Fabrication and moulding of cellular materials by rapid prototyping

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Abstract: Many biological materials (e.g. wood, cork, bone, ...) are based on cellular designs, since cellular architectures offer the possibility to optimise the properties (stiffness, density, strength, ...) of a structure according to the environmental conditions the structure is exposed to. By using Rapid Prototyping it is possible to fabricate cellular materials on a similar size scale as in natural material-structures. 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 direct light projection (stereolithography) in combination with gelcasting as 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.

Keywords: cellular materials; ceramics; moulding; rapid prototyping.

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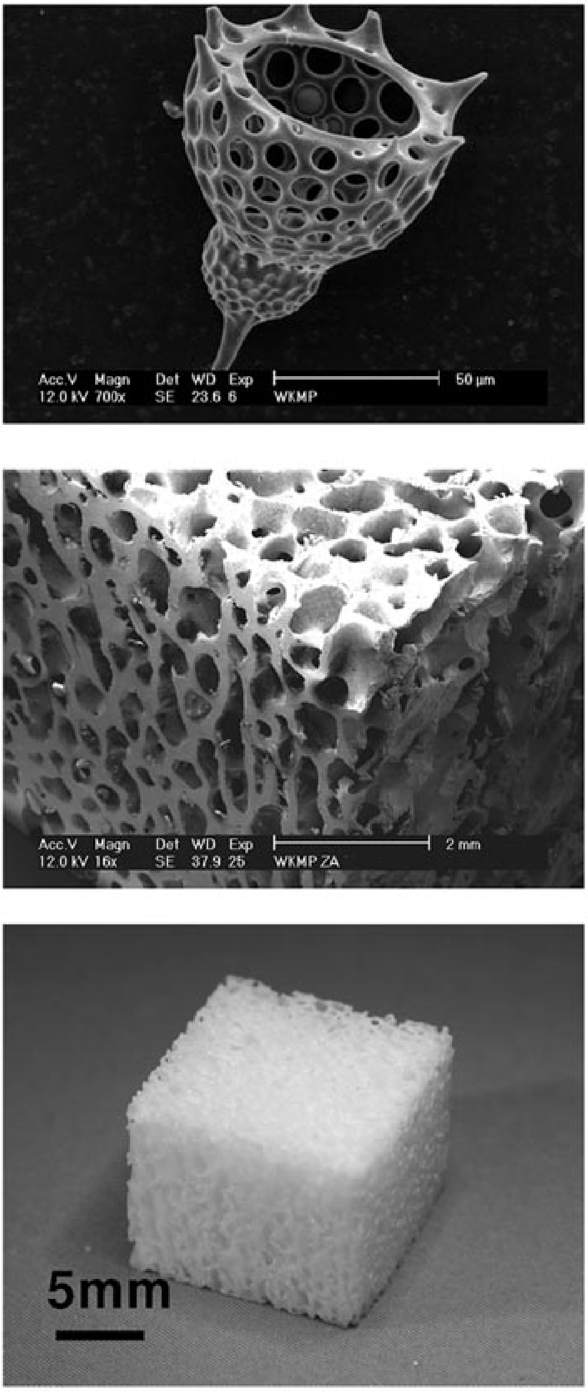
1 Introduction

Cellular solids are promising low-density materials and many natural material-structures, such as wood or bone, are based on cellular designs (Fratzl, 2002; Gibson and Ashby, 1997). Their micro-architecture is one of the determining factors for the mechanical behaviour, in addition to the apparent density and the properties of the bulk material. By varying these parameters, the mechanical properties and the overall weight of the structure can be tailored to a large extent. In Figure 1 some typical examples of such structures are shown.

In order to study the mechanical properties of such structures experimentally, it is necessary to have access to manufacturing techniques which are able to fabricate complex cellular structures with defined internal and external geometries out of various materials. Rapid Prototyping processes offer these capabilities and are therefore the most suitable route for the experimental investigation of such cellular materials.

