Neuburg Siliceous Earth

in 3D printing

SLA/DLP process (UV-curing)

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1 Introduction

Stereolithography (SLA) was already invented in the 1980s and is the oldest known 3D printing process.

The basic principle of both the SLA and DLP processes is the selective layer-by-layer curing of a photopolymer by a light source. In the SLA process (stereolithography), a (UV) laser is used for this purpose. The laser beam is directed via movable mirrors to the corresponding points one after the other, where it selectively cures the liquid photopolymer. The DLP (digital light processing) process uses a projector or LCD display as a light source instead of a laser, projecting an image of the entire layer to be cured. In this way, all dots of a layer are cured simultaneously, which means that the printing speed with the DLP process is normally significantly faster than with the SLA process.

Short production times together with high precision and surface quality enable the application for prototyping as well as the production of casting molds, filigree models and small series in many areas of industry and medical technology.

The photopolymers used are light-curing synthetic resins based on epoxy and acrylic, or more rarely vinyl.

The use of functional fillers such as Neuburg Siliceous Earth offers the possibility of adjusting the mechanical properties of the cured photopolymers.

The aim of this study is to present Neuburg Siliceous Earth as a mineral filler for light-curing 3D printing resins (SLA/DLP).

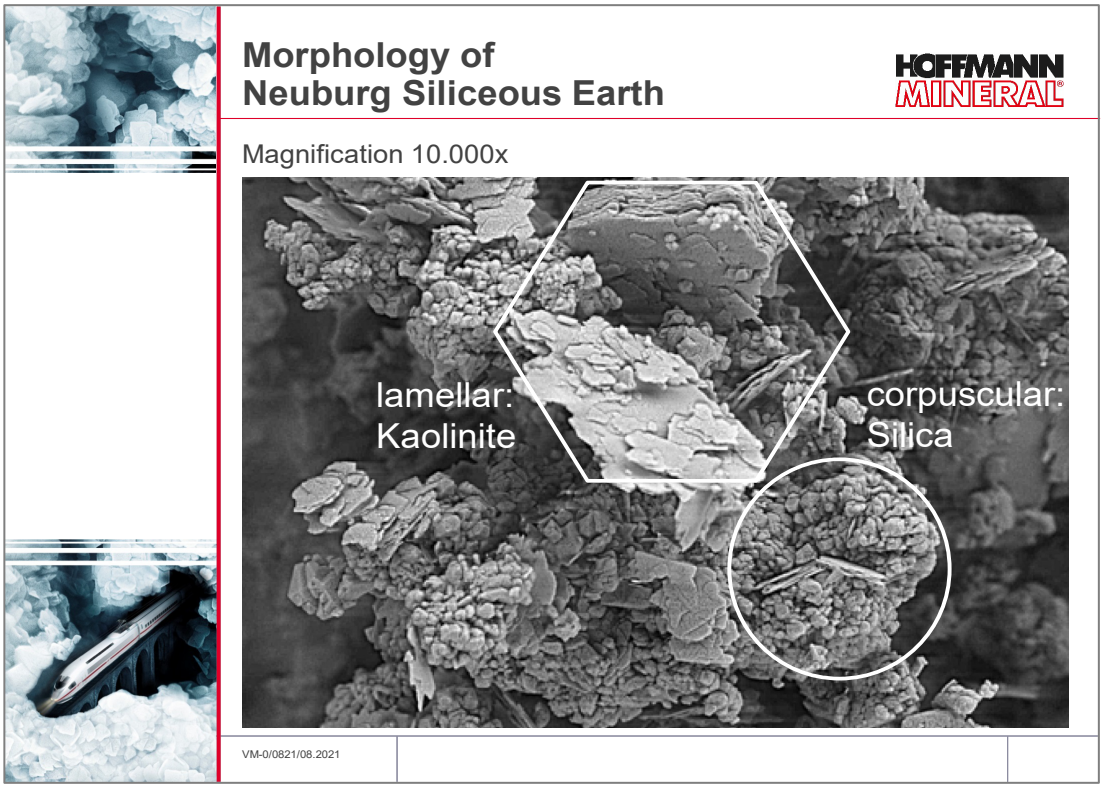
The mechanical properties were tested in an acrylate-based resin formulation.

