Water Soluble, Photocurable Resins for Rapid Prototyping Applications

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Summary: Rapid Prototyping (RP) is a suitable manufacturing method for fabricating structures with high geometric complexity and heavily undercut features. A special class of such structures which cannot easily be fabricated with traditional manufacturing methods are cellular materials [1].
Rapid Prototyping allows the fabrication of cellular materials on a similar size scale like in natural material-structures (e.g. trabecular bone). By using appropriate moulding techniques, these structures can be fabricated out of a wide variety of materials (polymers, ceramics, composites). In this work, several RP techniques are investigated regarding their suitability for the fabrication of cellular solids. The main focus is on using digital light projection (DLP, a variant of stereolithography) in combination with gelcasting [2] as a moulding technique. Besides using commercial light-sensitive resins, a class of newly developed water soluble resins has been evaluated regarding its usability as sacrificial mould material. These water soluble resins are compatible with a wide range of moulding techniques and therefore offer new routes for the fabrication of complex shapes out of more advanced materials than it is possible with currently used manufacturing techniques.

Keywords: digital light projection; photocurable polymers; rapid prototyping; stereolithography

Introduction

Rapid Prototyping (RP) has become a widely used tool for the fabrication and evaluation of physical prototypes during the product development cycle. RP is used since it can produce prototypes with arbitrary shapes quickly and at lower cost than traditional prototyping techniques. Recently RP has also been investigated regarding its ability to replace traditional mass manufacturing processes in applications where only one or a small number of individually

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shaped parts is required.

Especially for biomedical applications parts have to be shaped individually, and RP has for instance been considered for shaping cellular structures which later on serve as scaffolds for tissue engineering.[3]-[7].

If RP processes are to be used for such an application, several issues have to be considered:

- The process must be able to achieve the necessary feature resolution. In the case of cellular materials for biomedical applications the required cell size will typically range from 20µm to 500µm.
- Since most RP processes cannot shape advanced materials directly, the desired target material has to be moulded from a RP part. The mould material must be chemically compatible with the utilized part material and the mould must be easy to remove in order to obtain the final part.
- Cellular materials exhibit a lot of undercut features and the used RP process must be able to shape such features.

Table 1. Comparison of various RP processes.

	technical principle	Build speed	Feature resolution	Compatibility with moulding techniques	Ability to shape undercut features
Selective laser sintering	laser sintering of powder particles	++	+	+	+++
Fused deposition modeling	extrusion of thermoplastics	+	-	+	++
Wax inkjetting	inkjetting wax droplets	-	++	++	++
Stereolithography (Digital Light Projection)	photopolymerization	++	+++	+	++

In Table 1, several RP processes are compared regarding the above mentioned issues. Selective laser sintering (SLS) works with high build speeds and can easily shape undercut feature, but is somewhat limited regarding the achievable minimum feature size. Fused deposition modeling (FDM) extrudes wires with a thickness of around 0,25mm, smaller features (which might be necessary for the envisaged application) are hard to achieve. Wax inkjetting (e.g. the Modelmaker systems offered by Solidscape) uses wax materials which are compatible with most moulding techniques. If a two material system (support and build material) is used, overhanging structures can easily be built. Furthermore a good feature resolution can be achieved. The main problem with these systems is the fact, that two-material systems use only one inkjetting-nozzle per material, thus the build time for parts with complex shapes is extremely long. Stereolithography (SLA) offers excellent feature resolution and high build speed. Most cellular structures (see Figure 1) can be shaped without using support structures which have to be removed mechanically. Problems might occur if moulding techniques are to be used which do not allow a thermal removal of the SLA mould, since commercially available SLA-resins are heavily cross-linked and therefore insoluble in most solvents.

