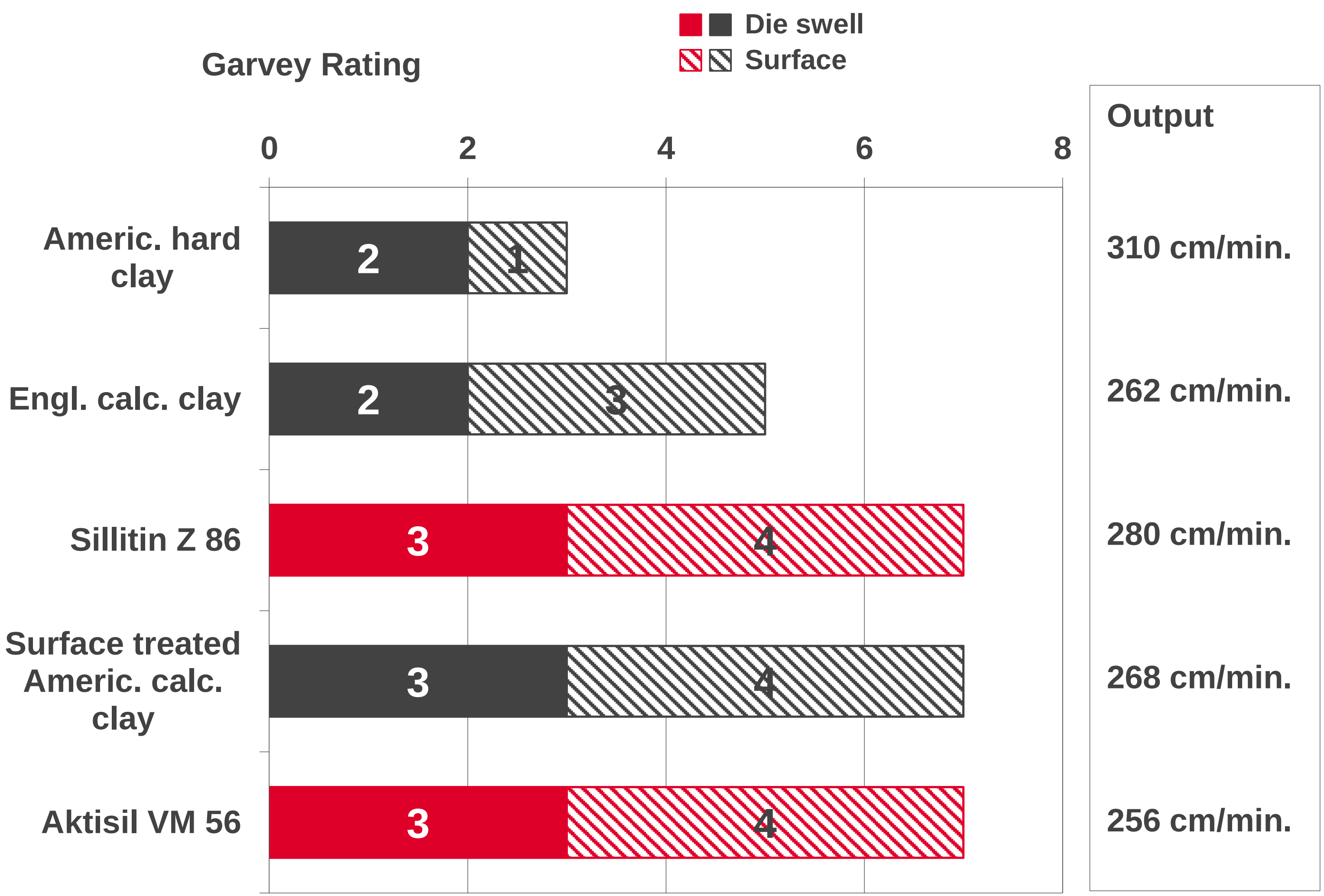
DIN 53 529-A3, Frank Linear Shear Vulcameter, 180 °C