Figure 1 Examples of natural cellular materials. The picture on the top shows a SEM image of a diatom, whose outer shell is based on a cellular architecture. The pictures in the middle and at the bottom show the trabecular structure of cancellous bone



2 Rapid prototyping processes

In this work RP processes are used to

- fabricate cellular solids with defined geometry and mechanical properties
- to fabricate cellular structures out of biomaterials which can serve as scaffolds for tissue engineering. The focus in this work is put on replicating the structure of cancellous bone.

In order to be suitable for this task, the used RP processes need to fulfil a number of requirements:

- the RP process should be capable of fabricating heavily undercut structures without the use of support material, which needs to be removed mechanically
- the achievable feature resolution should be close to the feature sizes, which are observed in cancellous bone. Typical diameters of trabecula in these materials range from 0.1 mm to 0.5 mm
- the used RP process should be compatible with various moulding processes since most biomaterials cannot directly be structured by RP.

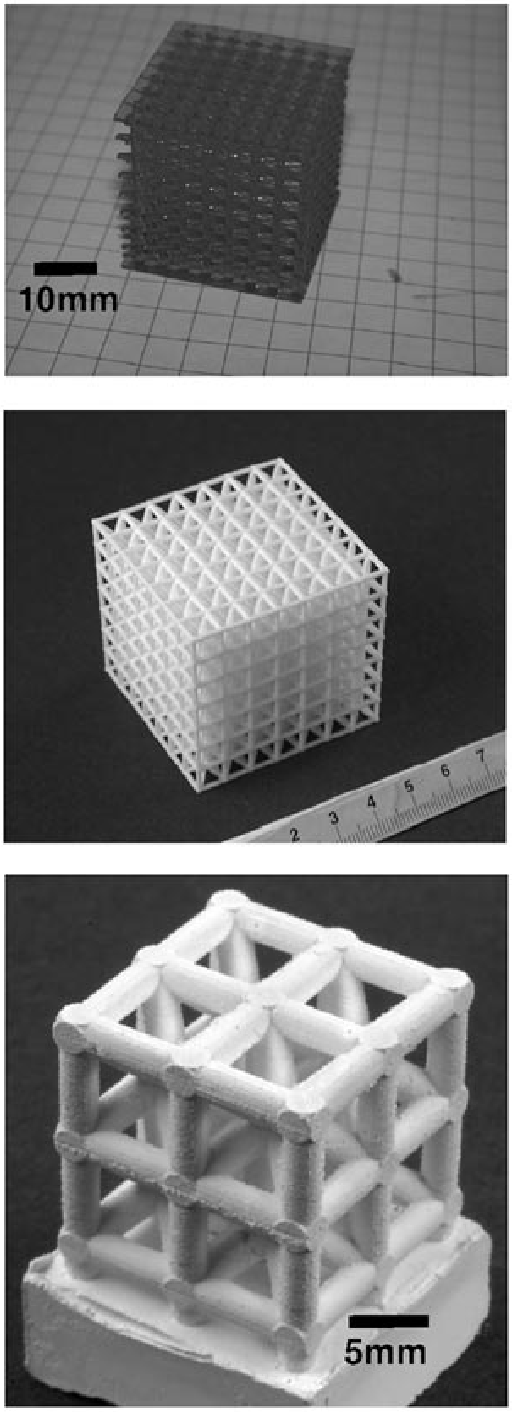
For this work, three different RP processes have been investigated regarding their suitability for the fabrication of cellular materials:

- selective laser sintering (SLS) is an appealing process due to the fact that the unsintered powder serves as support material and therefore the fabrication of structures with many undercuts presents no problem
- Digital Light Projection (DLP) (Bertsch et al., 1997) is a variant of stereolithography and uses a dynamical mask and visible light to expose photosensitive resins. Its main advantage is the very good feature resolution that can be achieved
- the Modelmaker system from Solidscape fabricates wax moulds with good feature resolution, which are compatible with a number of moulding processes.

