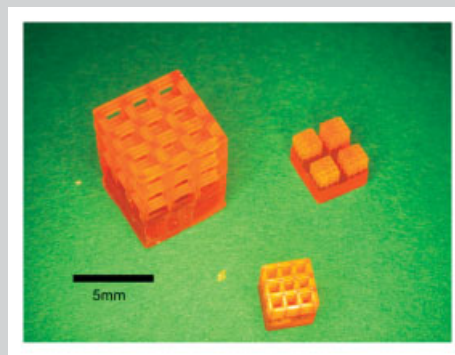


**Summary:** Rapid prototyping (RP) is a widely used manufacturing tool in the product development cycle. This Highlight article gives a brief overview of the currently available RP techniques with special emphasis on three-dimensional (3D) printing. The advantages and drawbacks of various RP processes regarding material quality, feature resolution, and surface quality are pointed out. New developments in the field of material development allow the use of polymer ionomers for 3D printing. Using polymer ionomers some of the drawbacks of 3D printing can be eliminated. In particular, the mechanical strength can be increased compared to traditional powder systems used for 3D printing. This article describes the chemical background of polymer ionomers and the relevance of these materials for future developments in RP.



Cellular structures made of photopolymerizable polymers.

## New Materials for Rapid Prototyping Applications

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### Why Do We Need New RP Materials?

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 a 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 shaped parts is required. Recently, Mühlhaupt and coworkers<sup>[1]</sup> presented a novel class of materials for RP and the following text will try to emphasize the importance of material developments for future applications of RP technologies.

Regarding the type of applications for which the RP models are used, the following groups of prototypes can be distinguished:

- i) Visual aids, which serve for visualizing design concepts and evaluate the ergonomics of a prototype.
- ii) Concept models that provide a certain functionality and are accurate enough to test whether individual parts fit properly within an assembly.
- iii) Master patterns for tooling and molding processes.
- iv) Functional parts that can be used to evaluate the functionality of certain parts before they are mass fabricated. Functional models need to fulfill high requirements regarding material quality and shape accuracy.
- v) Customized products, which are tailored according to specific requirements of the customer. Customized products are usually made in quantities between one and ten. Applications are mostly in the field of biomedicine, where individual shapes according to a patient's requirements have to be manufactured.

The field of visual aids, concept models, and master patterns is traditionally the 'home-ground' of RPs. Most RP processes are optimized for fabricating such prototypes. Since the market for classical prototyping services is saturated and prices for parts offered by RP service bureaus have fallen constantly,<sup>[2]</sup> the future growth of the RP industry will take place on two levels:

- i) Low-cost three-dimensional (3D) printers for design bureaus and engineering departments in small and medium-sized companies. These low-cost 3D printers

