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Development of binder systems for printing of medical metal and ceramic implants using FFF

Ralf Eickhoff*, Steffen Antusch*, Dorit Nötzel*, Thomas Hanemann*,**

* Materials Science and Engineering, Institute for Applied Materials, Karlsruhe Institute of Technology
** Laboratory for Material Processing, Department of Microsystems Engineering - IMTEK, University of Freiburg

Motivation

3D printing of metals and ceramics for patient-customized medical applications based on Fused Filament Fabrication (FFF) offers high product quality at low costs through the use of inexpensive commercial FFF printers and the low waste of powder. For a better usability and a higher level of detail, new feedstocks with water-soluble binder systems and superior properties were developed.

Process

Requirement and Modeling

First, the injury of the patient is analyzed and a suitable implant tailored to the patient's needs is modeled. For a better healing process and possible later implants, a bone-sparing approach is preferable.

Compounding

Before printing, the metal and ceramic powders must be mixed with the polymers for 2 hours at 160 °C to obtain homogeneous feedstocks. To control the homogeneity, the feedstocks are rheological characterized.

Extrusion and 3D Printing

To use the manufactured feedstocks in FFF printers, they must be shaped to filaments and wound onto common filament spools. Then the filaments are printed by using commercial FFF printers.

Debinding

After shaping, the binder must be removed in two steps. First, the PEG is dissolved in water. Then the remaining polymers are removed by pyrolizing.

Sintering

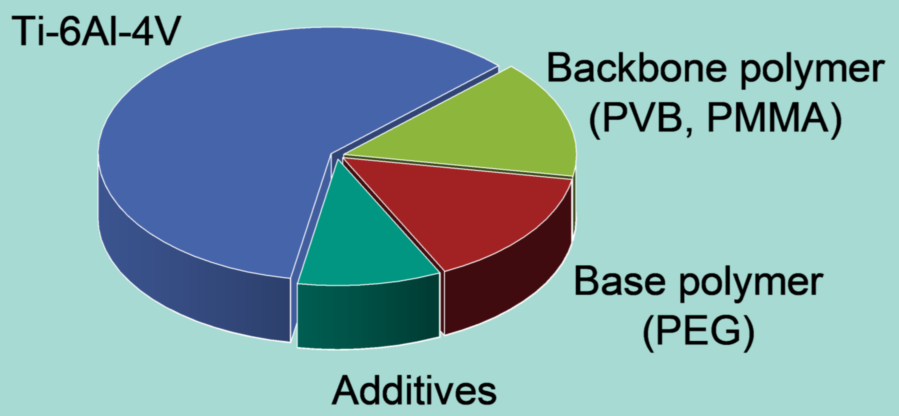
The sintering step densifies the parts. To avoid oxidation and contamination, this was done in an argon atmosphere. The ceramics were sintered in an oxygen atmosphere.

Testing and Implantation

2D and 3D measuring methods are used to check the quality and dimensional accuracy of the implants. After passing the control, the implants can be implanted.