Cellular structures, which have been fabricated with these processes, are shown in Figure 2. Each of the investigated processes offers distinct advantages and drawbacks.

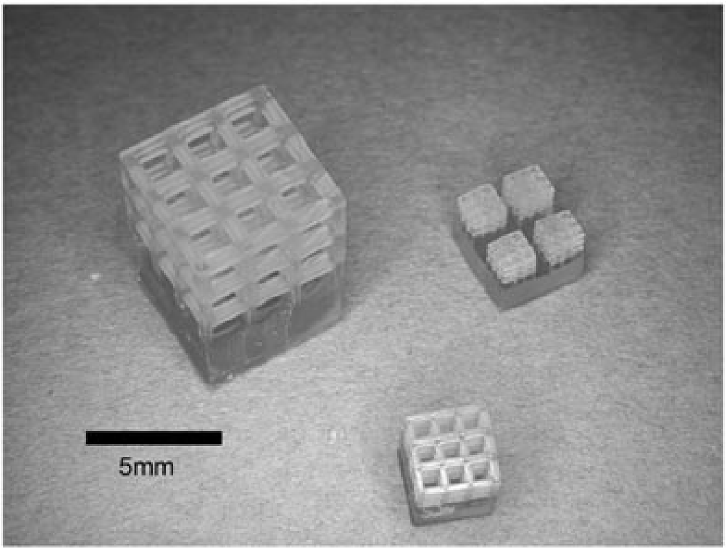
SLS is a very fast process, since many structures can be built at the same time due to the large build volume of the SLS machine. There are a number of various materials available, and especially for mechanical testing purposes (Stampfl et al., 2002b) the thermoplastic materials processes by SLS are a suitable choice. The possible feature resolution is not as good as with other processes, and there is only a limited compatibility with moulding processes, especially if ceramic parts have to be made. The minimal wall thickness (around 1 mm) is significantly larger than the typical diameter of the trabecula inside a cancellous bone.

Figure 2 Example structures made using digital light projection (top), selective laser sintering (middle), and ceramic part moulded from Solidscape ModelMaker parts (bottom)



DLP has a significantly better feature resolution than SLS. With the utilised machine (Perfactory Mini from Envisiontec) wall thicknesses down to 0.2 mm can easily be achieved (example structures made with this technique can be seen in Figure 3). The vertical build speed of these machines (around 18 mm/hour) is quite fast. However, due to the smaller build volume only fewer structures can be built at the same time, therefore the build time per structure is longer compared to SLS. Since DLP machines are significantly cheaper than SLS systems, DLP is more favourable in economic terms. Issues regarding the compatibility with moulding processes will be discussed in the next section.

Figure 3 Cellular structures with different feature resolutions made by Digital Light Projection



The Solidscape Modelmaker is appealing mainly in terms of achievable feature resolution and compatibility with various moulding processes. The feature resolution is better than in SLS, but slightly inferior compared to DLP. The Modelmaker system uses a sacrificial support material, which can be washed away after the build process (using Bioact). The remaining wax mould can be filled with various thermosetting resins (including ceramic slurries). After the resin has solidified, the wax mould can be dissolved in alcohol. Since the Modelmaker uses an ink-jetting system with one nozzle, complex parts with high resolution lead to an extremely long build-time. For academic purposes this build time is adequate, but for practical purposes the build speed for the fabrication of cellular solids is too low. If the build parameters are not carefully chosen, the wax mould will still exhibit a certain porosity, leading to flashes on the moulded part.

In Table 1 some of the key specifications of the used systems are summarised. The test part used for calculating the build speed was a cellular solid with the outer dimensions of $70 \times 70 \times 70\,mm^3$. Since the used SLS system can fabricate several of these structures at once, the total build speed was divided by the number of structures in order to get an estimate for the build duration of one structure.