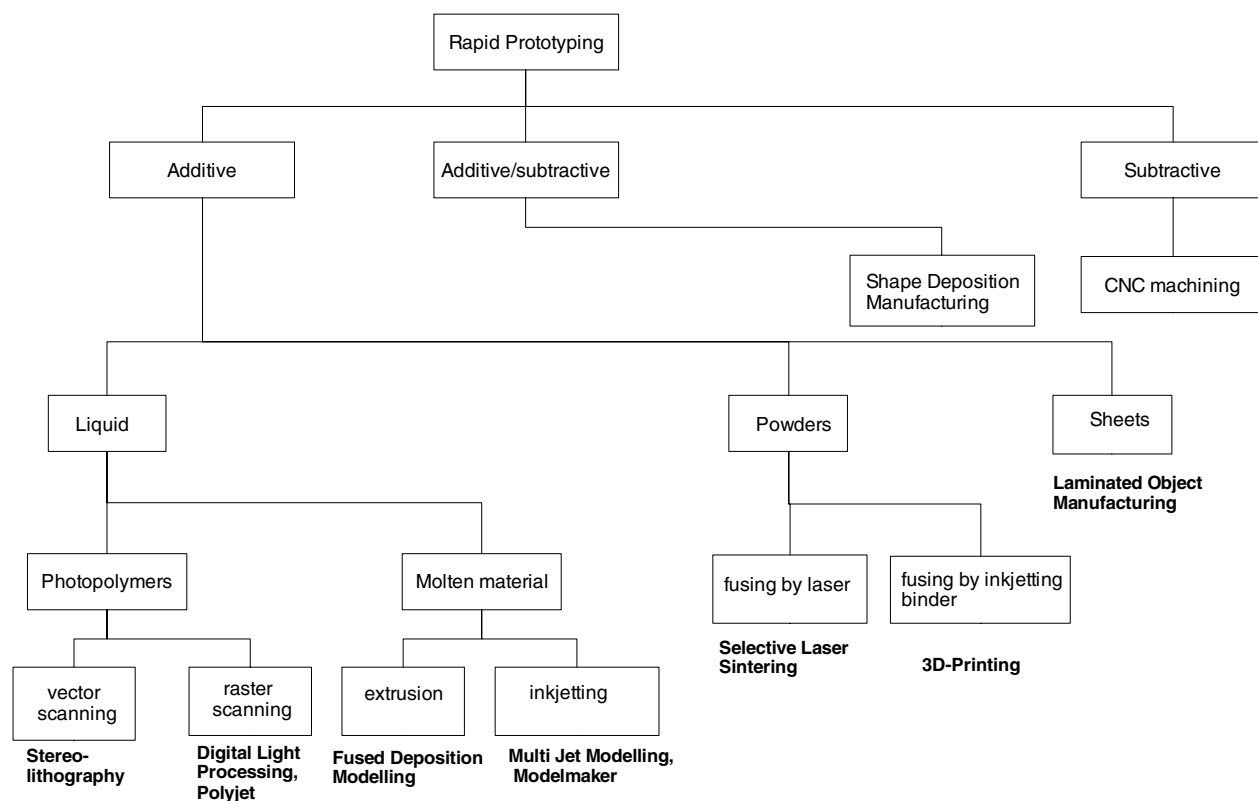


Figure 1. Classification of RP processes.

will probably rely heavily on components that are currently used in consumer electronics (e.g., inkjet heads from printers or digital mirror devices that are currently used in video beamers).

- ii) High-end applications where parts with excellent accuracy and/or feature resolution are required. In many cases the materials that these parts are made of have to fulfill specific functional and structural properties.

In Figure 1 most commercially available RP processes are depicted, categorized by the base material which is used (liquid, powder, etc.). It can be expected that the technology for the low-cost sector will be focused around the ink-jet-based processes (3D printing, multi-jet modeling, poly-jet, etc.) since these systems are mainly based on cheap components that are used in many other consumer-oriented applications. Current system prices for these technologies range between €25 000 and 50 000 for the simplest machine types.

The high-end applications will probably continue to rely on lithographic techniques, since stereolithography has a good track record regarding surface quality and shape accuracy. By number of installed systems, stereolithography, with a 40% share, is still the dominating technique<sup>[2]</sup> and recent advances in materials developments<sup>[3,4]</sup> have shown that functional materials can be shaped with lithographic techniques. One of the main advantages of lithographic techniques is their unrivaled feature resolution.

Commercially available systems allow the fabrication of parts with minimum wall thicknesses of around 100  $\mu\text{m}$  and feature resolution of around 20  $\mu\text{m}$ . An example of a cellular structure with minimum strut diameter of 200  $\mu\text{m}$  is shown in Figure 2.