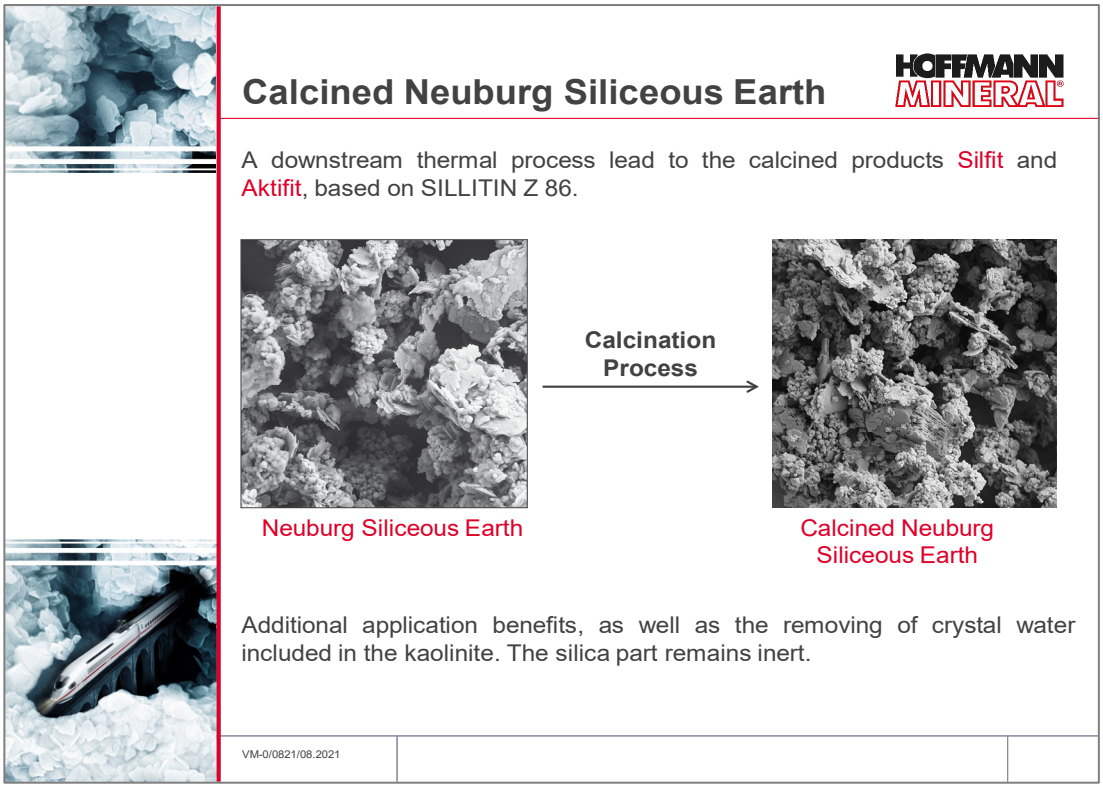
2 Experimental

2.1 Filler

Classic Neuburg Siliceous Earth is a natural combination of corpuscular Neuburg Silica and lamellar kaolinite: a loose mixture impossible to separate by physical methods. The silica portion exhibits a round grain shape and consists of aggregated primary particles of about 200 nm diameter.

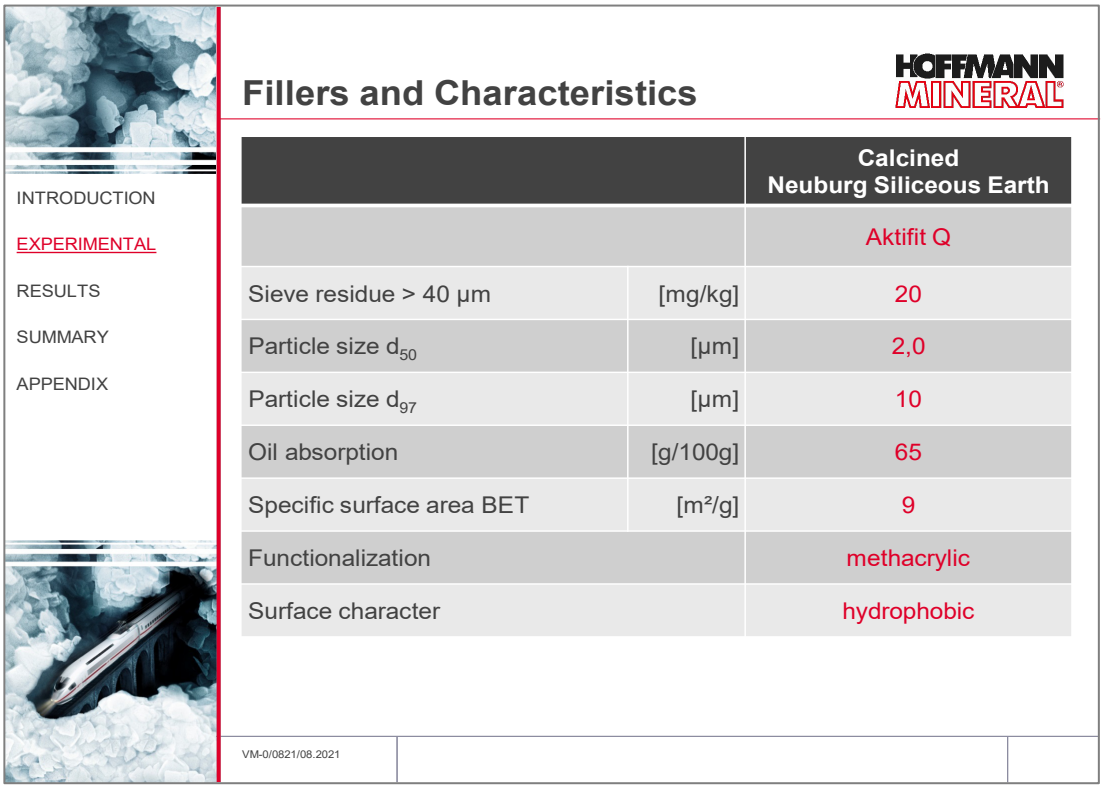
The special morphological composition of Neuburg Siliceous Earth, which represents a class of mineral on its own, in the following is illustrated by a SEM photograph:





The basis for the calcined Neuburg Siliceous Earth is the standard product Sillitin Z 86. In a thermal process, the water of crystallization in the kaolinite portion is removed and new, largely amorphous mineral phases are formed.
The resulting product Silfit Z 91 is characterized by high brightness and color neutrality.

