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Institute of Materials Science and Technology

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Additive Manufacturing of Filled and Unfilled Bio-Photopolymers

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Introduction

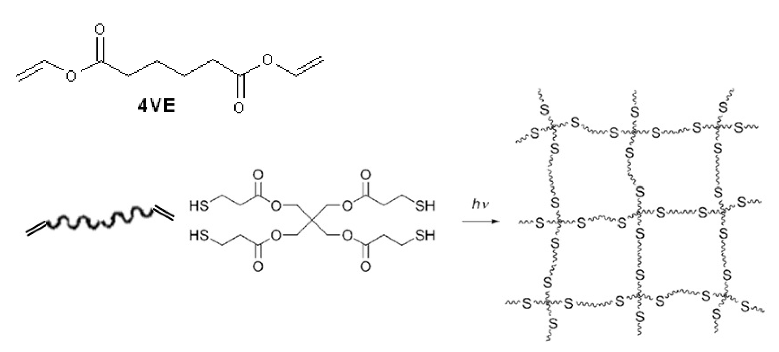
Additive manufacturing techniques offer unique possibilities in today's prototyping or even mass fabrication and are already used in different industrial sectors. Medical utilization seems to be one of the most promising application fields for these kinds of technologies today. As the development of these techniques proceeds and related machines and production units become cheaper, the demand of new working materials is growing in a significant way. In terms of medical applications as well as growing environmental concerns the need for new biocompatible or even biodegradable polymer materials is given. In this context the *Institute of Materials Science* and the *Institute of Applied Synthetic Chemistry* at the *Vienna University of Technology* are working together, developing new classes of biocompatible, photosensitive monomer solutions for their use in additive manufacturing processes.

Monomer resins based on vinyl-esters were investigated and polymerized in a 3D-printing process using DLP (Digital Light Processing) technology. By addition of special thiols monomer reactivity was increased *[1]* and the density of the resulting polymer network could be modified. Moreover biodegradability can be influenced by the amount of thiol added. To improve the overall mechanical behavior addition of glass microfibers as filling material was investigated. Mechanical characteristics of the so built biopolymer structures were tested including DMA (Dynamic Mechanical Analysis), 3-point bending tests and Charpy impact tests. Flexural modulus around 1GPa and flexural strength around 36MPa was achieved while impact strength values were reported to be up to $17 kJm^{-2}$.

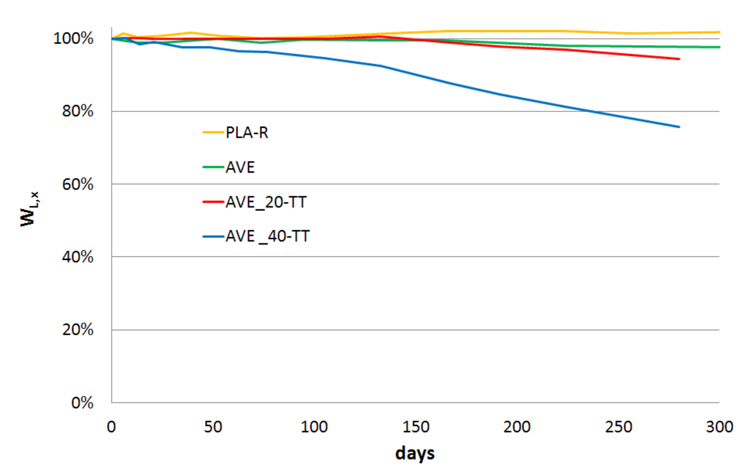
Biopolymers

For this study polymer materials for additive manufacturing processes were supposed to be biocompatible or even biodegradable. Therefore a new kind of bioactive duromer, based on vinyl-esters, was used. Biodegradability of adipic acid divinyl-esters (AVE) was proven in previous in-vitro tests *[2]* using simulated body fluid (SBF). The degradation speed could be influenced by varying the amount of thiol additives.