Mühlhaupt and coworkers<sup>[1]</sup> present a new class of materials for 3D printing (3DP). 3DP is an ink-jet-based technology that offers a number of advantages: 1) It is currently the fastest RP process. Through the use of commercial ink-jet heads and the development of appropriate binder systems, 3DP systems allow high build speeds that are more or less independent of shape complexity and part

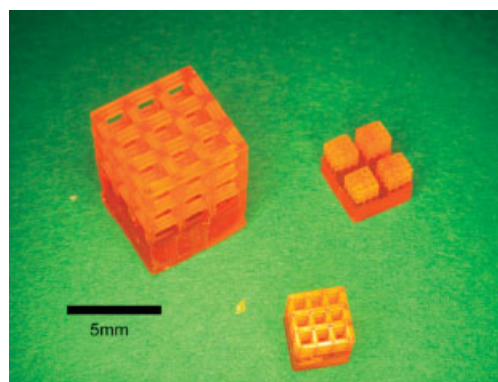


Figure 2. Cellular structures made of photopolymerizable polymers.

size. 2) 3DP systems are cheap since key components of these systems are also used in large-volume products like ink-jet printers. 3) 3DP is currently the only RP process that allows the fabrication of fully colored models.

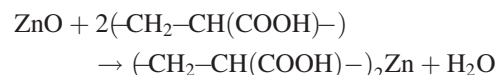
Up to now 3DP has also suffered from a number of drawbacks: 1) After the build process is complete, the part has to be removed from the powder bed. During this process fragile features of the parts might break off. 2) Without infiltration, 3DP parts are mechanically weak and their use as functional parts is limited. 3) Because of the use of powders, the surfaces of 3DP parts are fairly rough. The first and second drawbacks can potentially be eliminated by using polymer ionomers presented in ref.<sup>[11]</sup>

One of the major drawbacks of RP is that only a selected range of materials can be processed directly. In particular, in the field of biomedical applications post-treatment processes or molding techniques have to be used to obtain biocompatible and/or biodegradable parts. A fairly large number of biomaterials, e.g., bioceramics, biodegradable polymers, or silicones, are accessible by molding techniques (see, for example, ref.<sup>[5,6]</sup>). But from a practical point of view, direct methods are preferred. Direct printing of biopolymers and biocomposites has been achieved by using fused deposition modeling,<sup>[7]</sup> by 3D printing,<sup>[8,9]</sup> and by stereolithography.<sup>[10,11]</sup> Biopolymers which can be processed by these techniques are mostly based on poly(propylene fumarate), block copolymers of oligo ethylene glycol with lactic acid, or polycaprolactone.<sup>[12–14]</sup> Therefore, there is a strong demand for alternatives that can be processed easily. Mühlhaupt and coworkers<sup>[11]</sup> have recently shown that polymer ionomers are a promising class of materials that can be printed directly without the need of post-treatment processes.

## Chemistry and Material Properties of Zinc Ionomers

The concept of polyelectrolyte cements was developed in 1963, which led to the first application of zinc polycarbox-

ylate cements as dental filling materials.<sup>[15]</sup> This combination belongs to the class of materials known as acid–base reaction cements. The constituents are poly(acrylic acid) (PAA) and a deactivated zinc oxide powder. For deactivation ZnO is mixed with small amounts of magnesium oxide and fused at ca. 1 200 °C. By this pre-treatment, evaporation of oxygen gives a non-stoichiometric material  $\text{ZnO}_{(1-x)}$  where  $x$  is less than or equal to 70 ppm.<sup>[16]</sup> This and the addition of magnesium oxide reduces the reactivity towards the acid and, therefore, adjusts the setting time. The zinc ions released from the ZnO particles crosslink the PAA chains and effectively render them insoluble.



Crosslinking was reported to take place via a sort of “bridge” between the divalent zinc cation and the hydrophilic functional groups on the polymeric chain,<sup>[17]</sup> see Figure 3.