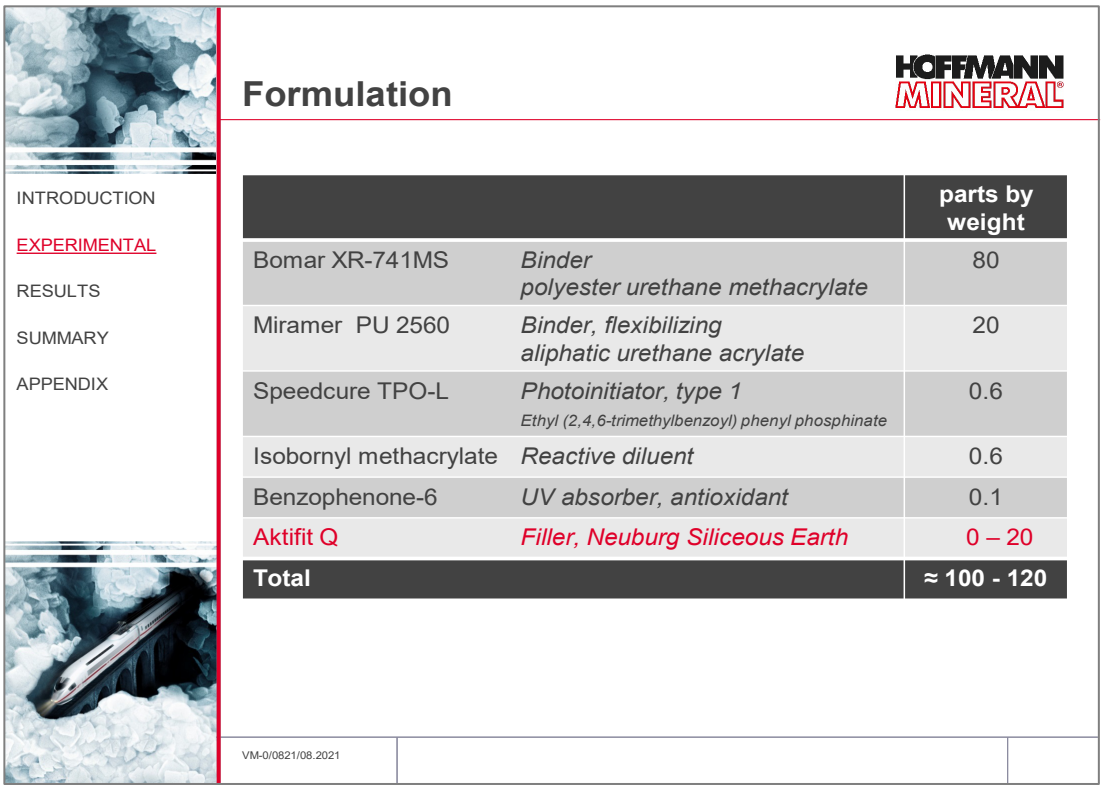
In preliminary tests, uncalcined and calcined grades as well as untreated and surface treated grades from the Neuburg Siliceous Earth product range were tested, Aktifit Q performing best. Aktifit Q is a calcined and methacryl-functionalized grade with hydrophobic surface character.



		Calcined Neuburg Siliceous Earth
		Aktifit Q
Sieve residue > 40 µm	[mg/kg]	20
Particle size d_{50}	[µm]	2,0
Particle size d_{97}	[µm]	10
Oil absorption	[g/100g]	65
Specific surface area BET	[m²/g]	9
Functionalization		methacrylic
Surface character		hydrophobic

2.2 Formulation

The table describes the composition of the formulations used.



		parts by weight
Bomar XR-741MS	*Binder polyester urethane methacrylate*	80
Miramer PU 2560	*Binder, flexibilizing aliphatic urethane acrylate*	20
Speedcure TPO-L	*Photoinitiator, type 1* *Ethyl (2,4,6-trimethylbenzoyl) phenyl phosphinate*	0.6
Isobornyl methacrylate	*Reactive diluent*	0.6
Benzophenone-6	*UV absorber, antioxidant*	0.1
Aktifit Q	*Filler, Neuburg Siliceous Earth*	0 – 20
Total		**≈ 100 - 120**

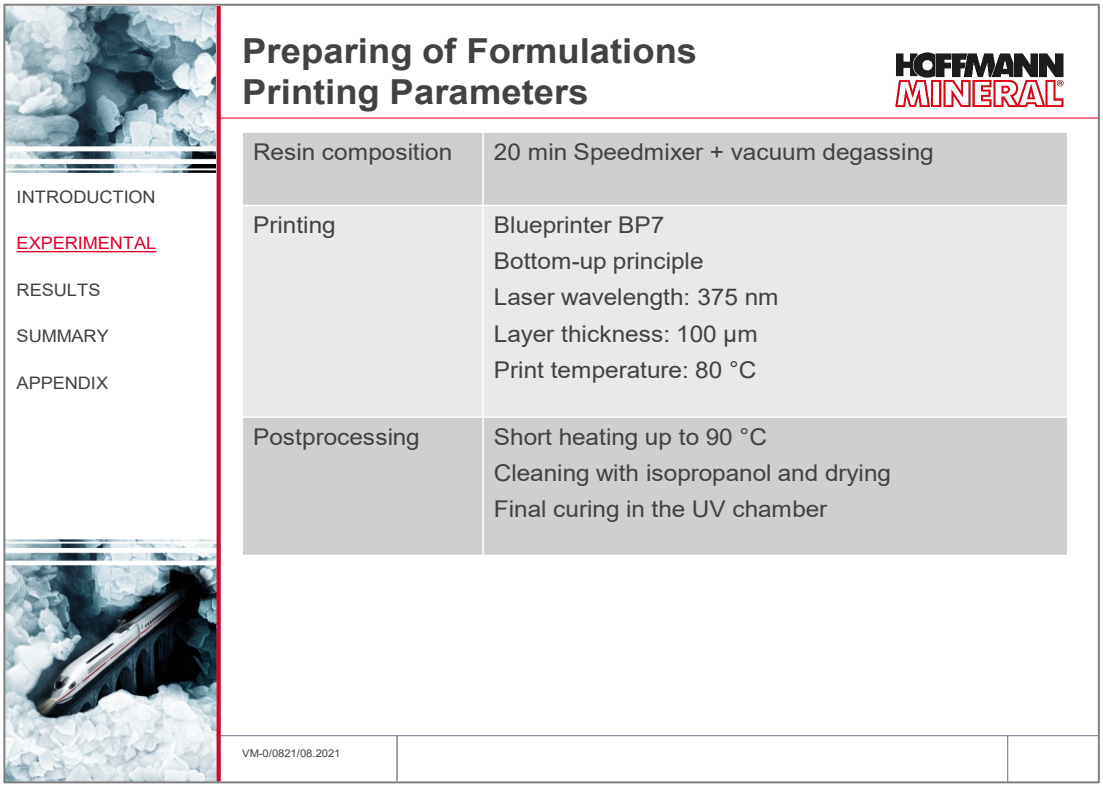
The main binder was Bomar XR-741MS, a high-viscosity polyester urethane methacrylate from Dymax. It is recommended for good heat deflection temperature, good adhesion and high hardness, as well as its resistance to yellowing.
To increase flexibility and toughness, the formulation contains Miramer PU 2560, an aliphatic difunctional urethane acrylate from Miwon.
A masterbatch was premixed from the next 3 raw materials - Speedcure TPO-L, isobornyl methacrylate and benzophenone-6. Speedcure TPO-L is a photoinitiator with absorption maxima at 274, 290 and 370 nm, benzophenone-6 serves as UV absorber or antioxidant, and isobornyl methacrylate is used in the masterbatch as reactive diluent.
Aktifit Q is the filler from the Neuburg Siliceous Earth product range already described.