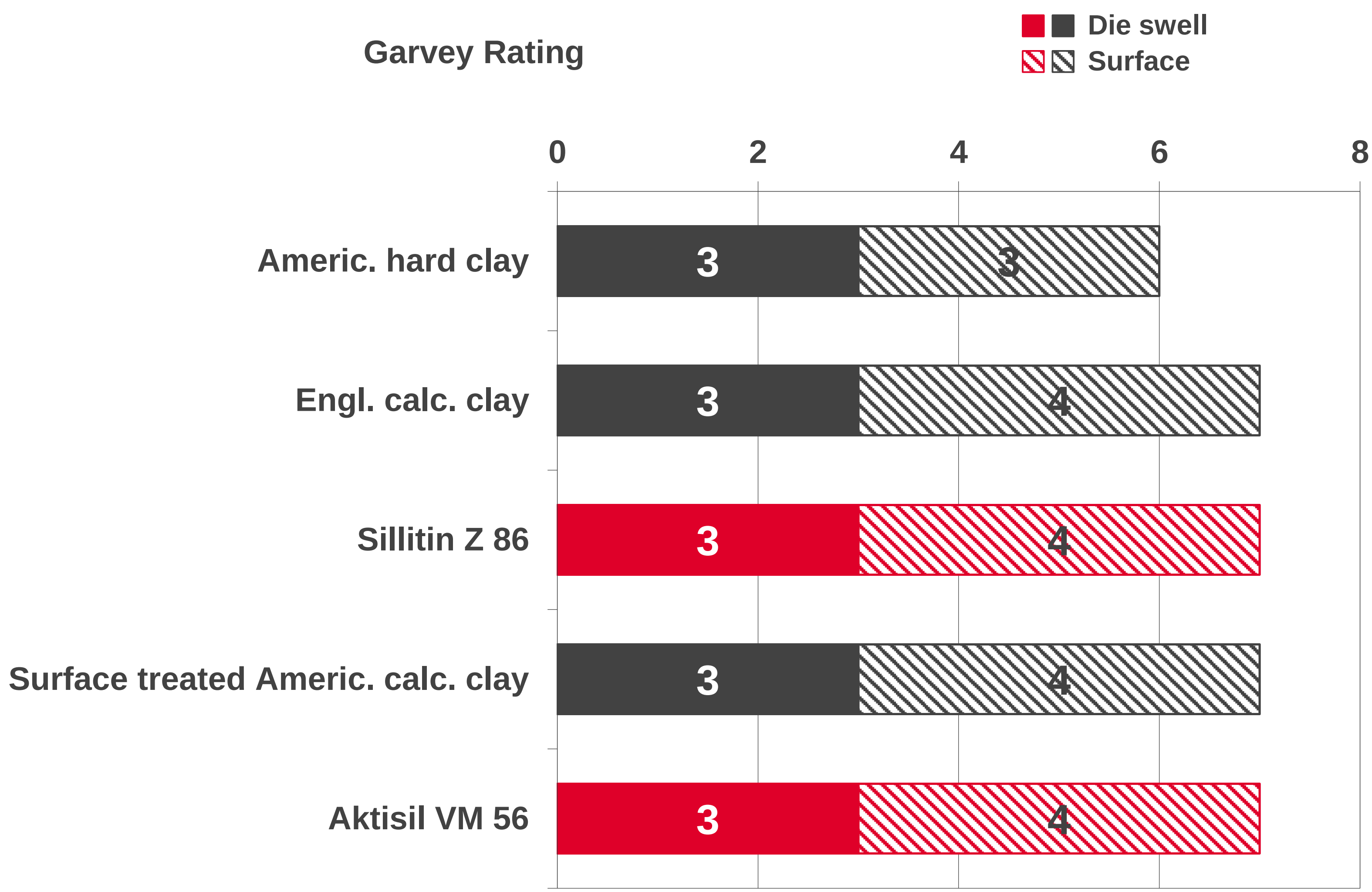
Garvey Extrusion 50 rpm
Filler Straight



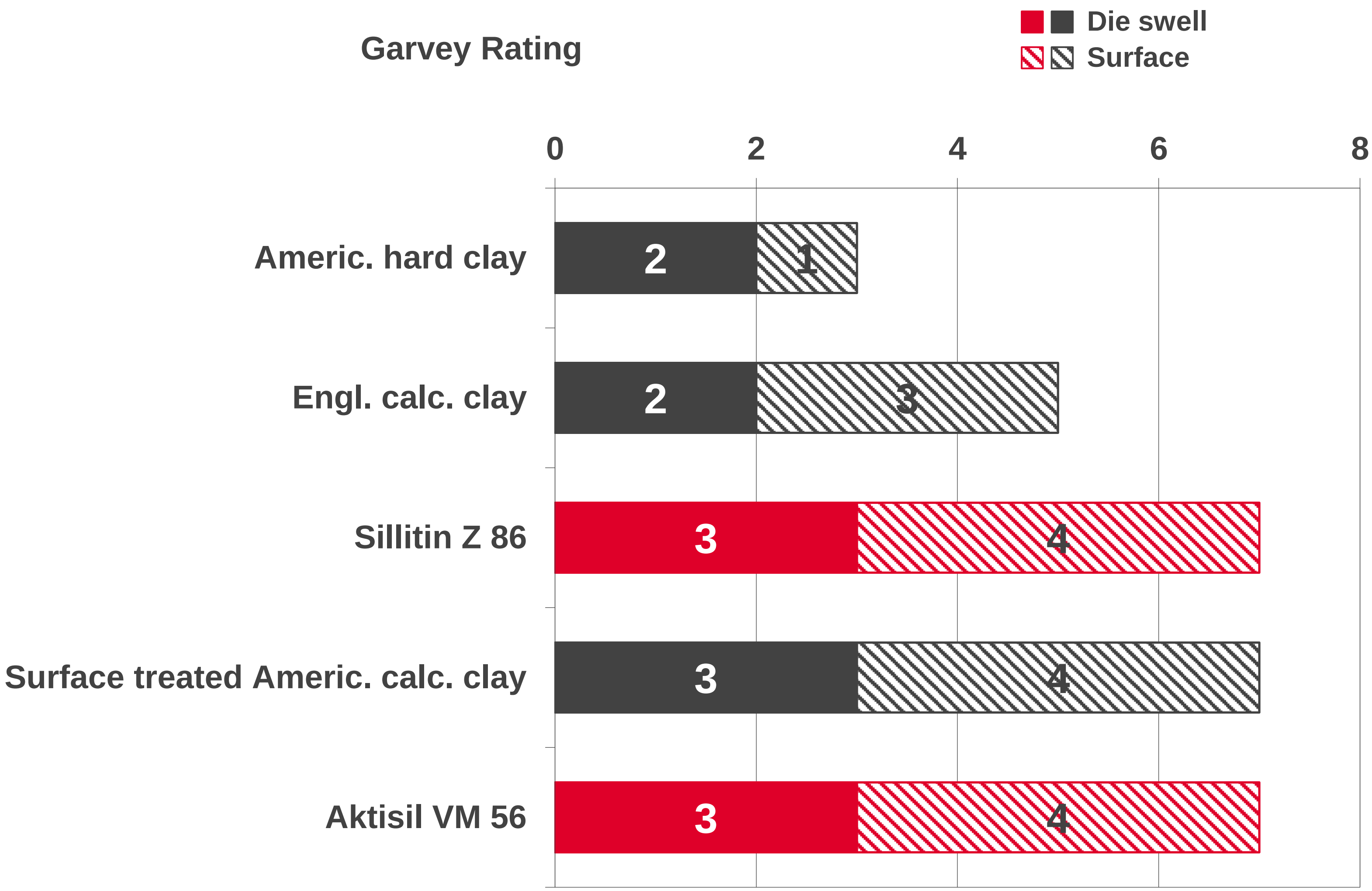
Garvey Extrusion 50 rpm
Blend with Whiting



