Non-toxic flexible photopolymers for medical stereolithography technology

Arthur Bens, Hermann Seitz, Günter Bermes and Moritz Emons
Center of Advanced European Studies and Research, Bonn, Germany

Andreas Pansky, Barbara Roitzheim and Edda Tobiasch
Department of Natural Sciences, University of Applied Sciences Bonn-Rhein-Sieg, RheinBach, Germany, and

Carsten Tille
Center of Advanced European Studies and Research, Bonn, Germany

Abstract

Purpose – To describe the development of a novel polyether(meth)acrylate-based resin material class for stereolithography with alterable material characteristics.

Design/methodology/approach – A complete overview of details to composition parameters, the optimization and bandwidth of mechanical and processing parameters is given. Initial biological characterization experiments and future application fields are depicted. Process parameters are studied in a commercial 3D systems Viper stereolithography system, and a new method to determine these parameters is described herein.

Findings – Initial biological characterizations show the non-toxic behavior in a biological environment, caused mainly by the (meth)acrylate-based core components. These photolithographic resins combine an adjustable low Young's modulus with the advantages of a non-toxic (meth)acrylate-based process material. In contrast to the mostly rigid process materials used today in the rapid prototyping industry, these polymeric formulations are able to fulfill the extended need for a soft engineering material. A short overview of sample applications is given.

Practical implications – These polymeric formulations are able to meet the growing demand for a resin class for rapid manufacturing that covers a bandwidth from softer to stiffer materials.

Originality/value – This paper gives an overview about the novel developed material class for stereolithography and should be therefore of high interest to people with interest in novel rapid manufacturing materials and technology.

Keywords Polymers, Resins, Mechanical properties of materials

Paper type Research paper

1. Introduction

One of best-known rapid prototyping processes, stereolithography, is widely spread and is often used in a broad field of technical applications nowadays, mainly within the aerospace, automotive and mechanical engineering industries (Wohlers, 2005). The technique of stereolithography uses a liquid photopolymer that is locally cured by a UV laser. Mechanical properties of the applied photopolymeric resin materials are mainly optimized to mimic stiff technical polymers like PP, PE or ABS. However, today standard stereolithographic resins are based on epoxies due to their good behavior according to accuracy and shrinkage. In the last years, one could see a growing need for resins with alternative material properties in order to enter new fields of application (DSM Somos Corp., 2006; 3D Systems Corp., 2006). A special focus lies on significantly softer stereolithographic materials. Initial efforts to such technical resins with a low Young's modulus (25-750 MPa) are currently showing up on the rapid prototyping market (DSM Somos Corp., 2006). Our focus of material development is clearly located in the medical technology area. This sector is growing very fast and steadily now, so our material and process research concentrates on the development of innovative materials and processes for this complex field of medicine and medical technology.

Common epoxy-based materials are not suitable for medical applications due to the known irritating and cytotoxic effects on human cells, resulting mainly from uncured epoxies in the cured polymer prototypes. To overcome these severe problems of the biological incompatibility, a new polyether(meth)acrylate-based resin material class has been developed and will be presented herein (Bens *et al.*, 2004, 2005a, b, c). The new resin class, called FlexSL®, is a flexible resin formulation for a broad range of hardness and elasticity adjustable to the requirements in

The current issue and full text archive of this journal is available at
www.emeraldinsight.com/1355-2546.htm

Rapid Prototyping Journal 13/1 (2007) 38–47

[DOI 10.1108/13552540710719208]

The authors thank the students from the University of Applied Sciences Bonn-Rhein-Sieg for their kindness to provide the data from the detailed biological experiments. Special thanks to Prof. M. Schulze for performing the GPC measurements and providing additional chemical data.

Received: 17 November 2005
Revised: 7 July 2006
Accepted: 25 July 2006

medical technology. The term "soft material properties" shall refer here to low values (25-750 MPa) up to mid values (Shore A 55-90) with an increased elongation at break.