2.3 Preparing of formulations and printing parameters

The formulations were prepared using a dual-asymmetric centrifuge, better known as a speed mixer.
For this purpose, the resins were heated to 90 °C and first mixed manually with the additive masterbatch and the filler before dispersion for 20 min in the Speedmixer. The formulations were then degassed under vacuum.

Printing was carried out with the Blueprinter BP7 developed at the Vienna University of Technology (TU Wien) at a temperature of 80 °C according to the bottom-up principle. The thickness of the layer applied per pass was 100 µm and curing was carried out using a laser with a wavelength of 375 nm.

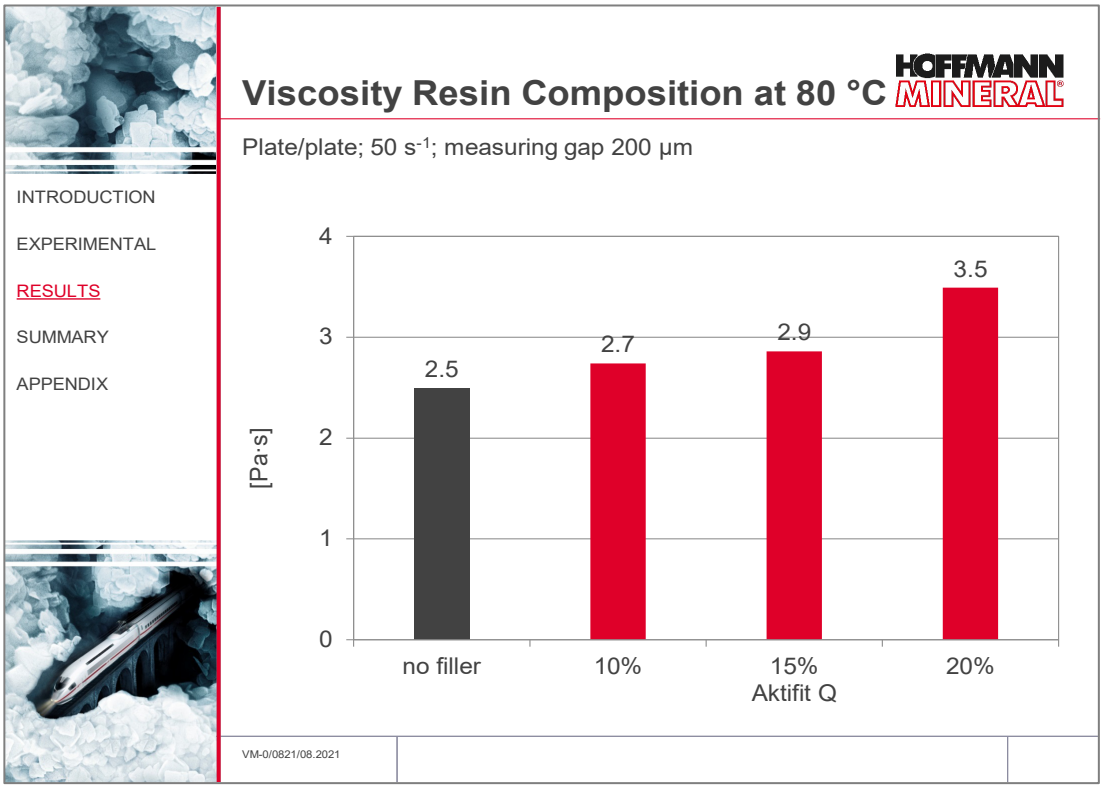
For post-processing, the component was removed from the printer while still warm, heated again to 90 °C, cleaned of resin residues with isopropanol and then dried in an oven. Final curing took place by continuous irradiation with UV light for 16.7 minutes under a nitrogen atmosphere.



