

# **Rheology control with Aktisil PF 777 in an epoxy system**

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## 1 Introduction

The objective of the study was to demonstrate possibilities to control the rheology via the good thixotrope properties of Aktisil PF 777.

## 2 Experimental

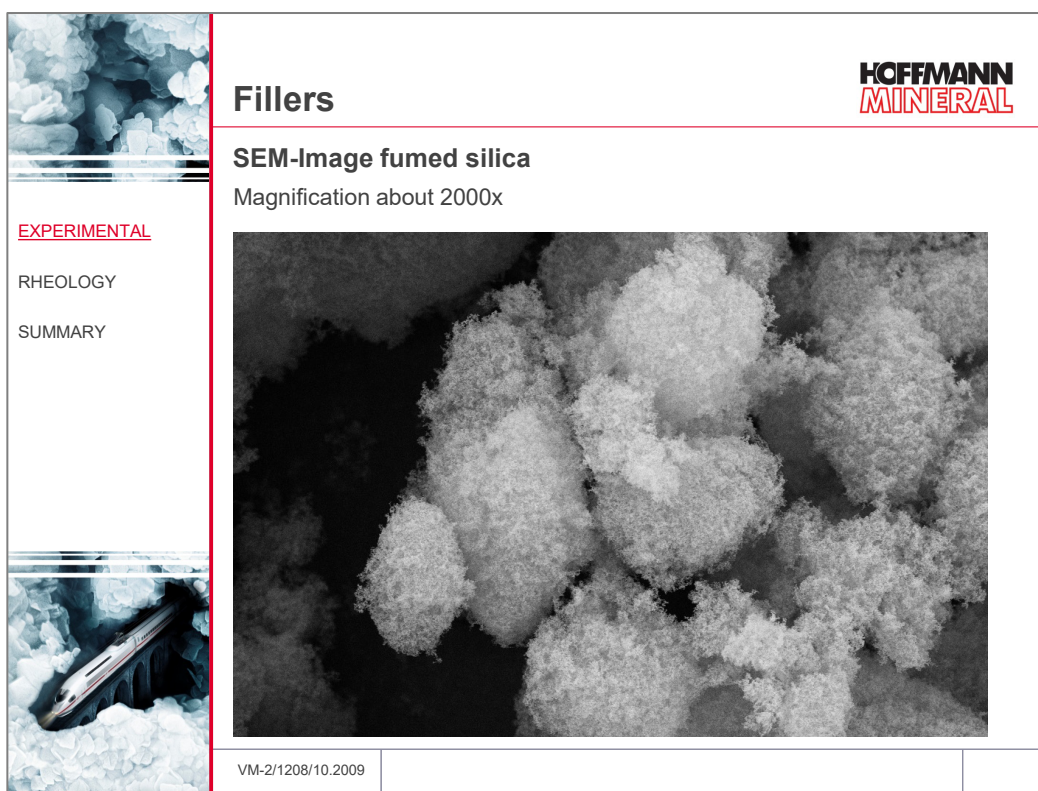
The reference chosen was a fumed silica treated with polydimethyl siloxane, with a BET surface area of 100 m<sup>2</sup>/g.

Out of the Neuburg Siliceous Earth products, the hydrophobically treated Aktisil PF 777 was tested, plus for comparison purposes the untreated base grade Sillitin Z 86.

### 2.1 Filler morphology and characteristics

#### Fumed silica


The picture shows the fumed silica used with an average primary particle size of 14 nm.



Neuburg Siliceous Earth

The 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, cryptocrystalline primary particles of about 200 nm diameter.