Depending on the individual application, FlexSL photopolymeric formulations (Figure 1) can also be modified with various components like special dyes, pigments and fillers. Depending on the individual formulation, the cured resins show Young's modulus in the range from 10 up to 2,000 MPa. Furthermore, other mechanical parameters (e.g. hardness) are customizable in a broad range. These properties will be presented in the following chapters.

The usage of resins in medicine and medical technology is currently widened. The current areas of use for medical rapid prototyping and medical rapid manufacturing are ranging from pre-surgical planning models, e.g. individual anatomical models (even with a realistic representation of hard and soft tissue), general surgical tools for the operating theater usage, to direct manufactured drilling and cutting guides (D'Urso *et al.*, 1999, 2000, D'Urso, 2006; Irsen *et al.*, 2004; Seitz *et al.*, 2004; SurgiGuides Materialise, 2006). The use of biocompatible (non-cytotoxic), sterilizable materials is therefore necessary for every usage within the operation theater. The production of non-toxic, biocompatible design and functional prototypes for medical device development is another field of interest in this industry. Biocompatibility of the processing material such as photopolymers for stereolithography is therefore an essential requirement for the fabrication of, e.g. custom-designed medical prototypes and devices (Tille *et al.*, 2005a, b).

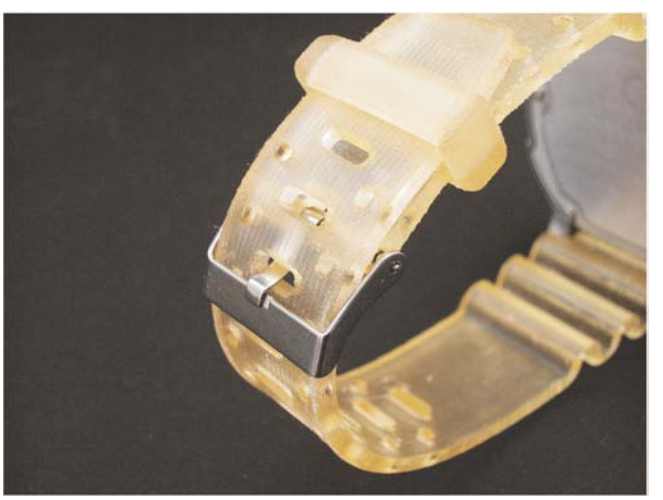
For this reason, we have started to investigate detailed pathways of cytotoxic agents from commercially available raw materials. The general biological characterization of a new medical material has to follow the ISO 10993 procedures, and we can show initial results in the corresponding chapter.

2. Materials composition

The basic FlexSL® resin class consists of mainly these components (Figure 2):

- very flexible oligomeric, polyether(meth)acrylate monomers with a high molecular weight;

Figure 1 Sample part (material: FlexSL SE-25), demonstrating the flexibility of the resin material



- polyfunctional polyether(meth)-acrylate monomers with a lower molecular weight;
- polyfunctional cross linking (meth)acrylates with lower molecular weight; and
- special selection of additives (photoinitiators, stabilizers and other processing chemicals).

There is also an option to add special dyes, pigments or organic and inorganic filler materials that can significantly alter the material properties into the direction of the customer needs. Figure 2 shows the basic chemical structures in a typical composition of a selected FlexSL resin formulation.

First, of all we have performed initial experiments to evaluate the possible bandwidth of material properties. This could be achieved by combining a very flexible oligomeric, polyether(meth)acrylate monomer with high molecular weight on the one hand with a short and therefore hard-segment polyfunctional cross linking polyether(meth)acrylate monomer or polyfunctional tri-acrylate with lower molecular weight on the other hand. Figure 3 shows the details of used compositions Flex-1 to Flex-20 of the initial tests.

3. Mechanical properties

All (meth)acrylates were weight into glassware equipment according to their percentage. Additionally, the photoinitiator was added to the (meth)acrylates mixture according to its weight percentage.

The initial formulations were mixed in complete darkness at room temperature and normal atmosphere for additional 24 h. For advanced FlexSL resin formulations (e.g. Flex-201, Flex-202) the components were weight into a stainless steel tank (3-12 l volume) and stirred with a laboratory dissolver from ATP engineering at 2,000-4,000 rpm for 30 to 90 min. All resins are kept for 24 h in darkness.