Garvey Extrusion 1 m/min. Filler Straight

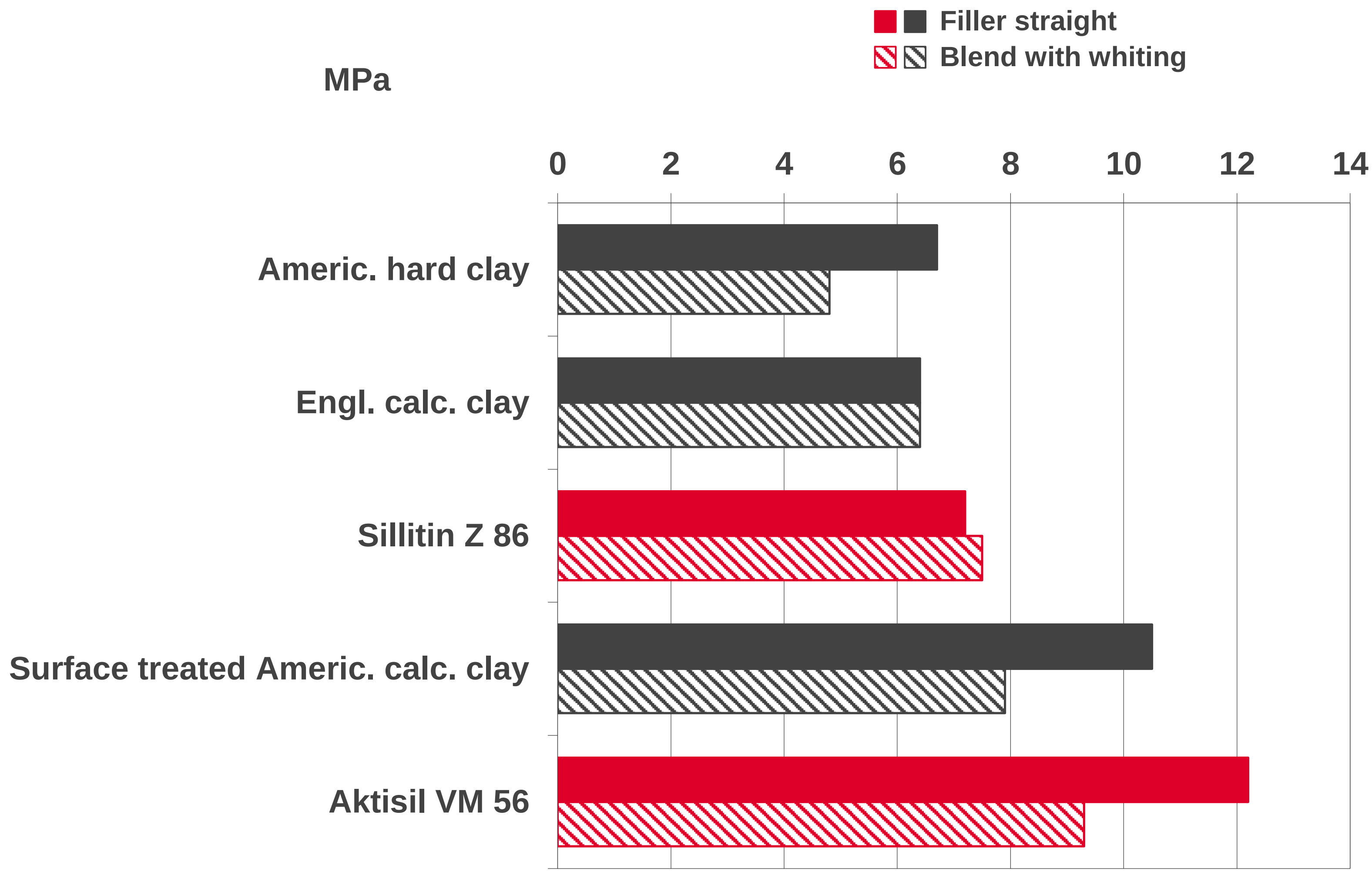


Garvey Extrusion 1 m/min.
Blend with Whiting



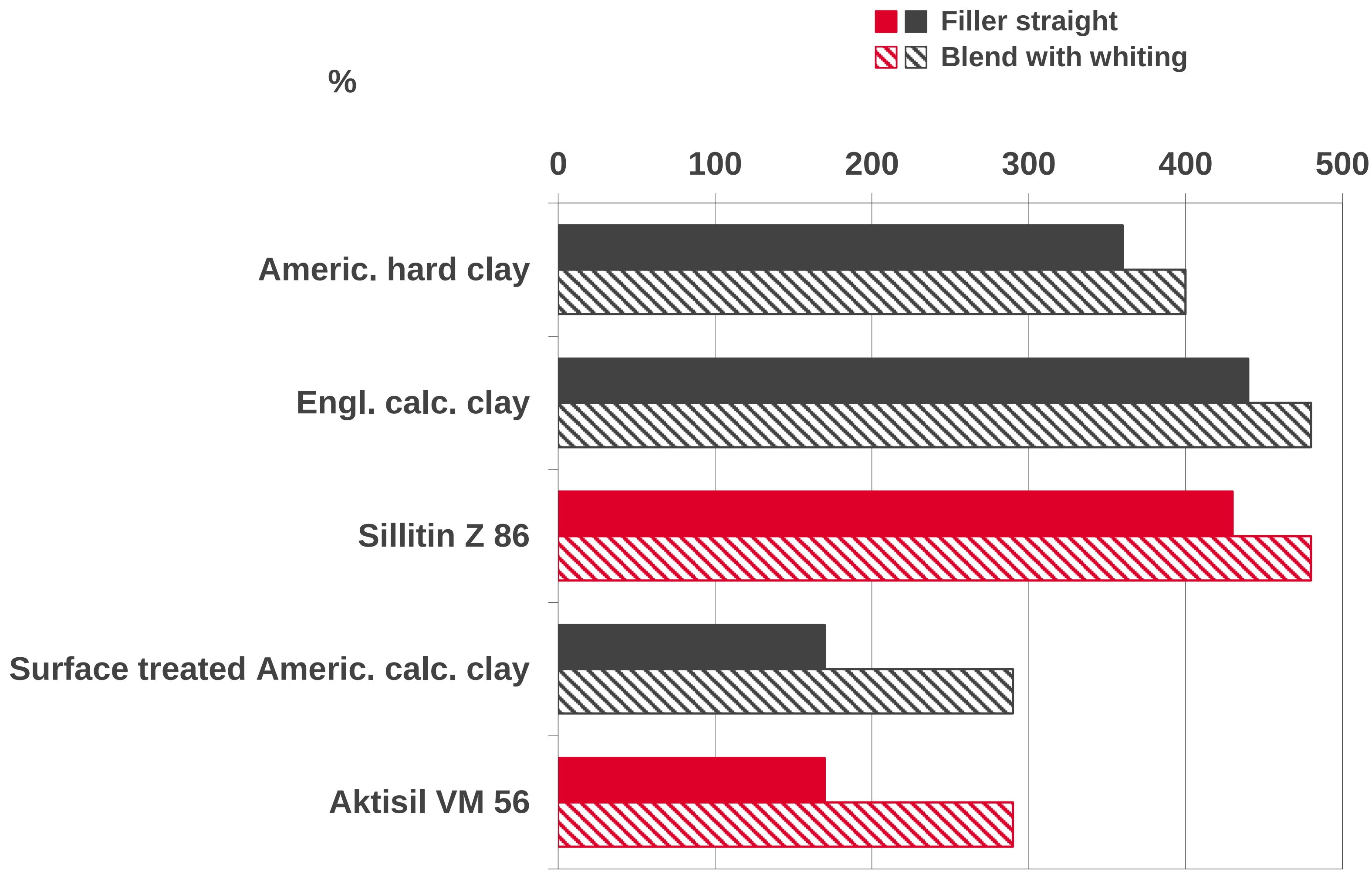
Tensile Strength

DIN 53 504, S2