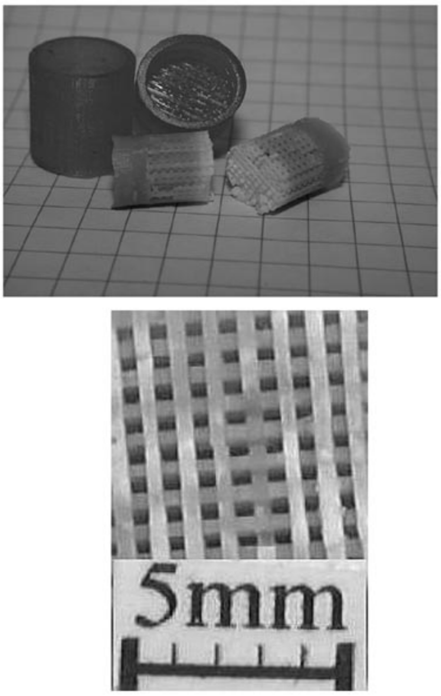
Table 1 Specifications of the utilised RP systems

System	*Resolution xy (mm)*	*Minimal layer thickness z (mm)*	*Build volume xyz (mm^3)*	*Vertical build speed (mm/hr)*	*Build duration for test part (hr)*
Envisiontec Perfactory	0.05–0.07	0.03	70×60×50	15–20	4
Solidscape Modelmaker	0.08	0.01–0.08	300×150×230	0.5–2.5	400
3D-Systems SLS		0.1	370×320×445	8	2.5

3 Moulding of ceramics

For biomedical applications, cellular materials offer an interesting route for the fabrication of scaffolding materials (Bibb and Sisias, 2002; Limpanuphap and Derby, 2002). Most materials that can be shaped directly by commercial RP systems are not suitable for these applications, since the ideal material should either be biodegradable or bioresorbable. It is, therefore, necessary to utilise appropriate moulding processes. For the use as bone scaffold, hydroxyapatite is a suitable material since it forms the ceramic base material of natural bone. For this work, moulds made by DLP (Figure 4) and the Modelmaker (bottom of Figure 2) have been used to fabricate ceramic parts by gelcasting.

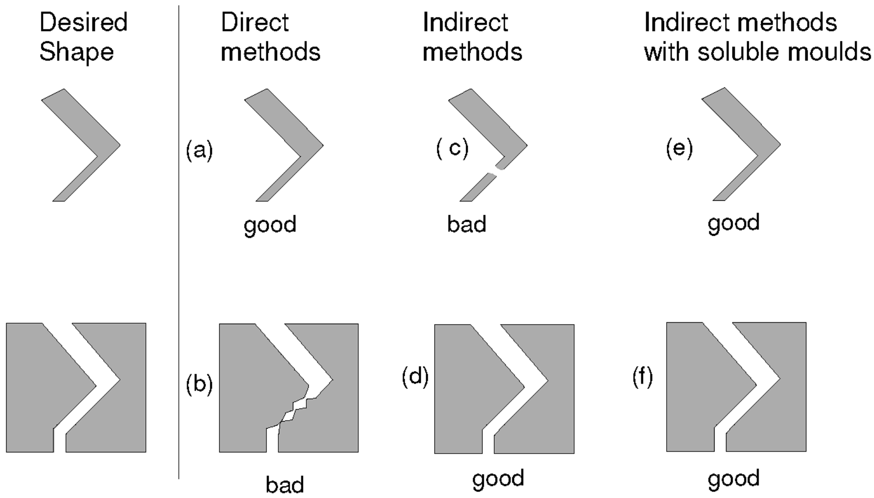
Figure 4 Cellular scaffolds out of hydroxyapatite. The top picture shows the moulds together with the sintered structures, the bottom picture gives a detailed view of such a structure