The samples of the initial formulations (Flex-1 to Flex-20 and Flex-1XX series) were cast into a silicone mould and were cured using an Hg high-pressure lamp (Lumatec SUV-DC-P) with 30 mW/cm^2 and an energy dose of 1.8 J/cm^2. The cured tensile test bars were cleaned with a paper and acetone. For the advanced FlexSL resin formulations (see above), the tensile probes were built on a 3D Systems Viper Si^2 stereolithography equipment.

For the development process, it was necessary to make a new resin vat design. A normal vat has a minimum volume of over 10 l (2 in. vat for the 3D Systems Viper Si^2), so to test the realistic behavior of the new resins we decided to reduce the resin volume by designing a smaller vat system, called X-vat (Figure 4). This makes it possible to process our resins on a build envelope of ca. 110 × 250 × 30 mm (3.0 l option) or 250 × 250 × 30 mm (5.0 l option). All critical process parameters, e.g. recoating styles, can be determined exactly like in a large vat. It is now possible to develop even individual resins with low production volume. Furthermore, for further cost reduction it was possible to design a micro- X-vat with a vat volume from 0.5 to 1.0 l that also fits in the SLA system.

All tensile probe samples were finally measured with a universal testing machine (Zwick-Roell) according to DIN 53504 and DIN EN ISO 527-1.

The Young's moduli of Flex-1 to Flex-20 shown in Figure 5 are an indication of variable material properties. On the left part of the diagram (Figure 5), the formulations Flex-01 to Flex-10 show the possible bandwidth of Young's moduli.