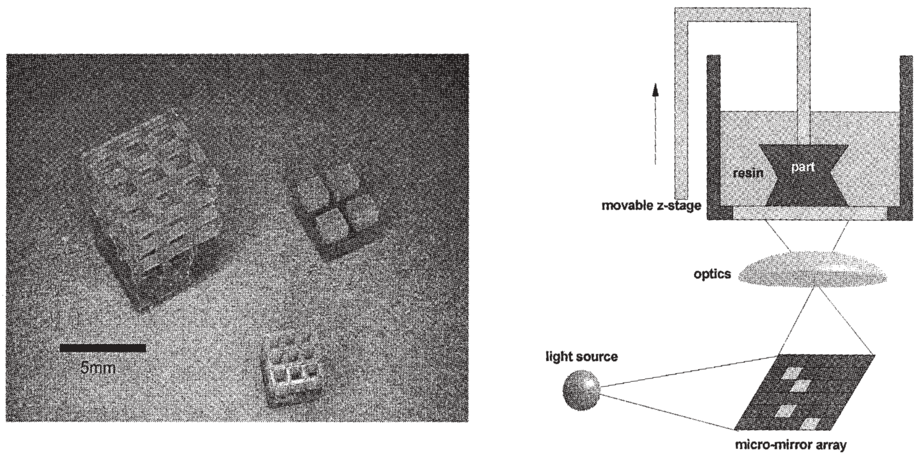
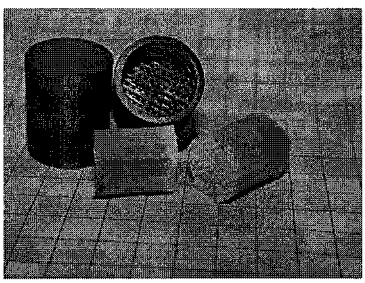


Figure 1. Cellular structures fabricated by digital light projection (left) and working principle (right) of the utilized machine.

Moulding techniques

Nevertheless, SLA seems to fulfil most of the criteria defined in Table 1, and therefore SLA and its variant digital light projection (DLP) are used in the following as primary shaping process (see Figure 1). Using the DLP moulds depicted in Figure 2, it is possible to fabricate ceramic parts using gelcasting. For this process the polymeric mould is filled with a ceramic slurry. The slurry contains monomers which start to polymerise after an initiator has been added. The slurry solidifies and the mould can be removed by thermal decomposition in order to obtain a ceramic green/brown part. After sintering, the final ceramic part is obtained (see Figure 2, right image). DLP (respectively SLA) is therefore a suitable method for the fabrication of cellular structure out of bioceramic materials. Nevertheless, the hydroxyapatite (HAP) structures shown in Figure 2 are not ideal for various biomedical applications due to two reasons:

- The HAP material is very brittle and mechanically weak. Therefore such structures are not suitable in applications where the structure is exposed to mechanical loads.
- During sintering, the HAP bioceramic will loose water and carbon dioxide. This change in chemical composition affects the bioresorbability of the material. Ideally, a fully bioresorbable HAP should not be exposed to temperatures that will lead to changes in the chemical composition.



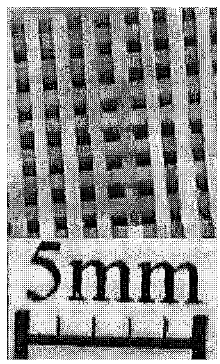


Figure 2: Mould together with gelcast HAP structures (left). Detail of sintered HAP structure (right).

Sacrificial photopolymers

In order to enable the fabrication of cellular structures out of advanced biomaterials using DLP moulds, a new route is proposed which is based on using soluble photopolymers. The basic principle of this technique is depicted in Figure 3: Using SLA (or DLP) a polymeric mould is built out of a sacrificial mould material (steps 1-3). The mould is then filled with the final part material (step 4). After the part material has solidified, the sacrificial mould is dissolved in an appropriate solvent (e.g. water) in order to obtain the final part. This type of process allows the fabrication of polymeric, composite or ceramic cellular materials using widely available lithographic techniques like SLA or DLP. Since commercially available resins are insoluble, this route is only viable if new photosensitive resins can be developed