In relation to medical applications low toxicity of monomer degradation products as well as low maximum molecular weight are of high interest. Vinyl-esters show promise because of their hydrolytic degradation into poly-vinyl alcohols and acetic acids.

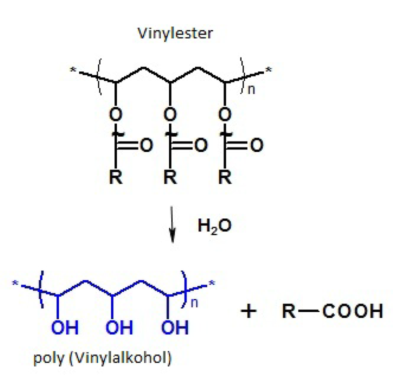


Adipic acid divinyl-ester (AVE) and *Pentaerythritol tetrakis (TT)* were combined to form a bioactive matrix system which can be easily modified in terms of biological degradation abilities.

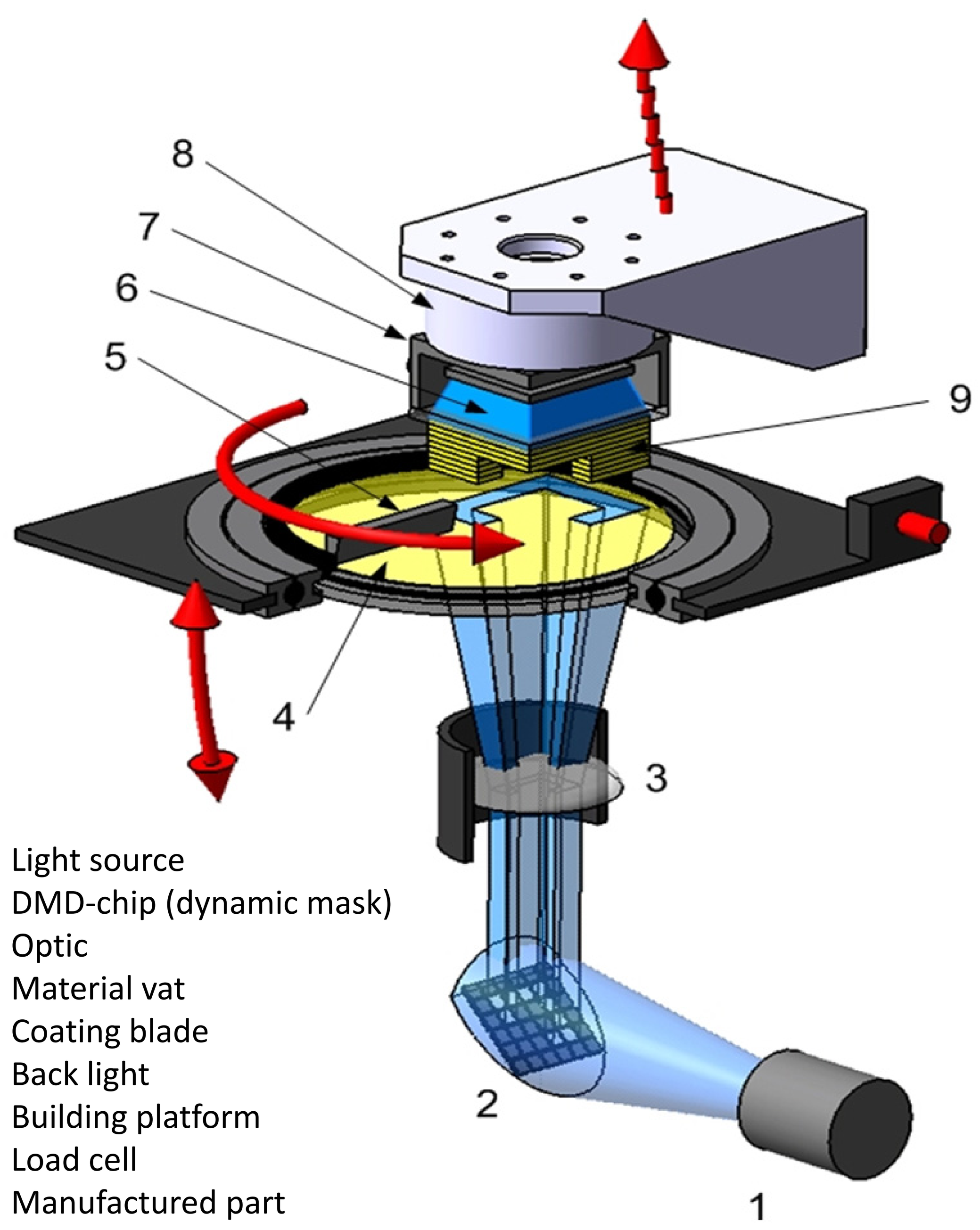


Source: *[3]*

Vinyl-ester monomers degrade in hydrolytic environments. Degradation products can be classified as non toxic as they form poly-vinyl alcohols and acetic acids. Degradation speed of vinyl-ester polymers strongly depends on the existing network density which can be modified by additives.



Additive Manufacturing

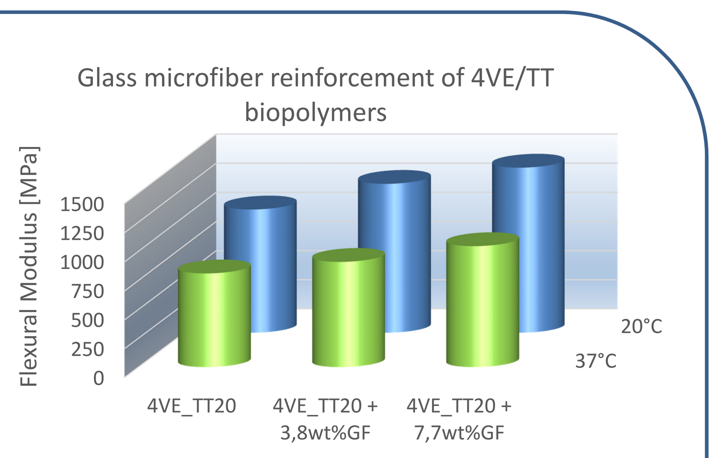


1. Light source
2. DMD-chip (dynamic mask)
3. Optic