Figure 2 Chemical structures of the two basic (meth)acrylate based components

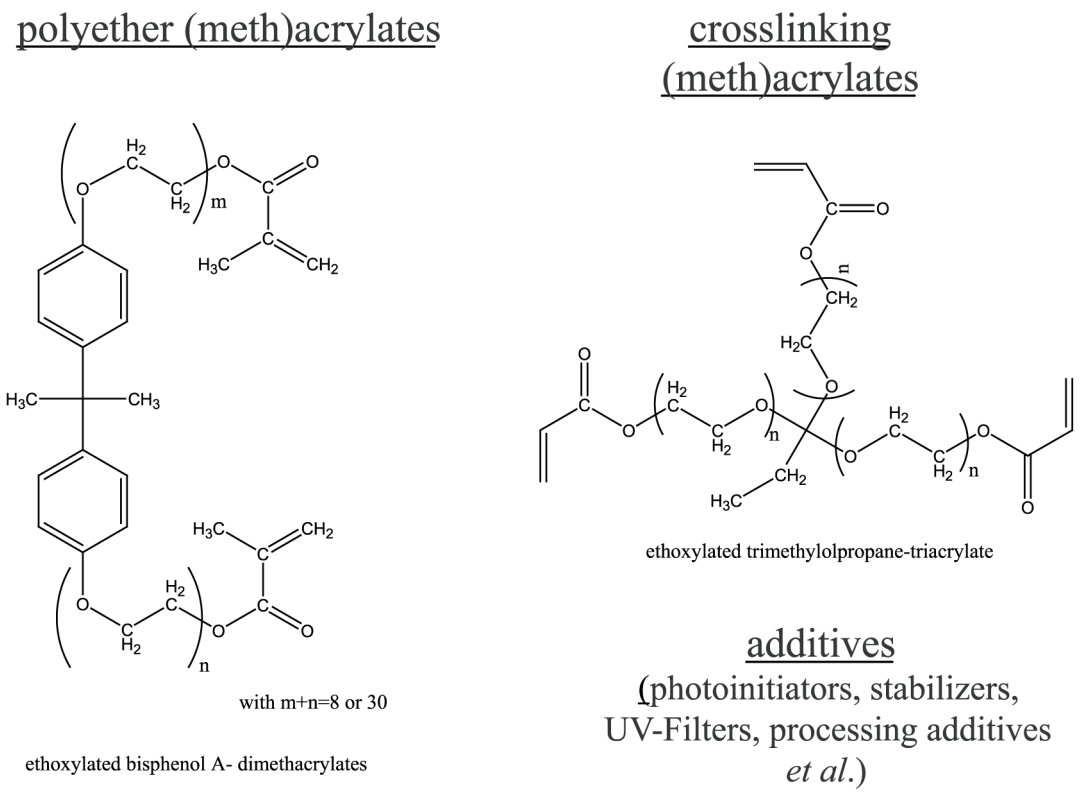
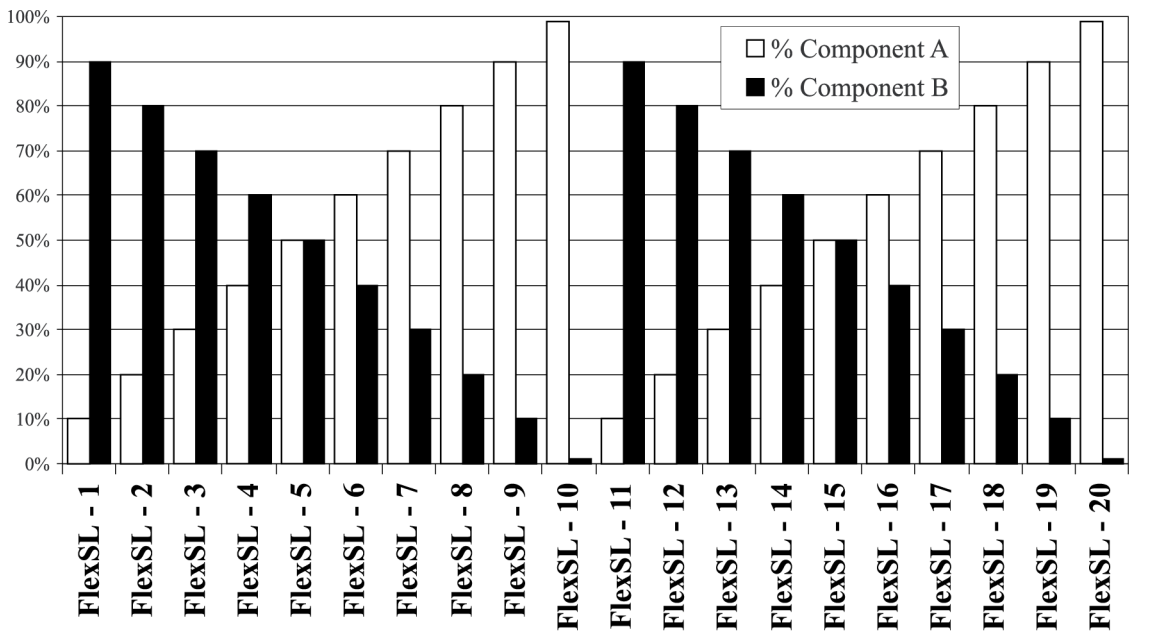
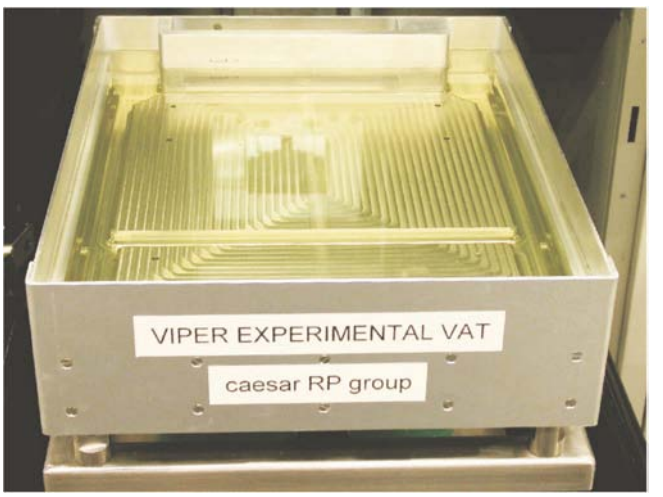


Figure 3 Composition (percent weight) of the initial formulations Flex-01 to Flex-20