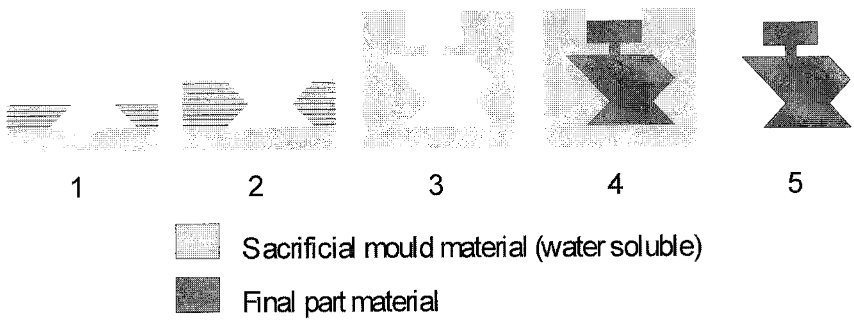


Figure 3: Proposed strategy for building parts with sacrificial photopolymers.

Water-soluble polymers [8] as sacrificial structures are easily accessible by photopolymerization of a wide range of commercially available monomers such as acrylic acid, methacrylic acid, acrylamide, dimethyl-acrylamide, dimethylaminoethyl methacrylate, vinylpyrrolidone etc. Important criteria for the selection of a suitable resin formulation are:

- Physical properties (solubility, viscosity) of the monomer
- Reactivity of the monomer
- Shrinkage during polymerization and
- Mechanical properties and solubility of the polymer.

The investigated resins where made up by the following constituents in order to fulfill the above requirements:

- Base monomer
- Co-monomer
- Filler
- Photoinitiator and
- Crosslinking agents.

Using these type of formulations, it is possible to fabricate structures with DLP which are soluble enough to be dissolved in alkaline solutions at slightly elevated temperatures (see Figure 4).

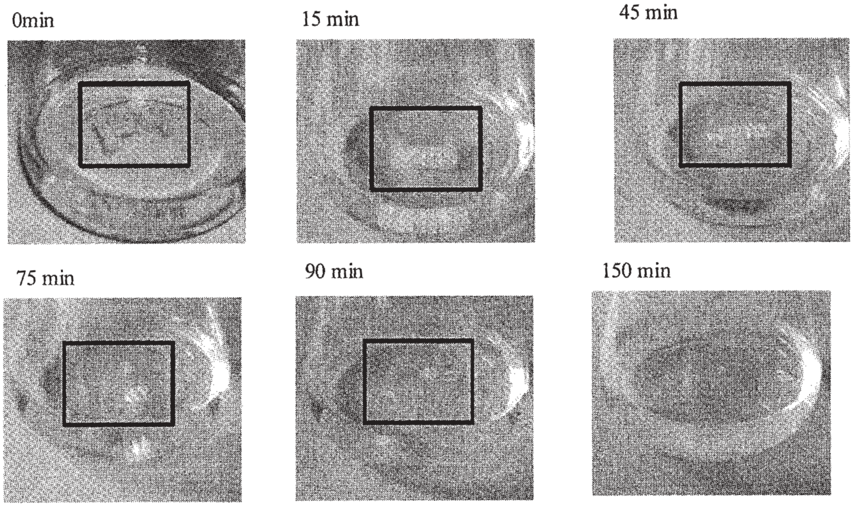


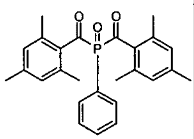
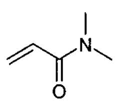
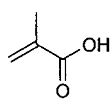
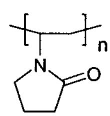
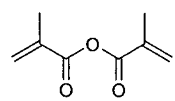
Figure 4: Dissolution of test structure in alkaline solution (1n NaOH) at 50°C.

Several issues (see Table 2) have to be considered in order to find the optimal formulation using the above mentioned constituents: The photoinitiator, which is responsible for the initiation of the polymerization process, has to produce radicals with high efficiency and high reactivity towards unsaturated compounds. By photo-DSC experiments, bisacylphosphine oxide (BPO) was found to fulfil these requirements. Besides good solubility, the DLP process requires that the photoinitiator absorbs light in the visible range of the spectrum.