4. Material vat
5. Coating blade
6. Back light
7. Building platform
8. Load cell
9. Manufactured part

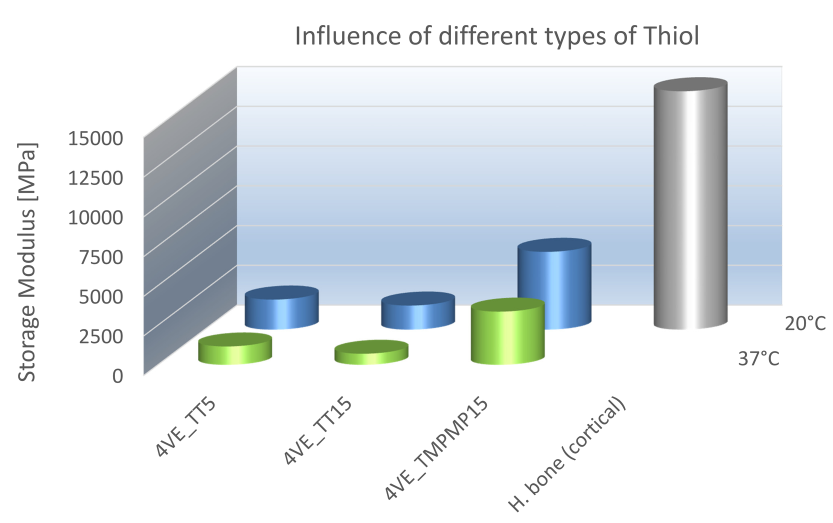
The additive manufacturing system used for this study is based on the DLP (Digital Light Processing) technology. A Digital Mirror Device (DMD) chip acts as an dynamic mask to expose a well defined area on the bottom of a transparent material vat above the optic system. The so generated pictures enable layer-wise polymerization of a photosensitive resin resulting in 3-dimensional objects. Curing takes place at wavelengths around 460nm which means blue visible light. The system combines high optical resolution allowing voxel geometries of $25x25x25 \mu m^3$ with the possibility to generate objects up to the size of a coffee cup. At the *Institute of Materials Science and Technology* at the *Vienna University of Technology* six generations of these *Blueprinter* machines have been developed and built to date.