3 Results

3.1 Viscosity

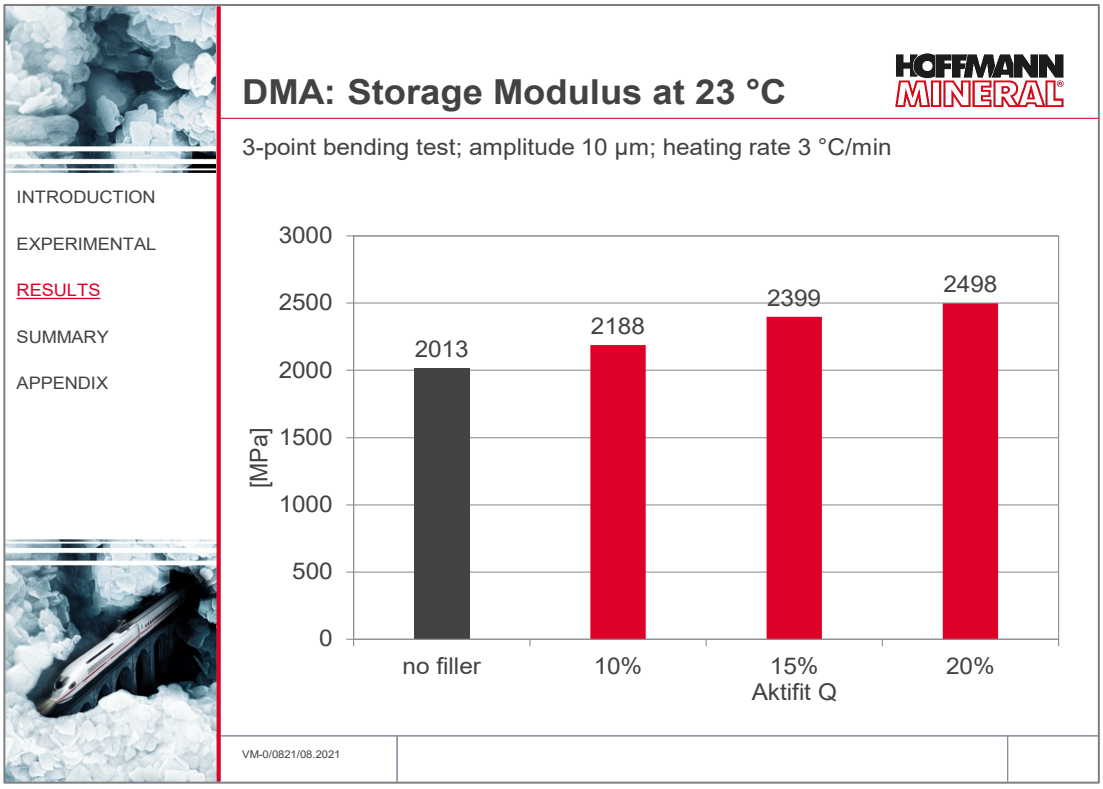
Viscosity was measured using a plate/plate system at a constant shear rate of 50 s^{-1} over a temperature range of 60-100 °C with a constant heating rate of 3 °C/min. The viscosity was evaluated according to the printing temperature at 80 °C.



Depending on the filler dosage, a slight increase in viscosity of up to approx. 30 % can be observed without negatively affecting the printing properties.

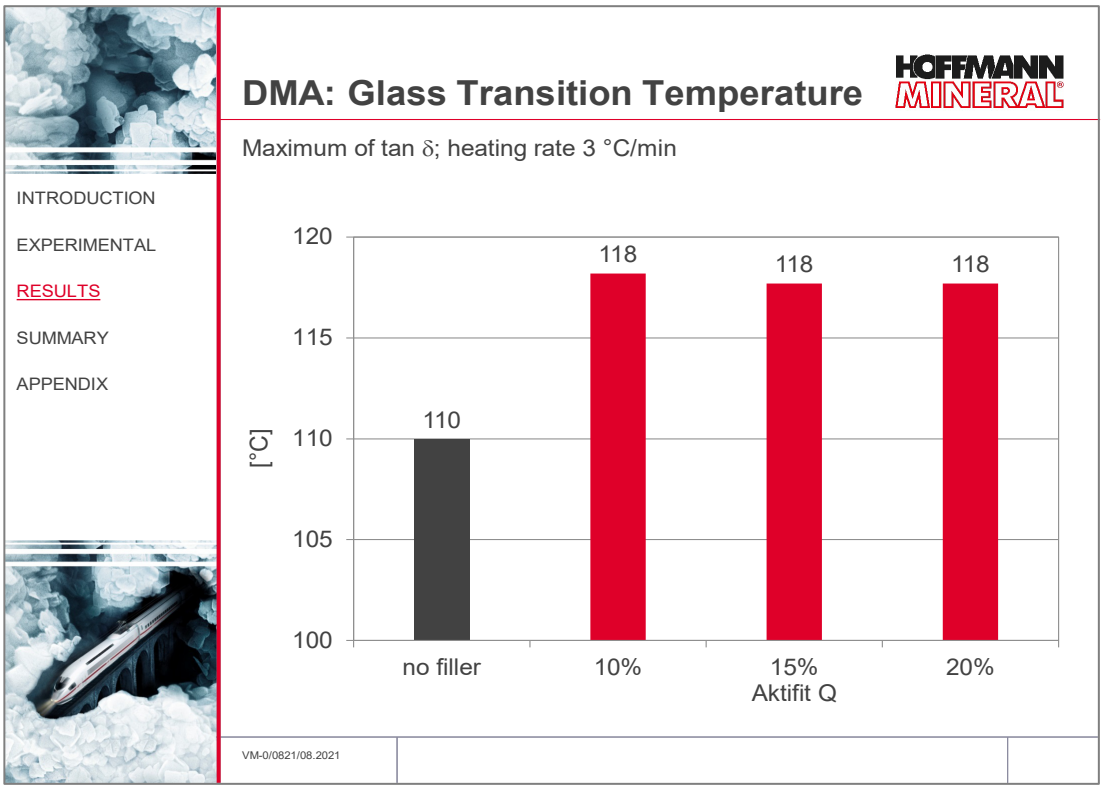
3.2 DMA analysis

In dynamic mechanical analysis (DMA), the viscoelastic behavior of a solid can be characterized. Stiffness and damping are thus determined as a function of temperature and frequency. For the measurement, the sample was subjected to a sinusoidal mechanical load in a 3-point bending test. The graph shows the storage modulus at 23 °C as a measure of the stiffness of the specimen.