The morphology of the Neuburg Siliceous Earth is illustrated in the following picture:



EXPERIMENTAL

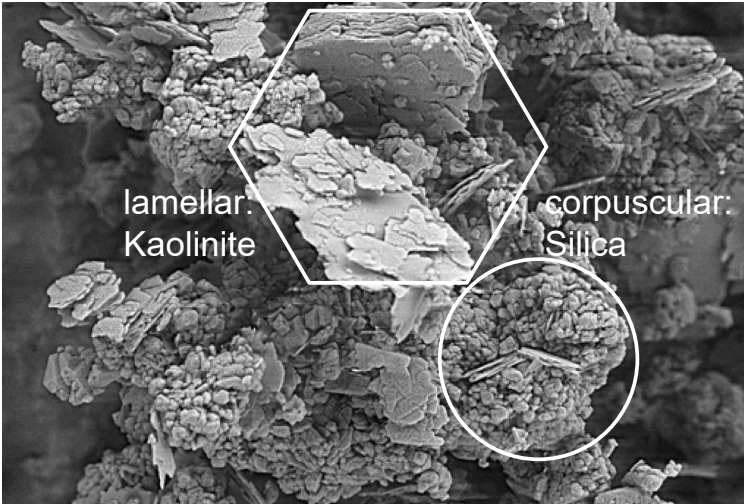
RHEOLOGY

SUMMARY

### Fillers

#### SEM-Image Neuburg Siliceous Earth

Magnification about 10000x




lamellar: Kaolinite

corpuscular: Silica

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The table summarizes the characteristic properties of the functional fillers used:



EXPERIMENTAL

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SUMMARY

### Fillers

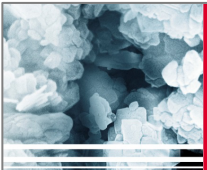
#### Characteristics

			Reference			Neuburg Siliceous Earth (NSE)	
			fumed silica			Aktisil PF 777	Sillitin Z 86
Particle size	d50	[µm]	---			2.2	1.9
	d97	[µm]	---			10	8
Surface area BET		[m²/g]	100 *			8	11
Surface treatment			polydimethyl-siloxane *			alkyl silane	none

\*manufacturer information

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This diagram shows in a simplified model the surface treatment of the filler with an alkyl silane. Of critical importance is the reaction of the silane with the filler surface, i.e. the formation of a covalent bond between the silane and the filler.



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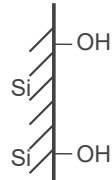
EXPERIMENTAL

RHEOLOGY

SUMMARY

## Fillers

### Surface treatment (simplified reaction model)




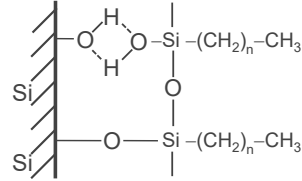
**Sillitin**

+


$$\begin{array}{c} \text{H}_3\text{C}-\text{O} \\ | \\ \text{H}_3\text{C}-\text{O}-\text{Si}-(\text{CH}_2)_n-\text{CH}_3 \\ | \\ \text{H}_3\text{C}-\text{O} \end{array}$$

**alkyl silane**





**Aktisil PF 777**

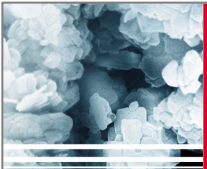


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## 2.2 Formulation

The dosages chosen were 4.5 pbw fumed silica resp. 50 pbw Aktisil PF 777, which in the total formulation with hardener led to similar rheological properties.

The hardener level for all tests was 14.5 pbw TETA on 100 pbw epoxy resin (corresponding to 104.5 pbw Component A with the silica, or 150 pbw Component A with the Neuburg Siliceous Earth).



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## Formulation

	fumed silica	Neuburg Siliceous Earth
Bakelite EPR 161 liquid unmodified epoxy resin bisphenol F type, EEW approx. 170	100	100
Rheology modifier / Filler	4.5	50
<b>Total (parts by weight)</b>	<b>104.5</b>	<b>150</b>

The filler was incorporated into the epoxy resin and dispersed in a planetary mixer for 20 minutes with 17 m/s circumferential speed under vacuum.

Hardener: TETA (triethylene tetramine)  
Mixing ratio: 14,5 parts by weight to 100 parts by weight epoxy resin



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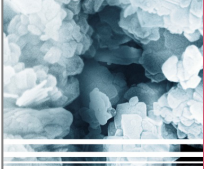

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## 2.3 Parameters rheology tests

For each test, the measuring device was newly loaded.