To keep build times as short as possible, the base monomer should be highly reactive as found for acrylate based monomers such as dimethyl-acrylamide (DMAA). In addition, the solubility of the polymer is of prime importance which is varied by the utilized base monomer and the degree of cross-linking. Using anhydride based monomers such as methacrylic acid anhydride (MAA), cross-links can be easily cleaved under alkaline conditions. It has been found that these structural elements are essentially necessary to obtain sufficient feature resolution due to limited radical diffusion. Especially at the beginning of the polymerization process, the same effect is obtained by application of fillers such as polyvinylpyrrolidone (PVP). The higher the viscosity of the resin, the less diffusion of radicals can occur and the more locally confined the photopolymerization will take place. Furthermore, the polymer has to be insoluble in its own monomer. Otherwise exposed features will get dissolved and the accuracy of the process decreases. Suitable comonomers as methacrylic acid (MA) reduce this unwanted behaviour of base monomers like DMAA. The mechanical strength of the obtained product is defined by the degree of cross-linking and the density of hydrogen bonds in the solid polymer.

By fine-tuning these parameters, compositions can be obtained which allow the fabrication of soluble cellular structures (see Figure 5, left images). These structures can serve as sacrificial moulds for various thermosetting polymers (e.g. silicone, Figure 5, right image) which can only be obtained by using a soluble mould material. Using this route, it is therefore possible to fabricate parts with severe undercuts by utilizing SLA moulds, and the accessible material spectrum can be expanded significantly.

Table 2. Properties of constituents.

	Photoinitiator: **BPO** 	**Base monomer: DMAA** 	**Comonomer:** **MA** 	**Filler:** **NVP** 	**Crosslinking agent:** **MAA** 
Reactivity	+ excellent addition rates to double bonds	+ acrylates show highest reactivity			
Mechanical strength			+ hydrogen bonds		+ degree of cross-linking
Solubility		+ excellently soluble	+ alkaline conditions	+ excellently soluble	- alkaline conditions necessary
Shrinkage				+	
Achievable minimum feature size	+ photo bleaching effect		+ monomer insoluble polymer	+ viscosity of the resin	+ limited radical diffusion

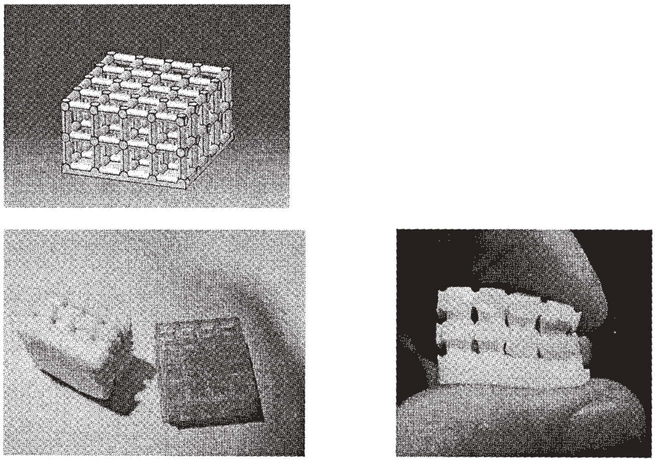


Figure 5. Cellular test structure made of water soluble photopolymer (left) together with moulded silicone structure (right).

Conclusion

It could be shown that RP is a suitable method for manufacturing cellular structures with defined internal and external geometries. Using commercially available photopolymers it is possible to shape ceramic cellular structures using stereolithography and appropriate moulding techniques. By developing sacrificial, water soluble photopolymers further materials can be made accessible to fabrication techniques based on stereolithography. The photopolymers developed for this work are suitable for the fabrication of sacrificial cellular structures. By tuning the composition of these photopolymers, solubility, feature resolution and mechanical properties can be varied according to the requirements of the application.

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