As expected, the stiffness of the specimens increases with increasing filler addition, up to 25 % at 20 % addition.

As a further measured value from the DMA, the glass transition temperature was determined from the maximum of the loss factor tan δ.

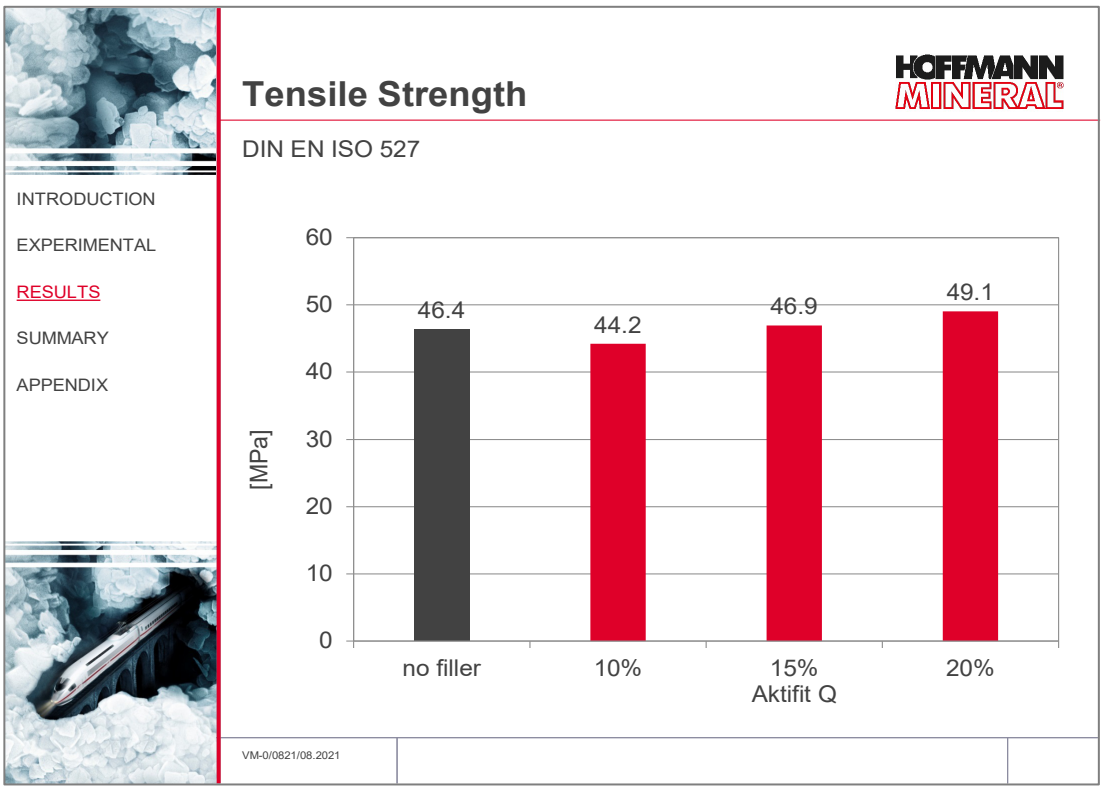


The addition of mineral filler leads to an increase of the glass transition temperature by approx. 8 °C (corresponds to approx. 7 %).

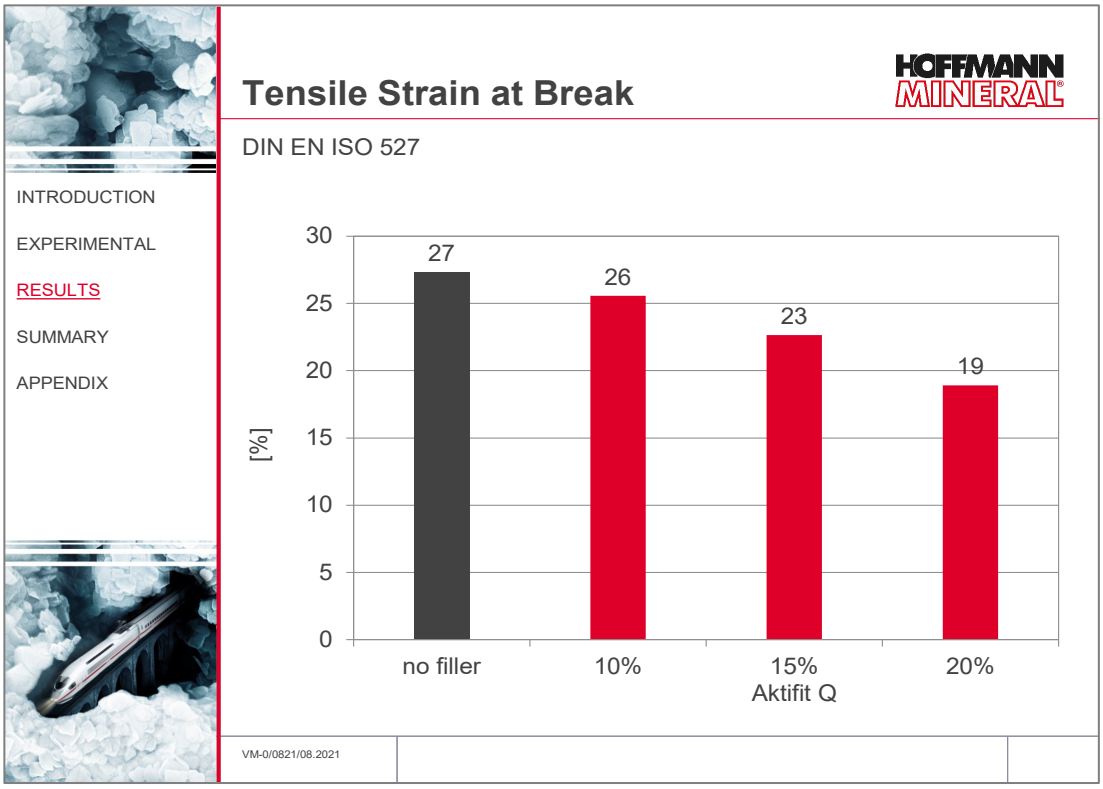
3.3 Mechanical properties

3.3.1 Tensile strength an tensile strain at break

The test was carried out according to DIN EN ISO 527 on special test specimens (similar to type 1 BB) up to the break of the specimens.