The set cement consists of unreacted metal oxide particles embedded in a zinc polyacrylate matrix. It should be noted that inclusion of magnesium oxide in the cement powder increases the water sensitivity of the materials because of non-specific binding.<sup>[18]</sup>

Low molecular weight and narrow distribution in the PAA is important to avoid “cob-webbing” in the cement mix.<sup>[19]</sup> The zinc–PAA cement is reasonable brittle, though it shows some plasticity for some time after formation.<sup>[20]</sup> It behaves in many ways like thermoplastic composites, as the chain length of the PAA had significant influence over the fracture properties<sup>[21]</sup> and Young’s modulus. Typical compressive strength is in the order of 80–100 MPa for a mixture consisting of three parts of a 40 wt.-% aqueous PPA and one part of metal oxide powder, which sets within 2–4 min.<sup>[20]</sup> The maximum strength is usually achieved after one week. The final porosity can be tuned by the chemical composition of the composite. A ZnO/PAA ratio of 0.6 resulted in minimal porosity.<sup>[22]</sup> Besides good physical properties, such formulations also have good adhesion properties, e.g., to tooth tissues where  $\text{Ca}^{2+}$  could also

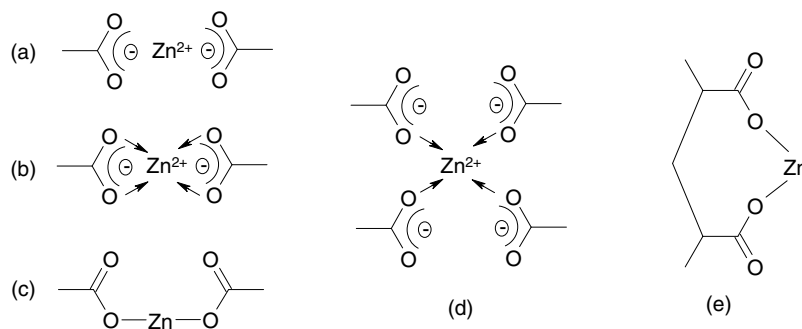


Figure 3. Possible modes of bonding of  $\text{Zn}^{2+}$  to carboxylate groups in zinc polycarboxylate cements: a) ionic, b) chelating bidentate, c) asymmetric unidentate, d) bridging bidentate, and e) chelate bidentate (eight-membered ring) (after Nicholson et al.<sup>[17]</sup>).

interact with the PAA chain. It should be noted that zinc ions are more strongly bound to polyacids as they have a smaller radius and greater electronegativity than calcium ions.

The zinc–PAA cements can be considered as good biomaterials because they are characterized by low toxicity. Zinc is fundamental for cell growth, development, and differentiation.<sup>[23]</sup> It is also known to assist in the prevention of bacterial infection<sup>[24]</sup> and to support wound healing.

Further developments were targeted towards glass–ionomer cements, because dental materials from zinc and other metal oxide cements were opaque and unaesthetic. Several excellent overviews have been published recently.<sup>[25–27]</sup> The first practical glass–ionomer cements were introduced in 1972. Important factors are the Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> ratio<sup>[28]</sup> and the application of tartaric acid to improve the setting properties.<sup>[29]</sup> The organic polymer consists of PAA or copolymers with itaconic acid. Poly(vinyl phosphonic acid)<sup>[30]</sup> or *N*-acryloyl-substituted amino acids<sup>[31]</sup> were described as suitable alternatives.

Future aspects of 3D printing using polymer ionomers might be seen in the application of glass ionomers for medical applications, since a further increase in strength and stiffness can be expected from such developments.<sup>[25]</sup>

Dual cure systems utilizing photopolymerizable monomers, e.g., hydroxyethyl methacrylate (HEMA), 2,2-bis[4-(2-hydroxy-3-methacryloxyprop-1-oxy)-phenyl]propane (Bis-GMA), or triethylene glycol dimethacrylate (TEGDMA) in resin-modified glass ionomers<sup>[25]</sup> can further improve and tune the mechanical properties towards the desired application. In addition, this concept may open the ability for 3D tuning of the material properties by selective irradiation of the composite material.

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