When testing the total formulation (with hardener), a new batch was prepared for each test; the batch size was about 8 g Component A plus the required amount of hardener.

The hardener was incorporated by manual stirring for about 1 minute, after which the batch was filled into the measuring device, and the test started after a total of 3 minutes.

  <u>EXPERIMENTAL</u>  RHEOLOGY  SUMMARY  	<b>Test parameters</b> <b>Rheological test</b> <ul style="list-style-type: none"><li>• Rheometer: MCR 300 from Anton Paar GmbH<ul style="list-style-type: none"><li>– Plate/plate-system, diameter 50 mm</li><li>– Gap 1 mm</li><li>– Temperature 23 °C</li></ul></li><li>• Viscosity<ul style="list-style-type: none"><li>– Preshearing 30 s at 50 s<sup>-1</sup></li><li>– 20 s rest phase</li><li>– Logarithmically increasing shear rate from 0.01 to 1000 s<sup>-1</sup></li><li>– Logarithmically decreasing shear rate from 1000 to 0.01 s<sup>-1</sup></li><li>– Only the downward curves were evaluated from 0.05 to 200 s<sup>-1</sup></li></ul></li><li>• Yield point<ul style="list-style-type: none"><li>– Preshearing 10 s at 5 s<sup>-1</sup></li><li>– 20 s rest phase</li><li>– Linear shear stress increase at 1.5 Pa/s</li></ul></li><li>• Structure recovery test<ul style="list-style-type: none"><li>– Preshearing in rotation for structure breakdown at 200 s<sup>-1</sup> for 100 s</li><li>– Structure recovery in oscillation at constant deformation of 0.01 % and constant frequency of 1.59 Hz (within the linear-viscoelastic range)</li></ul></li></ul>	
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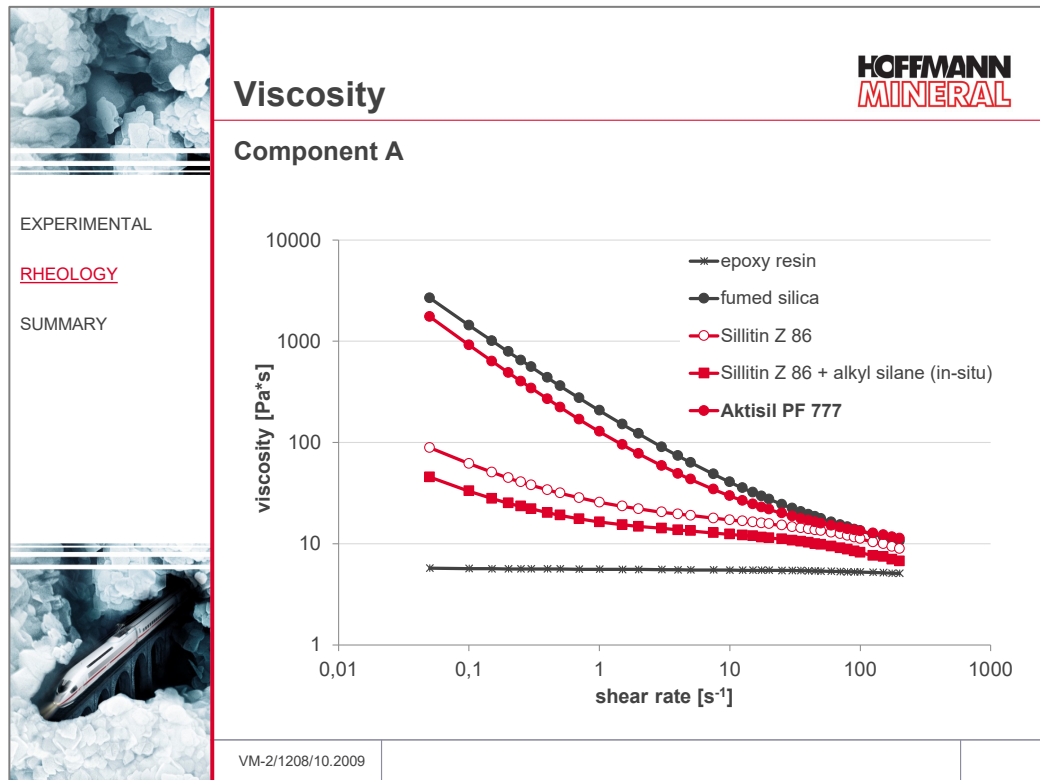
### 3 Results