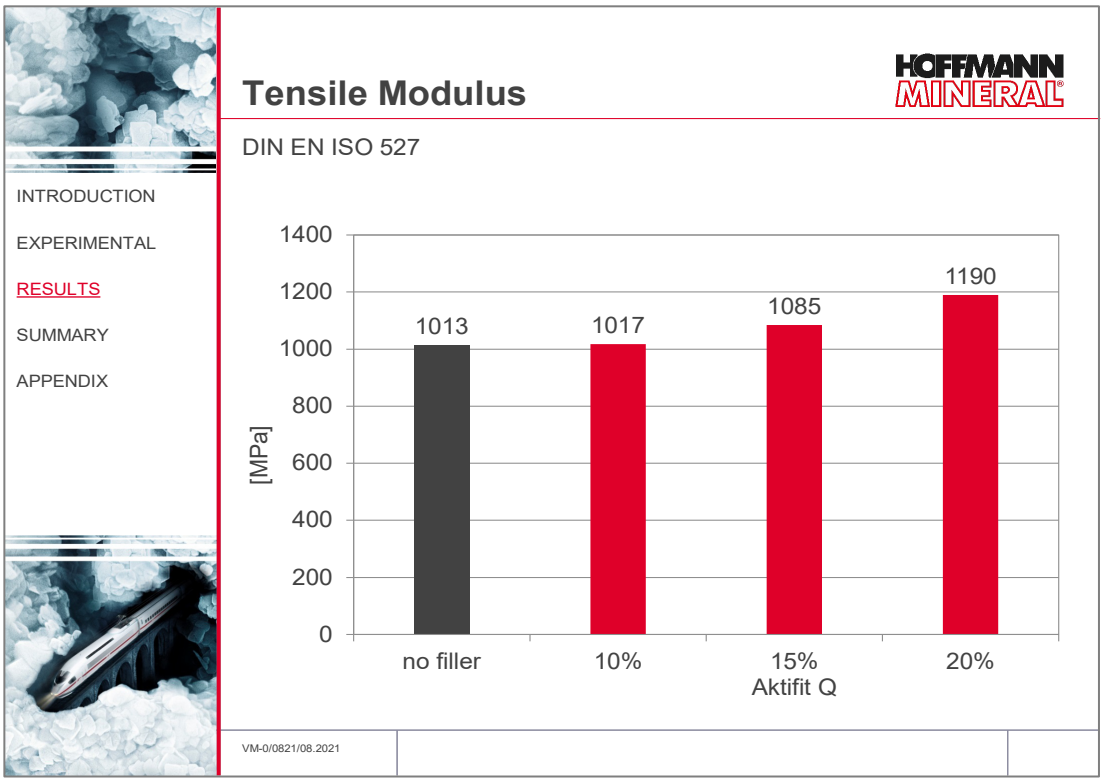
The tensile strength after the addition of Aktifit Q remains about on the level of the unfilled reference. At the highest dosage of 20 %, even a slight increase in strength can be observed.



In contrast, the strain at break drops by up to 30 relative % depending on the filler loading, but remains at a good level of 19 % at the highest loading.

3.3.2 Tensile modulus

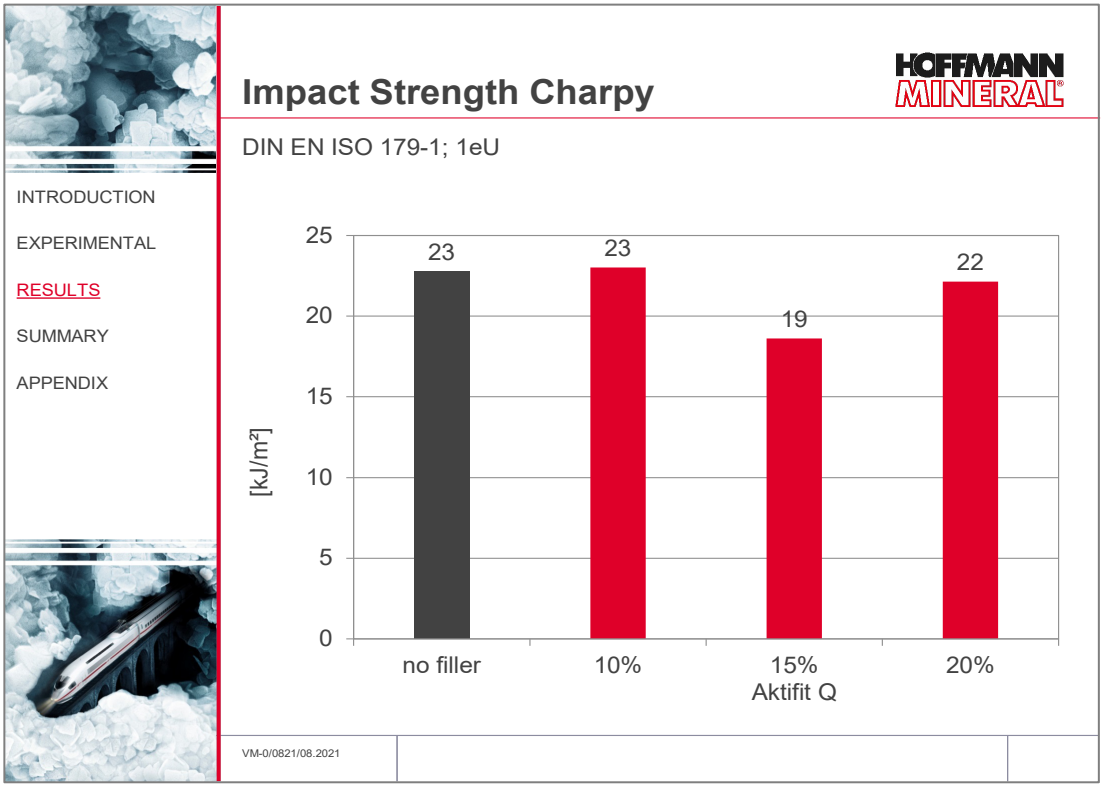
The tensile modulus was determined as a further indication of the stiffness of the specimens.