Notes: Component A: Bisphenol A ethoxylate – (15EO/phenol)-dimethacrylate; Component B: Trimethylolpropane-triacrylate (in the series of Flex-1 to Flex-10) and Bisphenol A ethoxyylate – (4EO/phenol)-diacrylate (in the series of Flex-11 to Flex-20); Component C: 1.0 % Irgacure 184 photoinitiator

Figure 4 X-vat design used in a 3D systems viper Si^2 stereolithography system



Flex-1 represents a rigid and Flex-10 an elastic formulation. The right part of the diagram shows different FlexSL formulations (Flex-11 to Flex-20) with a very low Young's moduli. Owing to the nature of component B a fine-tuning of the mechanical properties of the resin is possible.

In contrast to many commercial stereolithographic resins (Table I), the FlexSL family makes it possible to produce not only stiff but also soft models in a single process step without additional expensive process steps.

Starting from the initial formulations Flex-1 to Flex-20, new resin formulations (Flex-1XX and Flex-2XX series) have been developed. The focus here was on the optimization of critical material parameters (E_C and D_P) for the stereolithography process.

Furthermore, after different optimization steps a group of commercial resins was developed for technical (FlexSL® SE series) and medical (FlexSL® SM series) use (see below).

4. Processing parameters

Because of known difficulties in the recoating process with high viscosity resins resulting in insufficient part geometries, it was necessary during the development process to monitor and limit the dynamic viscosity of each formulation to approx. 1,500 mPas. Only for special applications, e.g. polymer and ceramic filled resin, this limitation can be exceeded by adopting special build style modifications. All measurements of dynamic viscosity were performed on a Thermo-Haake RS 600 rheometer system. Typical values for the dynamic viscosity of tested FlexSL resins are located in the range of 500-1,000 mPas.

The Windowpane technique (Jacobs, 1993) is widely used to capture the working curve of an unknown resin, that describes a resin's photolithographic behavior. In this method, the resin surface is exposed with a pattern of laser light using different energy doses. Each exposed area shows an individual thickness of the cured resin. A linear regression of the logarithmized relative energy dose in the working curve equation:

$$C_D = D_P \ln\left(\frac{E_{\max}}{E_C}\right) \quad (1)$$

leads to the characteristic resin values E_C (polymerization energy dose [mJ/cm^2]) and D_P (penetration depth [mm]) of a stereolithography resin.

Especially, the free-floating geometry that is exposed by the laser leads to a high distortion and thus a high error. An optimization of this standard method was necessary for an exact analysis of the influence of different photoactive compounds (e.g. photoinitiators) on the curing behavior especially for very thin layers, which might occur in micro

Figure 5 Mechanical properties (young's modulus) of cast FlexSL specimens (Flex-1 to Flex-20) according to DIN EN ISO 527-1