Composition

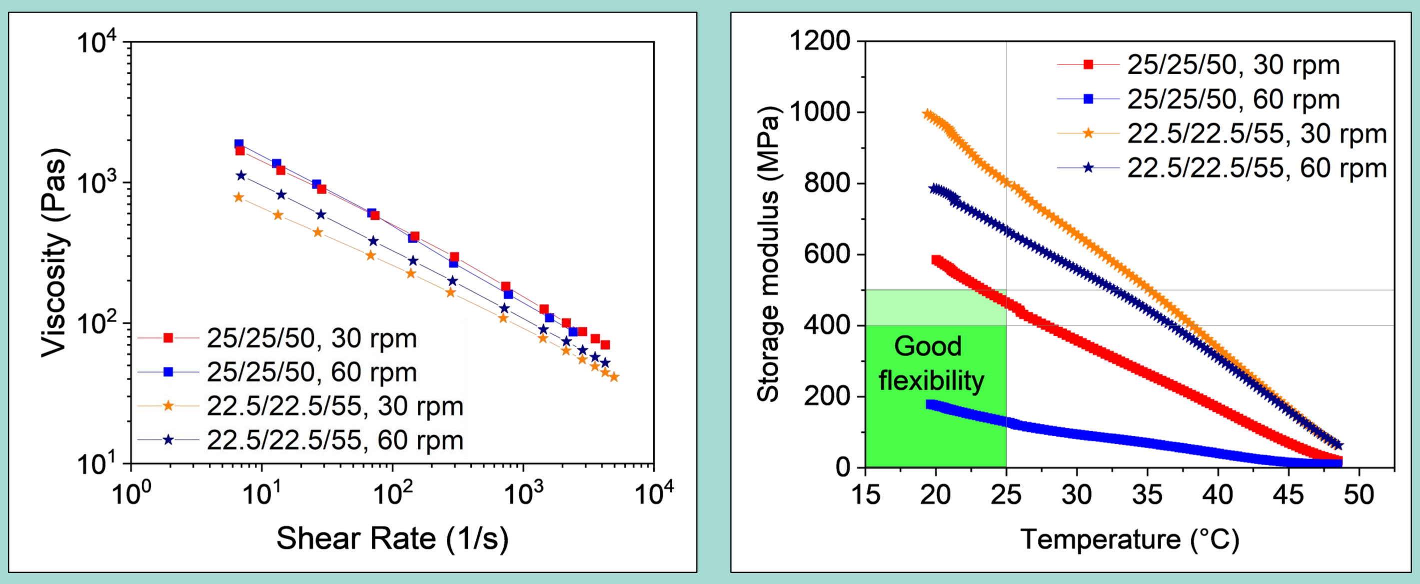
The feedstocks consist of minimum 60 vol.-% cobalt or titanium powder (CoCrMo or Ti-6Al-4V). This value was lowered for ceramics (ZrO_2) to 50 vol.%. The polymeric binder systems divide in high-viscosity backbone polymers (PMMA, PVB), a low molecular weight and water-soluble base polymer (PEG) and various non-hazardous additives (capric acid, lauric acid, stearic acid, ATBC).



Composition of a feedstock containing 60 vol.-% titanium

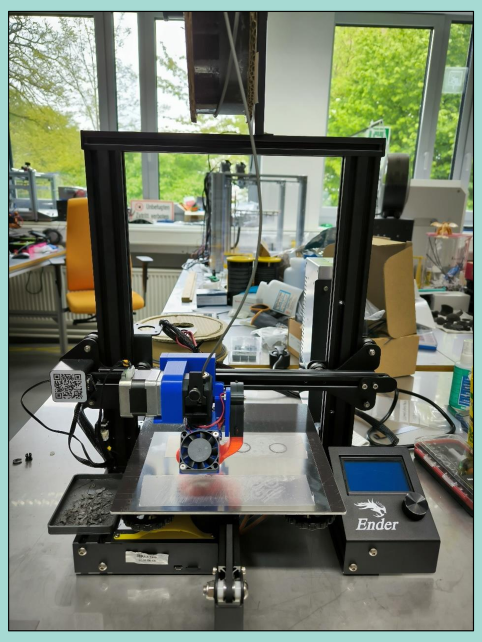
Rheology

For good processing properties and to achieve a high level of detail during printing, focus was set on the rheological behaviour of the feedstocks. The flow properties were measured using Capillary Rheology (CR) and the flexibility using Dynamical Mechanical Analysis (DMA). Not only the feedstock composition, but also the mixing parameters have a significant influence on the rheological properties. Mixing at a higher shear rate results in greater flexibility, while a higher PEG content leads to decreased flexibility.



CR at 160 °C (left) and DMA from 20 to 50 °C (right) of titanium feedstocks with 60 vol.% titanium powder and ATBC as the additive