#### 3.1 Rheology

##### Viscosity

In order to achieve the desired high viscosity at low shear rates, the addition of the liquid alkyl silane to the formulation with Sillitin Z 86 (in situ) proved not successful. Such an effect is only obtained with Aktisil PF 777, where the silane is fixed on the surface by chemical surface treatment.

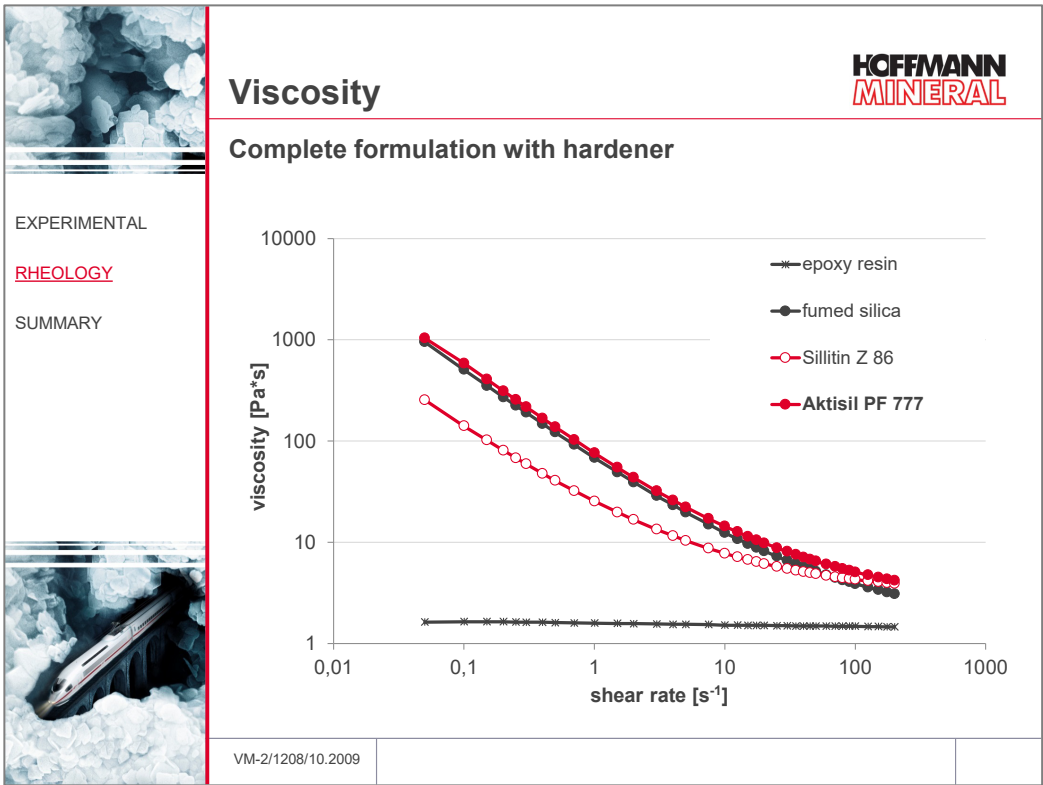
Even with Aktisil PF 777 at the chosen dosage, Component A does not quite reach the high viscosity at low shear rates as is the case with fumed silica. But with increasing shear rates, the viscosity graphs become more and more similar.



More close to practical conditions, the other rheological tests were only carried out on total formulations (with hardener).