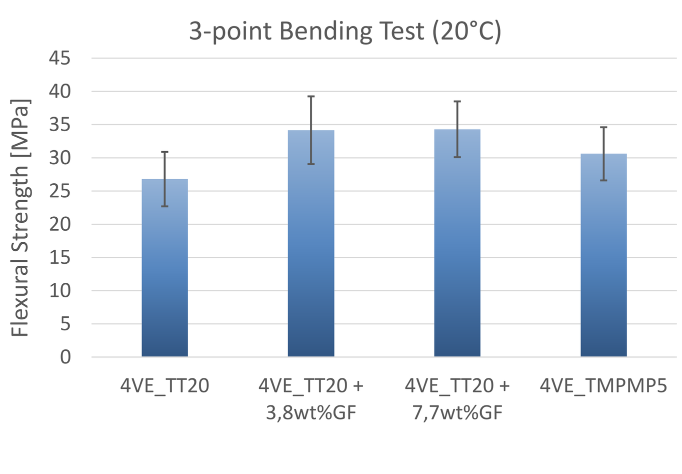
Mechanical Properties

Different mechanical analysis were conducted to characterize material properties of vinyl ester based biopolymers. Test specimen were printed using our Blueprinter machines. Anisotropic mechanical behavior due to the layer-wise building process was observed but could be minimized by adapting exposure parameters.



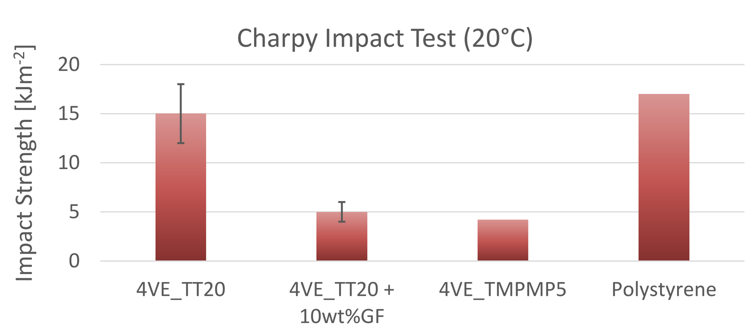
Flexural moduli of different 4VE/thiol formulations were tested using DMA (Dynamic Mechanic Analysis) method to allow a first mechanical characterization of this class of biomaterials. The influence of glass microfiber reinforcement has also been tested. Furthermore different thiols were tested to increase the stiffness of the resulting biopolymers. Modulus values can therefore be adapted in a wide range to fulfill requirements given to soft tissue and bone replacement materials. Results for 20°C and 37°C are shown on the right.