3D printing

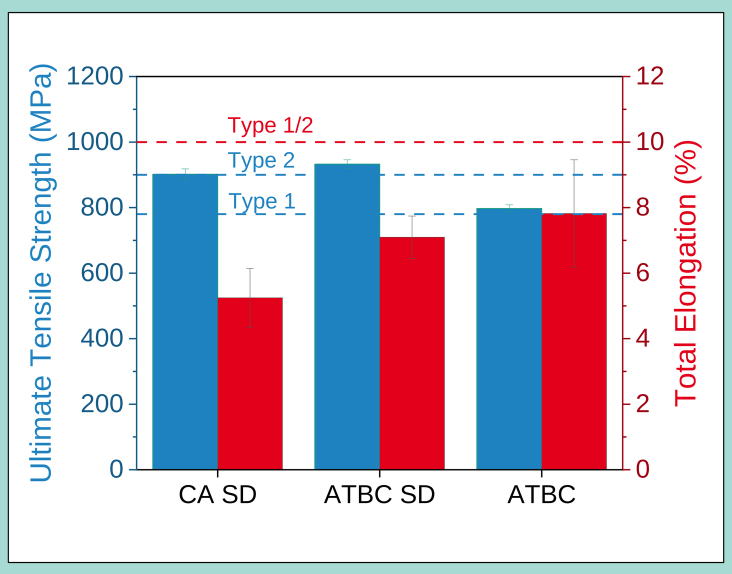


To obtain green bodies with a high level of detail, the commercial printer must be slightly modified. These modifications include for instance a spring steel sheet for a better removal of the samples or a dual gear extruder to allow printing of soft filaments.

Modified Creality Ender 3

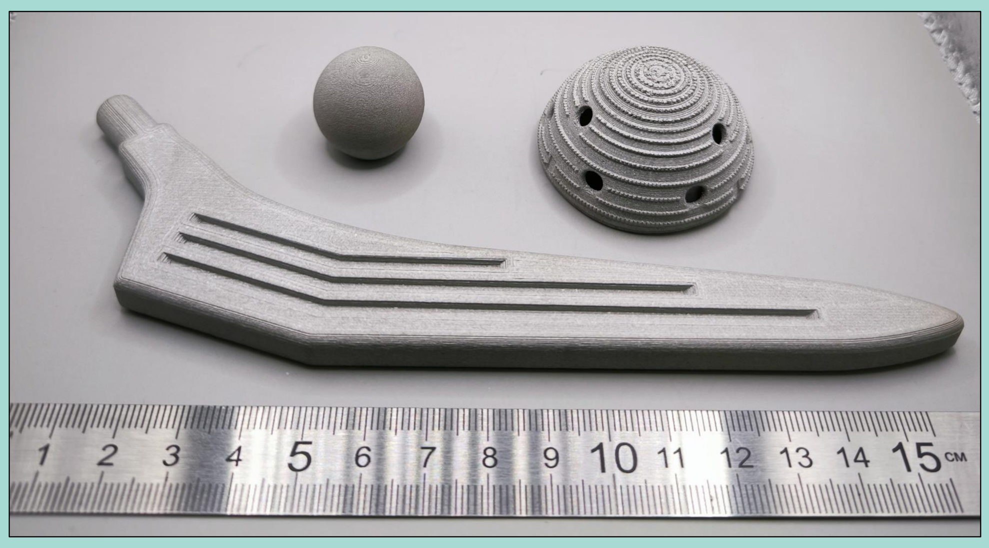
Properties of the final parts (Ti-6Al-4V)

- Relative densities between 95 and 100 % (depending on used binder system)
- Low contamination with oxygen and carbon according to ASTM F2885-17
- UTS meets the standard of ASTM F-2885-17, elongation below the required value of 10 %

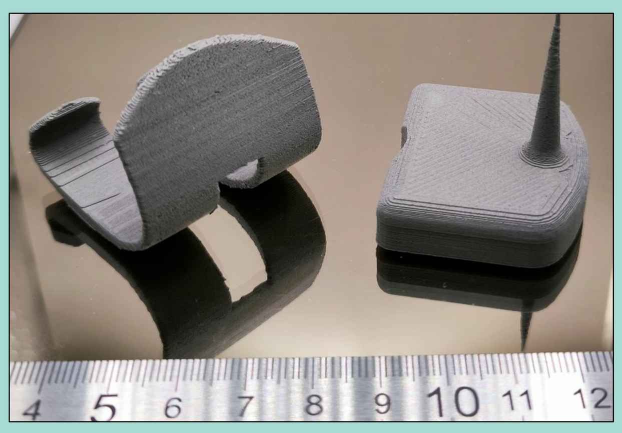


Mechanical properties of feedstocks with capric acid (CA) and ATBC. SD stands for a slow heating rate of 0.2 K/min during thermal debinding instead of the usual 1.5 K/min. Type 1 (sintered) and 2 (sintered and densified) are defined in the standard.

Printed and sintered implants



Hip implant (Ti-6Al-4V)



Knee implant (CoCrMo, green body)

Dental implant (ZrO_2)

Dental and skull implant (Ti-6Al-4V)

ralf.eickhoff@kit.edu