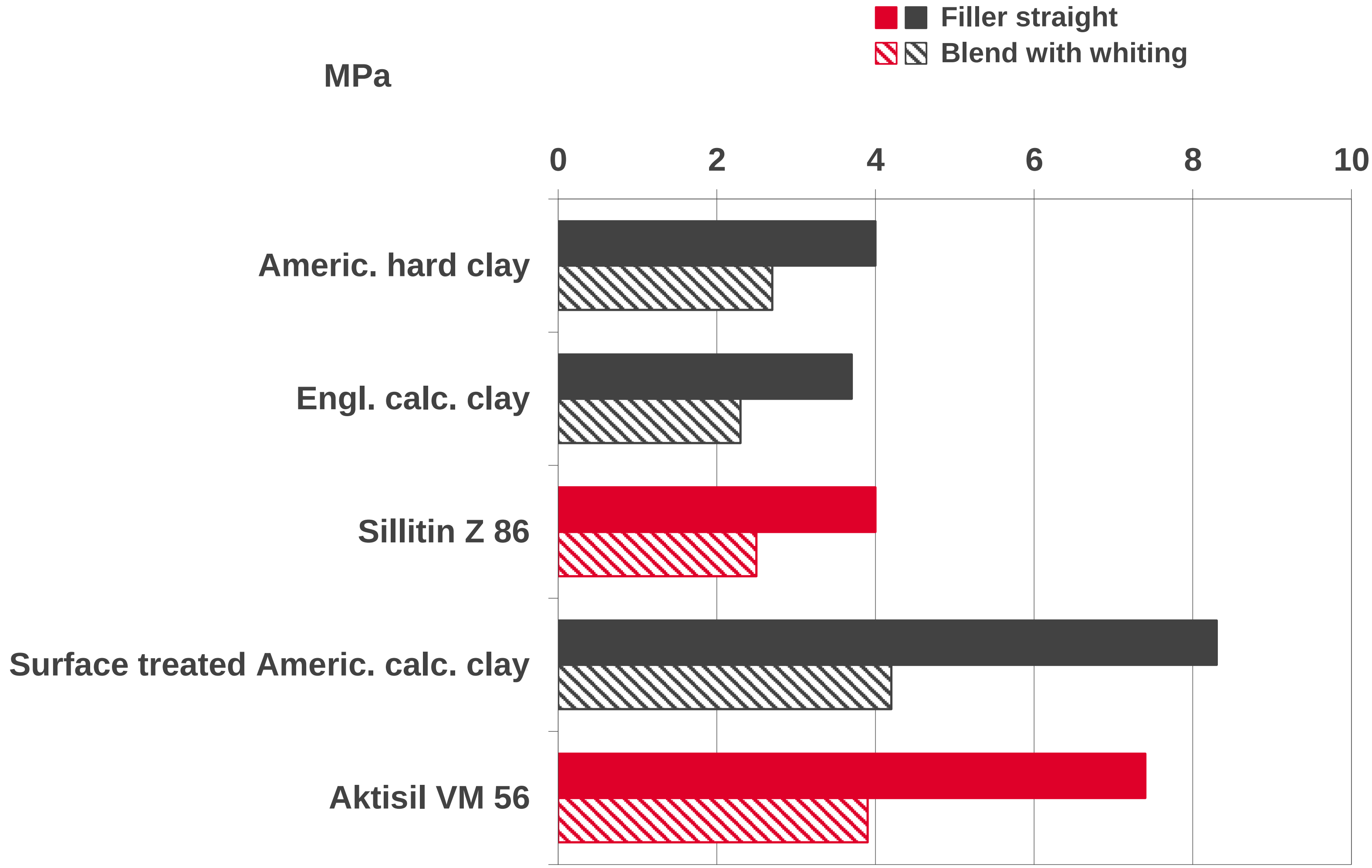
Elongation at Break

DIN 53 504, S2



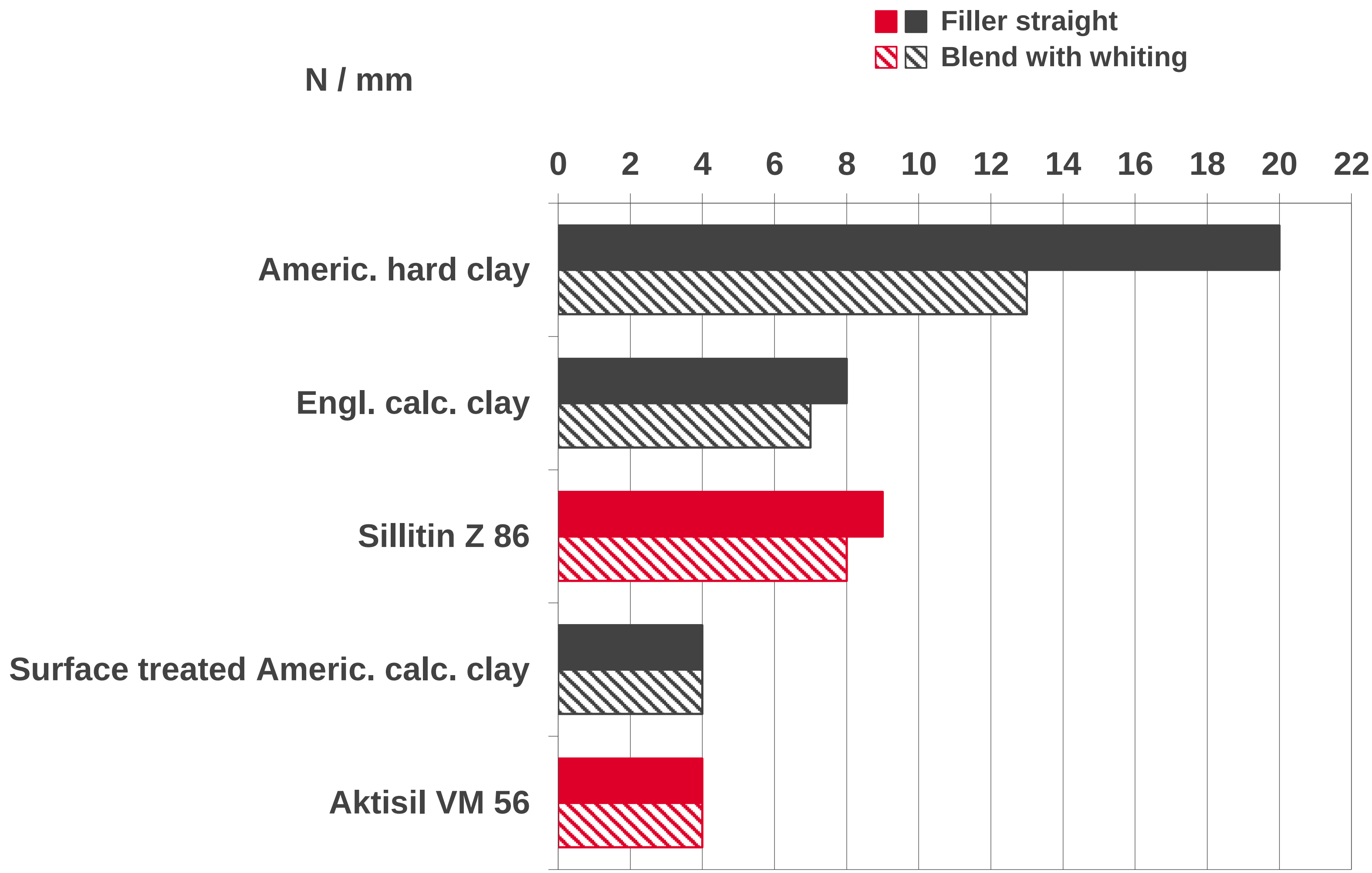
Modulus 100 %

DIN 53 504, S2



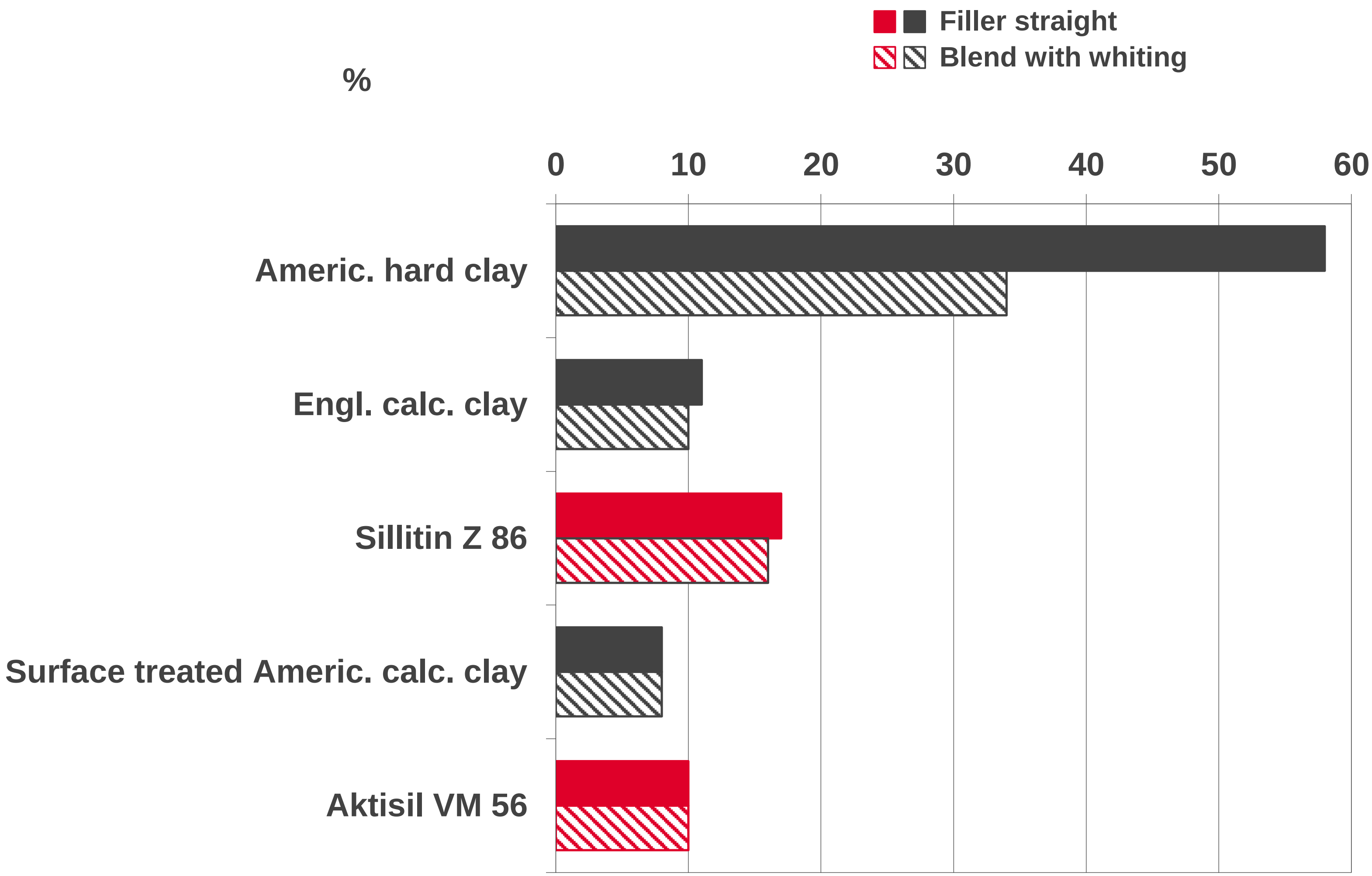
Tear Resistance

DIN 53 507-A, F_{max}, 500 mm / min.