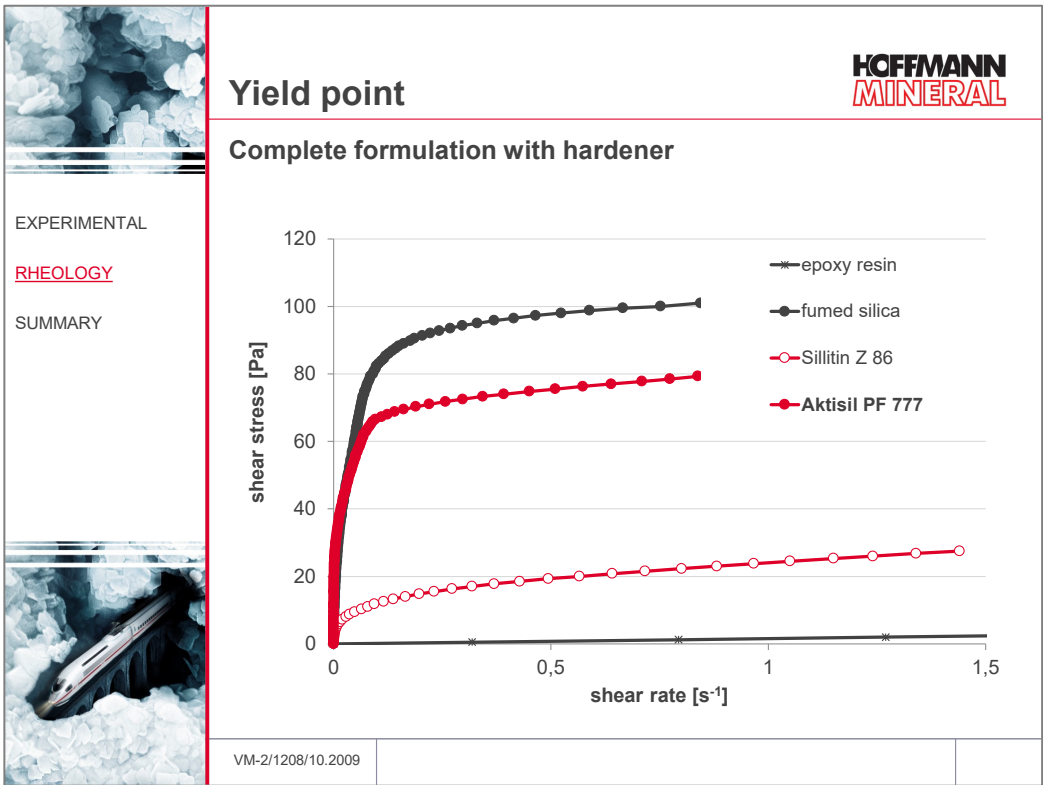


After adding the hardener, the viscosity graphs of Aktisil PF 777 and fumed silica are practically identical.



### Yield point

Despite the identical viscosity traces, the yield point with Aktisil PF 777 comes out somewhat lower than with the fumed silica. The epoxy resin without filler as well as the formulation with Sillitin Z 86 do not exhibit any resp. only a very low yield point.





## Structure recovery

After breaking down the structure by shear, the structure recovery is determined under oscillation. The diagram shows the complex shear modulus  $G^*$  and on the second y-axis the loss factor  $\tan \delta$  dependent on time.