Gelcasting is a ceramic forming process, which uses thermosetting ceramic slurries, which solidify, inside a mould (Young et al., 1991). Gelcasting in combination with RP has been used to fabricate ceramic parts for biomedical (Chu et al., 2002) and engineering (Stampfl et al., 2002a) applications. Slurries based on organic and inorganic solvents have been developed. The parts shown in Figure 2 and Figure 4 have been manufactured with a water-based slurry described in Young et al. (1991). Commercial ceramic powders together with water-soluble monomers and dispersing agents are mixed into water. The solid loading of the ceramic particles is around 50 volume%. Before casting, an initiator is added and the slurry is cast into the mould where it solidifies at slightly elevated temperatures (~50°C). After solidification, the solvent (water) has to be dried off and at the next step the binder is thermally decomposed in order to obtain a brown part, which can be sintered.

The parts were debinded in an ambient atmosphere by ramping up the temperature from 50°C to 600°C in 30 hr. Sintering was done at 1250°C (for hydroxyapatite parts) and 1550°C (for alumina parts), respectively. During drying the green part will slightly shrink (around 1–3% linear). In the case of DLP moulds (which are removed thermally during debinding) this shrinkage of the ceramic part can cause cracks in delicate features since the dimensions of the mould remain constant whereas the ceramic part shrinks (see Figure 5(c)). When Modelmaker moulds are used, the wax mould can be dissolved in alcohol prior to drying of the green part.

Figure 5 Comparison of advantages and drawbacks of direct and indirect RP processes



4 Direct versus indirect processes

By using ceramic filled photocurable resins (Dufaud and Corbel, 2002; Jiang et al., 1999), it is possible to directly shape a ceramic green part without using secondary moulding processes. By using such a method, cracks due to thermal mismatch between mould and green part can be avoided (see Figure 5(a)). Problems with these methods can occur if structures with internal channels have to be fabricated, since the uncured slurry is not easily removed from these channels (Figure 5(b)). Best results for parts, which exhibit internal channels as well as delicate features, can be expected by using soluble moulds (Figure 5(e) and (f)).

Soluble moulds can be removed by an appropriate solvent instead of decomposing the mould thermally. The currently used resins for DLP and stereolithography are based on strongly cross-linked acrylates and epoxies. These materials are practically insoluble in commonly used solvents and if soluble materials are required new resins have to be developed.

In the following section initial results on water-soluble photo-curable resins are presented. This class of materials offers new possibilities for applications where the direct fabrication of the desired shape is not possible (e.g. if special materials are required) and where conventional moulding processes cannot be applied (e.g. if the parts are too heavily undercut for silicone moulding).

5 Sacrificial photocurable resins

Water-soluble polymers (Molyneux, 1983) as sacrificial structures are easily accessible by photopolymerisation (Gruber, 1992; Liska, 2002) 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:

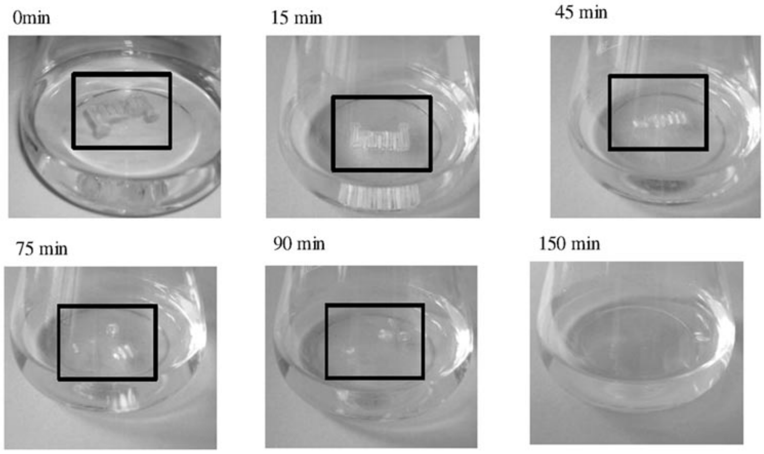
- physical properties (solubility, viscosity) of the monomer
- reactivity of the monomer
- shrinkage during polymerisation
- mechanical properties and solubility of the polymer.