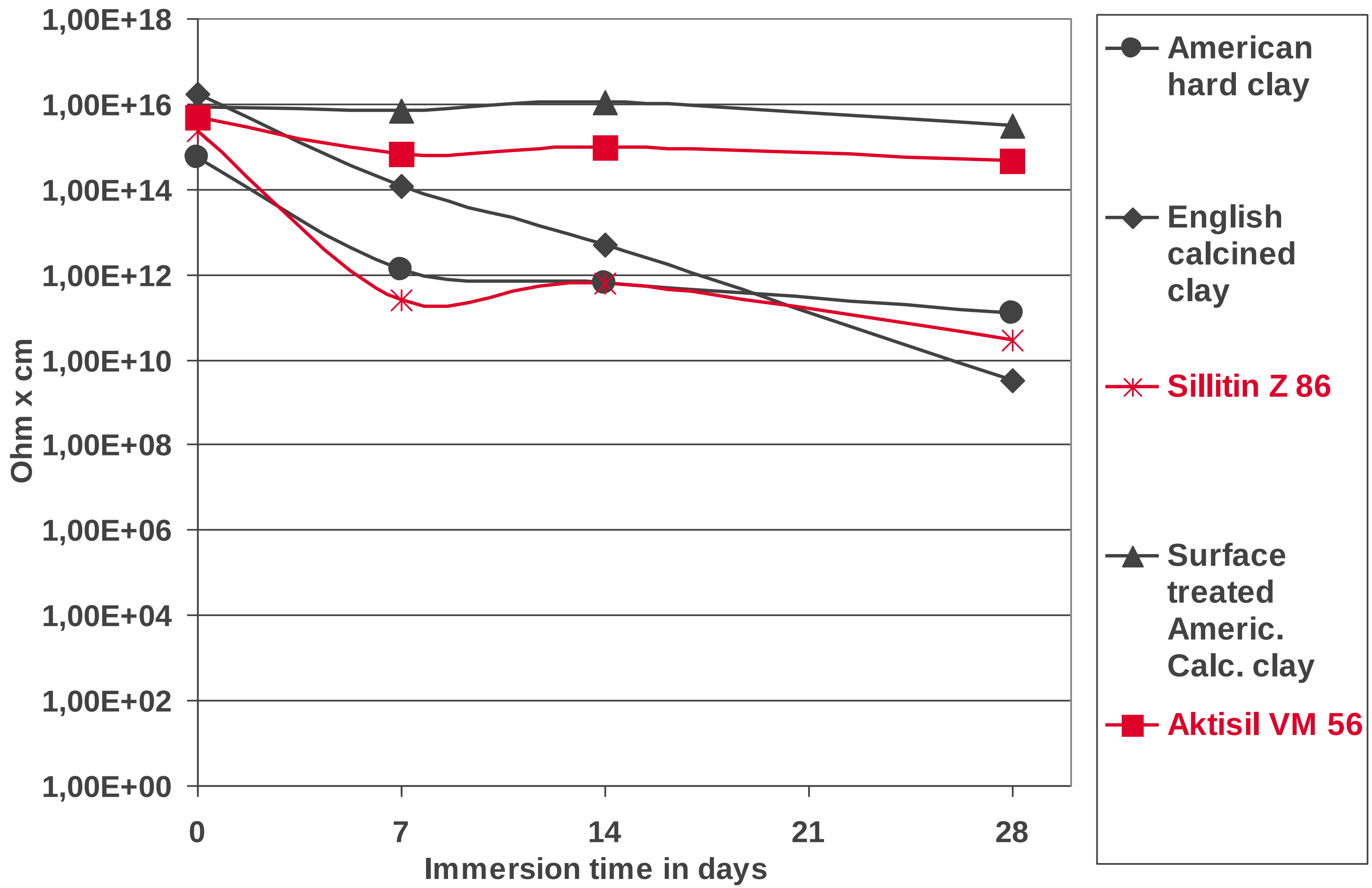
Compression Set

DIN 53 517 I, 24 h / 100 °C



Volume Resistivity
Filler Straight

Immersion in Deionized Water at 70 °C



Volume Resistivity
Blend with Whiting

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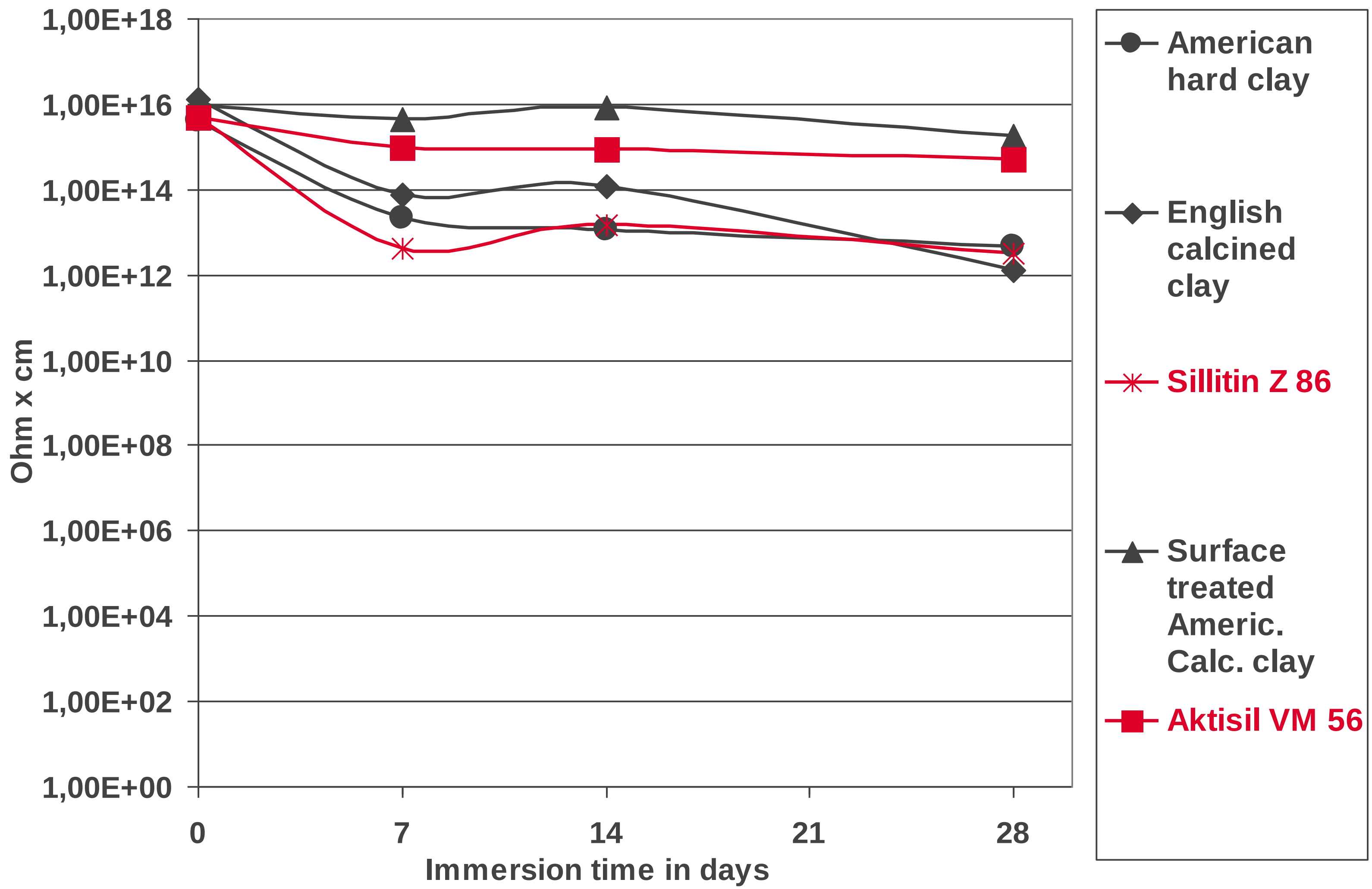
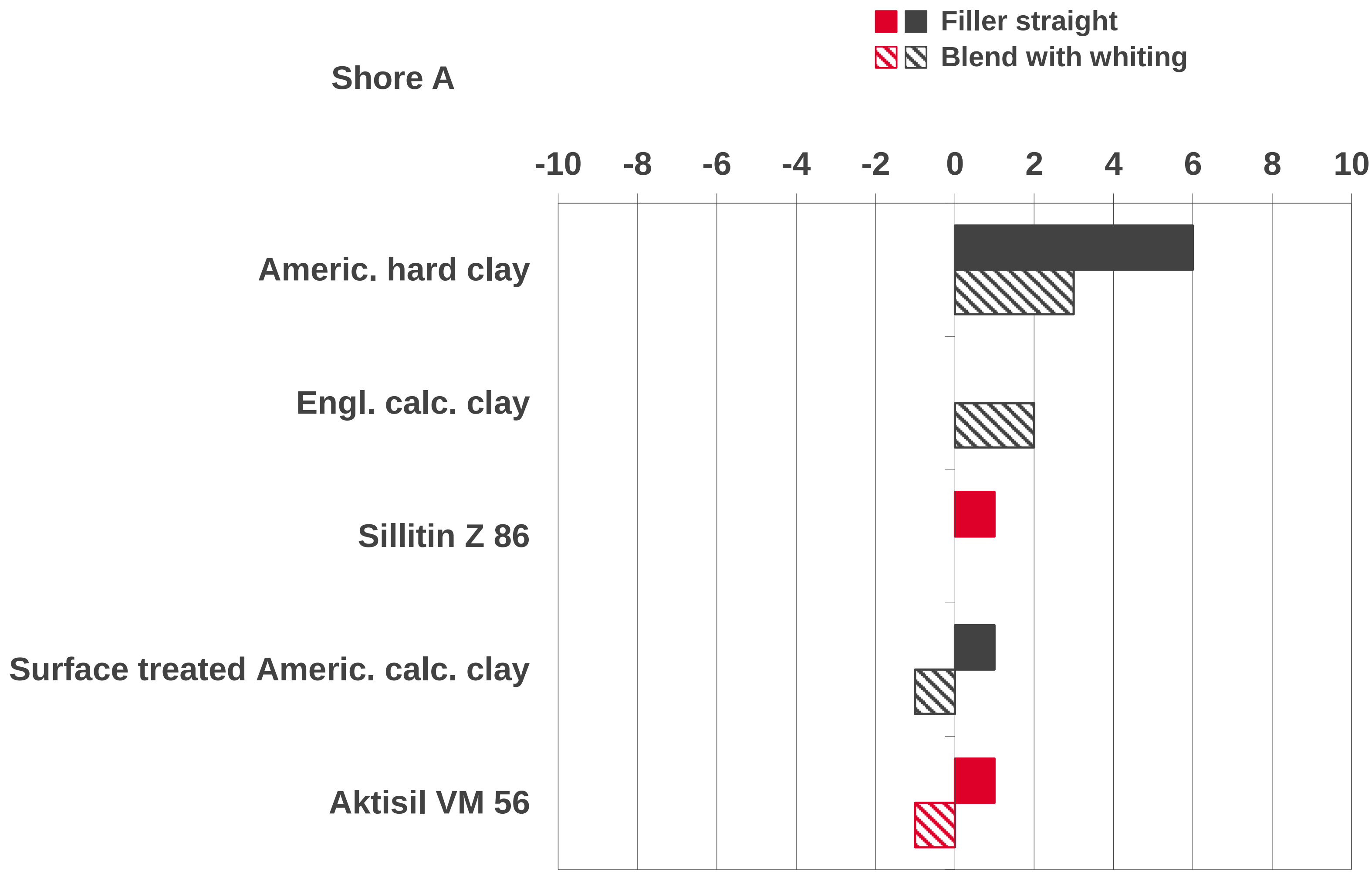
Immersion in Deionized Water at 70 °C