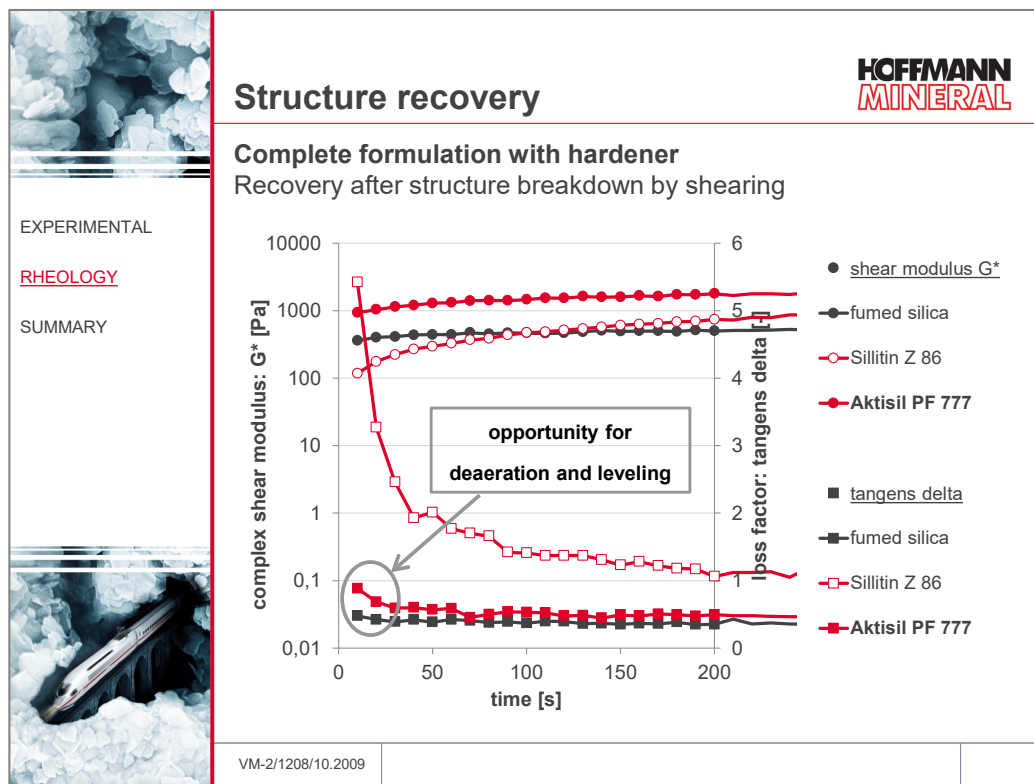
The complex shear modulus is composed of an elastic and a viscous contribution, and indicates the overall rigidity of the sample under oscillating deformation.

Aktisil PF 777 leads to a higher complex shear modulus than fumed silica.

The loss factor is the quotient of the viscous and the elastic contributions, and therefore describes the structure of the sample. With results  $>1$  the viscous part is predominant, and the material behaves rather like a liquid. By contrast, loss factors  $<1$  indicate substances with a higher elastic contribution and thus the characteristics of solids. The smaller the loss factor, the more the characteristics of a solid are prominent.

As evident from the change of the loss factor after shearing (structure breakdown), Aktisil PF 777, unlike the fumed silica, does not give rise to a rapid structure recovery, and therefore offers a sufficiently wide time window for good deaeration. In the end, a structure similar to fumed silica will be obtained.

Structure recovery with Sillitin Z 86 comes out markedly weaker and at a lower level, i.e. mostly viscous in nature.



## 3.2 Storage stability

The component A was stored for 6 months at ambient temperature. After this, the rheological tests were repeated.

After the storage, a slight diminuation of the structure recovery was observed with Aktisil PF 777.

This effect could be offset by adding 1% hexadecyl trimethoxysilane (based on the Aktisil PF 777 content).<sup>1</sup>

<sup>1</sup> Hexadecyl trimethoxysilane: e.g. Dynasylan 9116 from Evonik Degussa GmbH.  
On principle, also other alkylsilanes with appropriately long alkyl groups should be suitable.

## 4 Summary

As distinct from surface-treated fumed silica, Aktisil PF 777 offers the following advantages:

- easier and more precise dosing in view of the higher amount added
- markedly lower tendency towards dust formation
- as a result of the delayed structure recovery after shearing, a favorable time window for efficient deaeration

In further studies, Aktisil PF 777, apart from the rheological effects, offered some additional benefits:

- as a result of the hydrophobic nature, good wetting and easy dispersion in binders of low polarity
- improved anti-corrosion protection
- reduced swelling
- increased resistance to chemicals and moisture
- very low or no sedimentation tendency

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