Analogously to the storage modulus, the increase in stiffness can be determined as a function of the filler addition, at 20 % filler addition approx. 17 %.

3.3.3 Impact strength

The test was carried out according to DIN EN ISO 179-1 on unnotched specimens with a 2J pendulum.



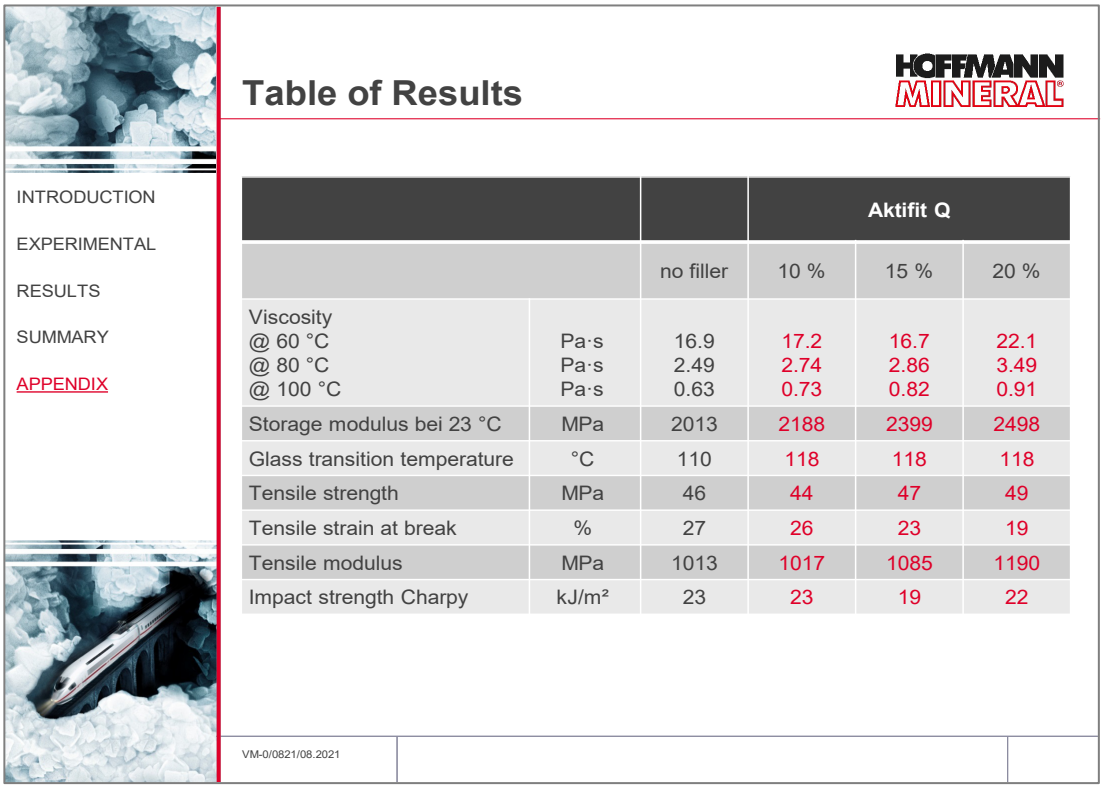
Despite the addition of Aktifit Q, impact strength remains approximately comparable to the unfilled control formulation without filler.

4 Summary

Aktifit Q can be easily incorporated into the system and dispersed. Compared to the unfilled printing resin, the viscosity of the liquid formulation remains at a comparable level or increases only slightly. There is no disturbing influence on the UV crosslinking. The addition of the filler increases the stiffness of the components while largely maintaining strength, strain at break and impact strength. Depending on the resin system used, a higher glass transition temperature may result, which should also lead to better heat distortion temperature.

Aktifit Q is therefore suitable as a mineral filler for use in light-curing 3D printing resins (SLA/DLP). The recommended dosage is 10-20 %.

5 Appendix



INTRODUCTION

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Table of Results

HOFFMANN MINERAL

			Aktifit Q		
		no filler	10 %	15 %	20 %
Viscosity @ 60 °C @ 80 °C @ 100 °C	 Pa·s Pa·s Pa·s	 16.9 2.49 0.63	 17.2 2.74 0.73	 16.7 2.86 0.82	 22.1 3.49 0.91
Storage modulus bei 23 °C	MPa	2013	2188	2399	2498
Glass transition temperature	°C	110	118	118	118
Tensile strength	MPa	46	44	47	49
Tensile strain at break	%	27	26	23	19
Tensile modulus	MPa	1013	1017	1085	1190
Impact strength Charpy	kJ/m²	23	23	19	22

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