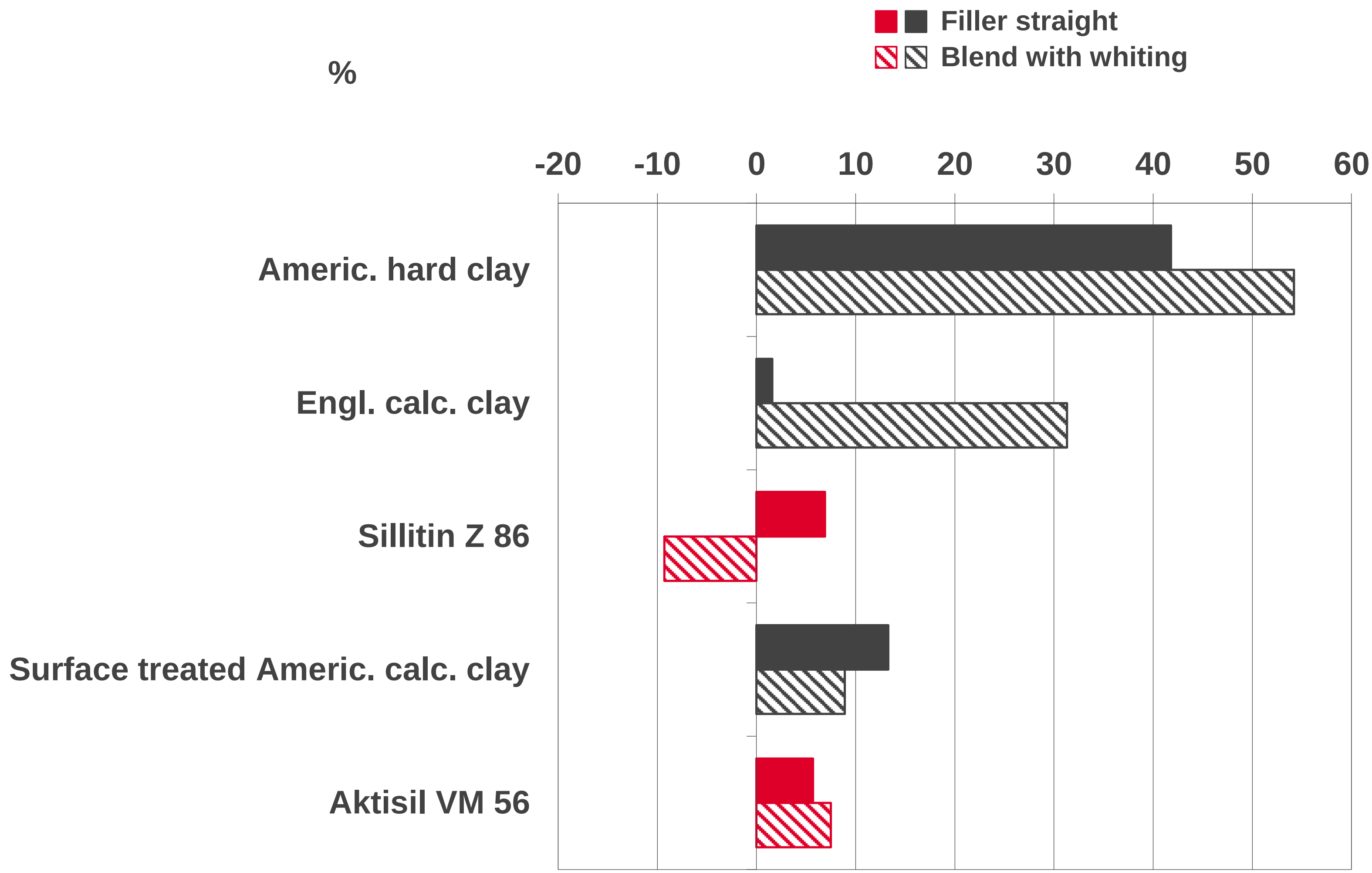
Hot Air Aging
Change of Hardness

168 h / 100 °C



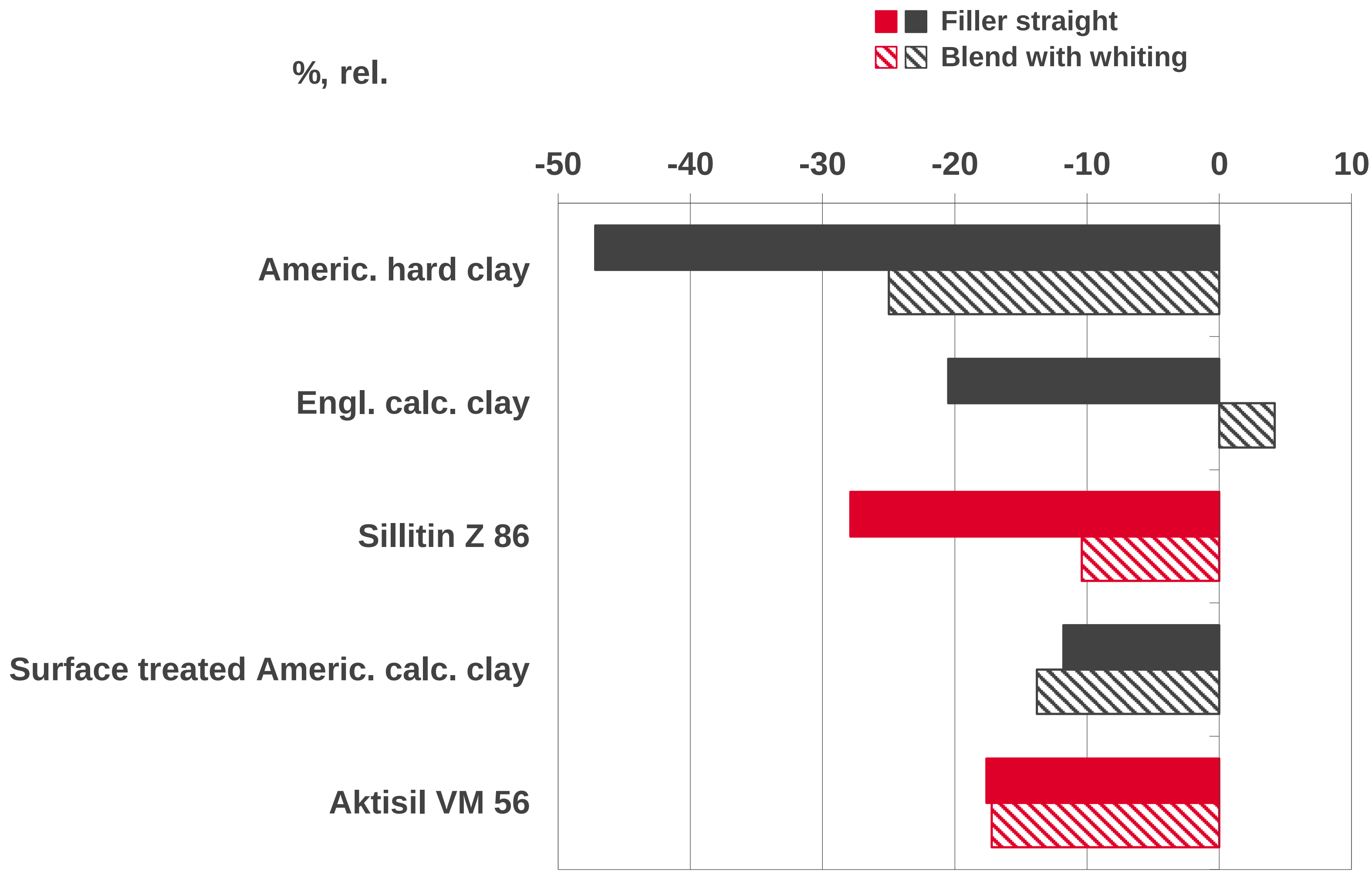
Hot Air Aging
Change of Tensile Strength

168 h / 100 °C



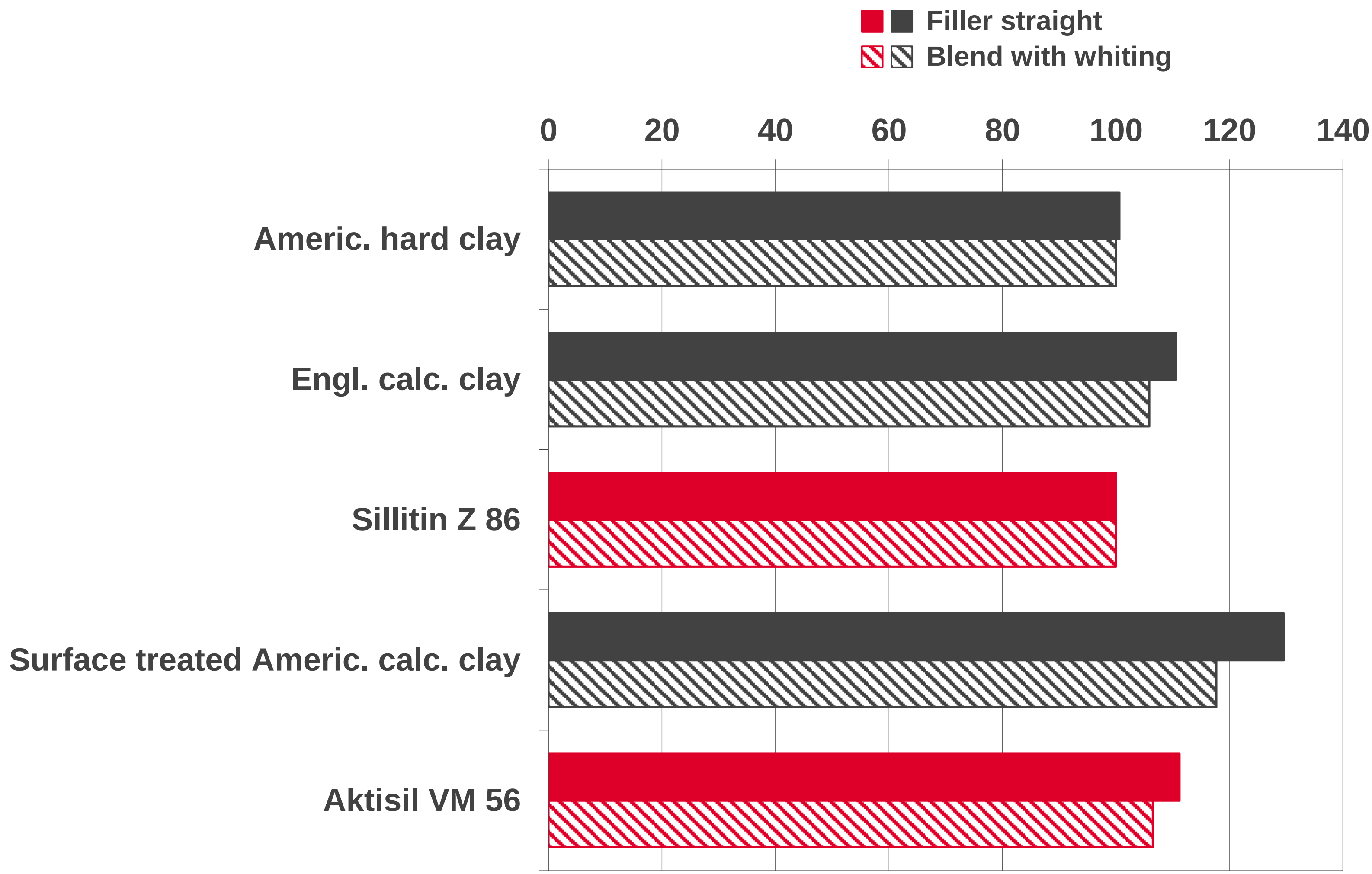
Hot Air Aging
Change of Elongation at B.

168 h / 100 °C



Compound
Raw Material Cost Indices

Germany 2009, Sillitin Z 86 = 100, Volume Related



Summary

Untreated Fillers

- American hard clay, straight as well as in blend with whiting, comes out very unsatisfactory in mixing and processing, leads to high compression set, high tear strength, low volume resistance, poor extrusions and high changes of properties upon aging.
- English calcined clay is easy to mix and process, gives very good compression set, good extrusion properties, but suffers from a sharp decrease of the volume resistance upon water immersion.
- Sillitin Z 86 too is easy to mix and process and largely comes close to the calcined clay. With respect to extrusion, however, Sillitin Z 86 is markedly superior, in particular in the blend with whiting. Also cost aspects should speak for the Neuburg Siliceous Earth grade.