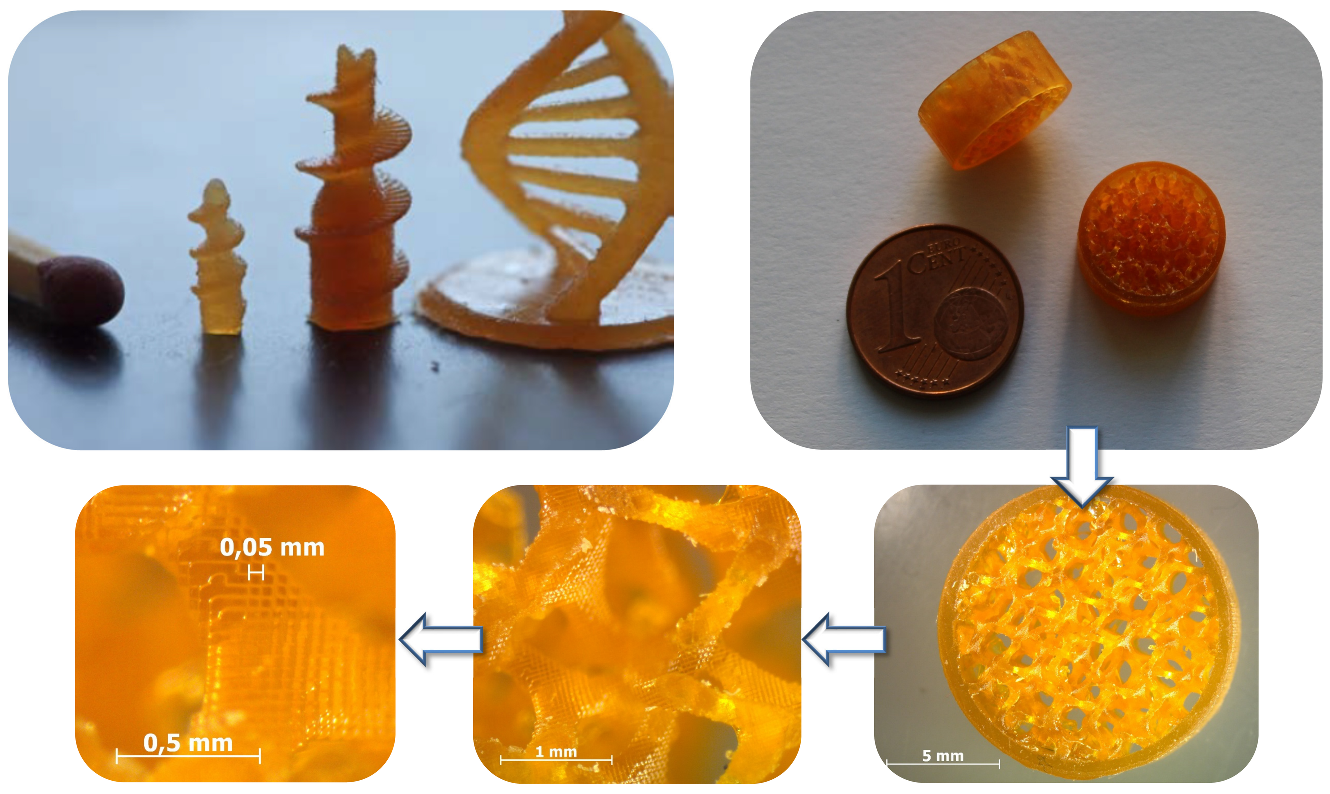


In order to determine material strength 3-point bending tests were conducted at laboratory conditions (20°C). As expected increasing bending strength was observed due to glass microfiber reinforcement. However biopolymer-microfiber bonds seem to be open for further improvement by using better fiber coating substances.

Charpy impact tests were conducted to evaluate the impact strength of different biopolymer formulations. At room temperature some unfilled 4VE/thiol formulations have shown impact strength values similar to Polystyrene.



Printed Parts



In Cooperation with the *Institute of Applied Syntethic Chemistry, Vienna University of Technology*

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[2] Husár, B., Polymer Chemistry, 2011. Biomaterials Based on Low Cytotoxic Vinyl Esters for Bone Replacement Application
[3] Mautner, A., PhD Thesis, 2012. Development of Low Cytotoxic Photopolymers