The investigated resins were made up by the following constituents in order to fulfil the above requirements:

- base monomer
- co-monomer
- filler
- photo-initiator
- cross-linking agents.

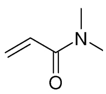
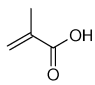
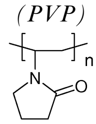
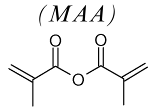
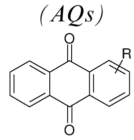
Using these types of formulations, it is possible to fabricate structures with DLP, which are soluble enough to be dissolved in alkaline solutions at slightly elevated temperatures (see Figure 6).

Figure 6 Dissolution of test structure in alkaline solution (in 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 polymerisation 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.

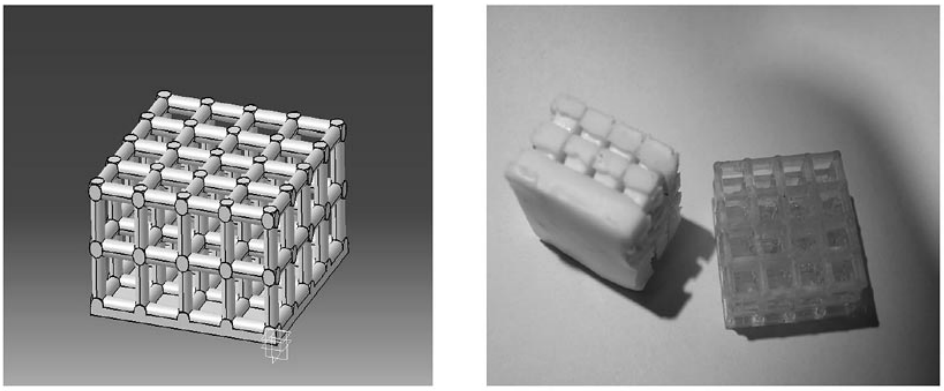
Table 2 Properties of constituents

	Base monomer (DMAA) 	*Co-monomer (MA)* 	*Filler (PVP)* 	*Cross-linking agent (MAA)* 	*Light absorber (AQs)* 
Reactivity	+ highest reactivity				– decreases reactivity
Mechanical strength		+ hydrogen bonds		+ degree of cross-linking	
Solubility	+ excellently soluble	+ alkaline conditions	+ excellently soluble	– alkaline conditions!	
Shrinkage			+		
Achievable minimum feature size	– polymer soluble in monomer	+ polymer insoluble in monomer	+ viscosity of the resin	+ limited radical diffusion	+ + increases resolution

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 utilised 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 polymerisation 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 photopolymerisation 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 co-monomers, such 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 7, right image). These structures can serve as sacrificial mould for various thermosetting polymers (e.g. silicone, Figure 7, right image), which can only be obtained by using a soluble mould material. Using this route it is possible to fabricate parts with severe undercuts by utilising SLA moulds, and the accessible material spectrum can be significantly expanded.

Figure 7 CAD-design of a cellular test structure (left). The right picture shows the cellular test structure made of water soluble photopolymer together with the moulded silicone structure



6 Conclusions

It could be shown that RP is a suitable manufacturing method for the fabrication of cellular solids. In combination with appropriate moulding methods a wide variety of engineering materials can be made accessible. For the fabrication of ceramic cellular solids, DLP (or stereolithography) seems to be the most suitable method regarding economical aspects as well as build speed and achievable feature resolution.

It could be shown that water-soluble photo-curable polymers can be shaped with DLP. These materials offer new routes for the fabrication of sacrificial moulds. In contrast to conventional moulds made by DLP (which need to be removed by thermal decomposition) these sacrificial moulds can be dissolved at temperatures close to room temperature and are, therefore, more suitable for moulding temperature sensitive materials (e.g. composites).

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