Summary

Surface Treated Fillers

- Surface treated American calcined clay provides a very good property profile with respect to incorporation, processing, mechanical and electrical properties as well as extrusion characteristics. However, the costs here present themselves very high.
- Aktisil VM 56 too comes off with a very good property profile which regard to incorporation, processing, mechanical and electrical properties as well as extrusion characteristics. The price/performance ratio without doubt speaks in favor of Aktisil VM 56.

Summary

- Among the untreated fillers, the American hard clay came off, straight or in the blend with whiting, as the weakest filler. The English calcined clay and Sillitin Z 86, when used straight, give very similar results to each other, however, in the blend with whiting, Sillitin Z 86 proved superior. Including cost considerations, **Sillitin Z 86 results as the best suited filler.**
- When looking at the total property profile of the two surface treated fillers, Aktisil VM 56 has to be confirmed on equal level with the calcined clay. Including cost considerations, **Aktisil VM 56 must be judged the best suited product in this comparison.**

Summary
At a Glance

	untreated						surface treated			
	American hard clay		English calcined clay		SILLITIN Z 86		surface treated American calcined clay		AKTISIL VM 56	
	straight	blend with whiting	straight	blend with whiting	straight	blend with whiting	straight	blend with whiting	straight	blend with whiting
Incorporation	-	0	++	++	++	++	++	++	++	++
Processing (Extrusion)	0	--	++	+	++	++	++	++	++	++
Cure behavior	+	0	-	-	+	+	+	+	+	+
Mechanical properties	0	-	+	+	++	++	+	+	++	++
- Hot air aging	--	0	++	++	0	++	++	+	+	+
Electrical properties dry	0	+	++	++	+	+	++	++	++	++
- After water immersion	0	+	--	+	-	+	++	++	+	+
Cost	+	+	0	0	++	++	0	0	++	++
Total assessment	-	0	+	+	+	++	+	+	++	++

++ = very good; + = good; 0 = satisfactory; - = poor; -- = very poor

Results

Raw Compound Properties

M. 432		untreated						surface treated			
		American hard clay		English calcined clay		SILLITIN Z 86		surface treated American calcined clay		AKTISIL VM 56	
		straight	blend with whiting	straight	blend with whiting	straight	blend with whiting	straight	blend with whiting	straight	blend with whiting
Mixing time	min.	30	25	19	20	21	19	20	20	25	17
Mooney viscosity DIN 53 523, Part 3 ML (1+4), 120 °C	ME	83	52	69	52	67	44	53	45	55	49
Mooney scorch DIN 53 523, Part 3 ML +5, 120 °C	min.	6.7	25.6	11.3	38.2	6.4	22.6	14.7	26.3	10.0	14.0
Linear shear vulcameter (Frank) DIN 53 529, A3 180 °C											
t_5	min.	0.6	1.1	1.3	1.4	1.1	1.3	1.3	1.4	1.1	1.2
t_{90}	min.	8.2	11.6	13.7	14.5	10.3	8.6	9.8	9.7	8.9	8.9
t_{90} + 10 % (Cure time)	min.	9	13	15	16	11	10	11	11	10	10

Results

Cured Rubber Properties

M. 432		untreated						surface treated			
		American hard clay		English calcined clay		SILLITIN Z 86		surface treated American calcined clay		AKTISIL VM 56	
		straight	blend with whiting	straight	blend with whiting	straight	blend with whiting	straight	blend with whiting	straight	blend with whiting
Hardness DIN 53505-A	Shore A	71	67	73	66	72	67	73	69	74	69
Tensile strength DIN 53 504, S2	MPa	6.7	4.8	6.4	6.4	7.2	7.5	10.5	7.9	12.2	9.3
Modulus 100 % DIN 53 504, S2	MPa	4.0	2.7	3.7	2.3	4.0	2.5	8.3	4.2	7.4	3.9
Modulus 300 % DIN 53 504, S2	MPa	6.3	4.2	4.7	3.2	5.2	3.6	-	-	-	-
Elongation at break DIN 53 504, S2	%	360	400	440	480	430	480	170	290	170	290
Rebound DIN 53 512	%	43	51	54	57	55	56	52	55	53	57
Tear resistance DIN 53 507 A, Fmax 500 mm/min	N/mm	20	13	8	7	9	8	4	4	4	4
Compression set DIN 513 517 I 24 h/100°C	%	58	34	11	10	17	16	8	8	10	10
Density DIN 53 479	g/cm³	1.47	1.48	1.48	1.48	1.48	1.48	1.48	1.49	1.47	1.48

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Extrusion ASTM D 2230

M. 432		untreated						surface treated			
		American hard clay		English calcined clay		SILLITIN Z 86		surface treated American calcined clay		AKTISIL VM 56	
		straight	blend with whiting	straight	blend with whiting	straight	blend with whiting	straight	blend with whiting	straight	blend with whiting
Output rate 1m/min Rating Torque	Nm	3131 70	2111 60	3142 80	2132 70	31436 0	3142 80	3444 70	3142 80	3143 60	3142 80
Screw speed 50 rpm Rating Output Torque	 cm/min. g/min. Nm	2111 336 232 80	2111 310 228 80	3142 242 204 100	2132 262 216 80	3142 244 206 90	3142 280 238 90	3142 258 218 80	3142 268 234 80	3142 248 212 85	3142 256 224 90

Extrusion ASTM D 2230

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Volume Resistivity, DIN IEC 93

M. 432		untreated						surface treated			
		American hard clay		English calcined clay		SILLITIN Z 86		surface treated American calcined clay		AKTISIL VM 56	
		straight	blend with whiting	straight	blend with whiting	straight	blend with whiting	straight	blend with whiting	straight	blend with whiting
unaged	Ωcm	5.6x 10^{14}	4.1x 10^{15}	1.7x 10^{16}	1.3x 10^{16}	2.3x 10^{15}	4.9x 10^{15}	8.0x 10^{15}	9.3x 10^{15}	5.0x 10^{15}	4.6x 10^{15}
after aging in deionized water at 70 °C											
7 days	Ωcm	1.3x 10^{12}	2.1x 10^{13}	1.2x 10^{14}	7.2x 10^{13}	2.5x 10^{11}	4.2x 10^{12}	6.6x 10^{15}	4.3x 10^{15}	6.3x 10^{14}	9.8x 10^{14}
14 days	Ωcm	5.9x 10^{11}	1.1x 10^{13}	4.8x 10^{12}	1.2x 10^{14}	6.3x 10^{11}	1.5x 10^{13}	1.1x 10^{16}	8.0x 10^{15}	9.6x 10^{14}	8.7x 10^{14}
28 days	Ωcm	1.2x 10^{11}	4.4x 10^{12}	3.2x 10^{9}	1.3x 10^{12}	2.9x 10^{10}	3.1x 10^{12}	3.1x 10^{15}	1.8x 10^{15}	4.5x 10^{14}	5.2x 10^{14}

Results

Properties after Aging in Hot Air 168 h / 100 °C

M. 432		untreated						surface treated			
		American hard clay		English calcined clay		SILLITIN Z 86		surface treated American calcined clay		AKTISIL VM 56	
		straight	blend with whiting	straight	blend with whiting	straight	blend with whiting	straight	blend with whiting	straight	blend with whiting
Hardness Change	Shore A Shore A	77 + 6	70 + 3	73 ± 0	68 + 2	73 + 1	67 ± 0	74 + 1	68 - 1	75 + 1	68 - 1
Tensile strength Change	MPa %	9.5 + 42	7.4 + 54	6.5 + 2	8.4 + 31	7.7 + 7	6.8 - 9	11.9 + 13	8.6 + 9	12.9 + 6	10.0 + 8
Modulus 100 % Change	MPa %	7.2 + 80	4.6 + 70	4.5 + 22	3.0 + 30	5.6 + 40	3.1 + 24	9.4 + 13	4.8 + 14	8.4 + 14	4.7 + 21
Elongation at break change	% %, rel.	190 - 47	300 - 25	350 - 21	500 + 4	310 - 28	430 - 10	150 - 12	250 -14	140 - 18	240 - 17

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