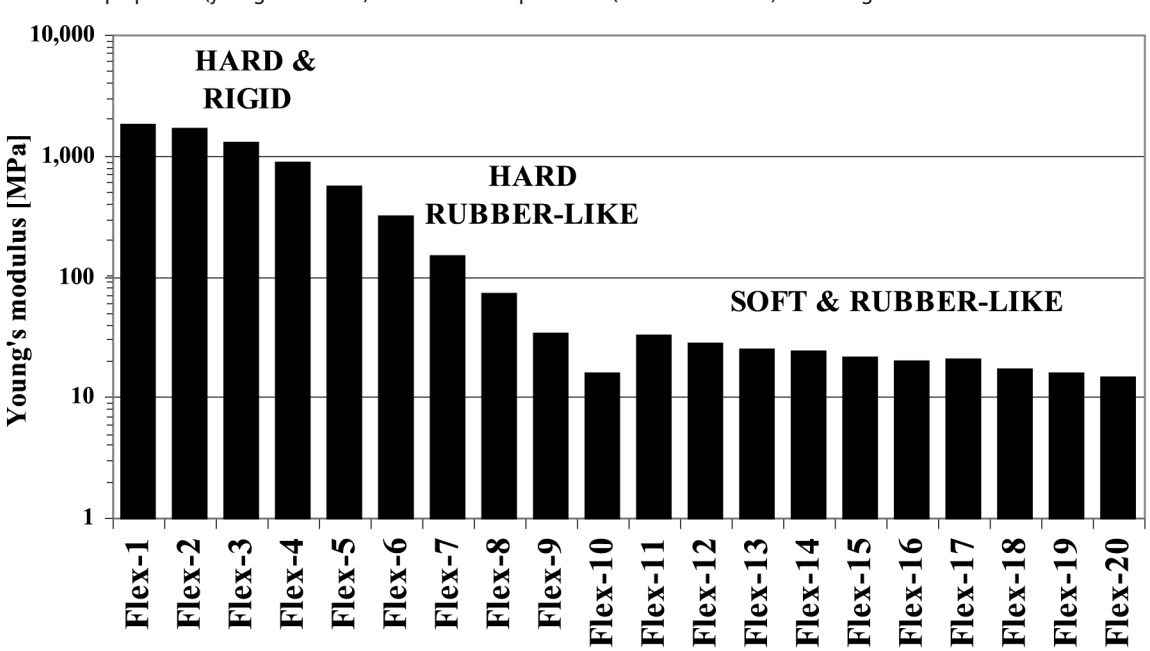


Table I Typical mechanical properties of the FlexSL® material class and selected examples

	FlexSL® family	FlexSL® SE/SM-25	FlexSL® SE/SM-50	FlexSL® SE/SM-1500	Typical SL resin *	Huntsman SL Y-C9300
Young's modulus (MPa)	15-1800	20	46	1365	1,400-2,800	1,315 (calculated from flexural modulus)
Tensile strength (MPa)	2-50	2.5	4.9	39	30-110	45
Elongation at break (percent)	2-15	14.3	12.7	4	5-10	7
Shore A/D hardness	Shore *A* 50-95	74 A	66 A	73 D	Shore *D* 75-95	75 D

Notes: *N.b.: material properties of the comparison materials taken from Huntsman Advanced Materials (UK) and 3D systems Corp. datasheets (Huntsman Advanced Materials (USA) 2006 and 3D Systems Corp., 2006)

stereolithographic applications. The novel developed protocol called quartz-glass window method uses a $120 \times 120\,\mathrm{mm}^2$ optical quality quartz-glass window. In a first step, the absorbance of the quartz-glass plate has to be determined with a UV dosimeter, placed directly under the quartz-glass plate, to calculate a correction factor for the absorbance of laser light of the quart-glass itself. The quartz-glass window is thereafter fixed in a box with a distance of >2 mm to ground. Then a small liquid resin sample (approx. 50 ml) is poured carefully without air bubbles beneath the glass window. Then the box is placed in the build chamber of a stereolithography apparatus and a predefined pattern is exposed with an increasing energy dose in the individual cells of the pattern. Remaining resin is allowed to drip off for 20 min and the cured structure is then gently rinsed with sufficient TPnB solvent (Dow Corning). After drying the wet quart-glass plate on a clean double-folded double-layer tissue for six times, each 30 s, the plate is cleaned from the back. The irradiated side containing the hardened pattern is post-cured for 10 min in a UVA-oven. With the help of a height measuring instrument with a predefined small contact force of 1.0 N, the thickness of each cured area within the exposed pattern is measured against the quartz-glass surface. This method allows a significantly higher precision (approx. $\pm 5\,\mu$m) in comparison to the standard Windowpane method. It allows now also a fast, cost-effective and reliable measurement to control the quality of stereolithography resins regularly, which could be also of interest for customers with an increased sense for quality control.

Using the described quartz-glass window protocol, the photolithographic parameters of a set of advanced FlexSL resins (Flex-1XX series; see Figure 6) were characterized. For the chosen Irgacure 369 photoinitiator, the resins (Flex-101 to Flex-107) show that the values for D_P can be easily adjusted from 23 to 173 μm by changing the photoinitiator concentration. The lower D_P values are of interest for a high-resolution resin used for micro stereolithography. In this experiment, the E_C values range from 0.5 to 6.0 mJ/cm^2. Using another photoinitiator (Irgacure 907) for the Flex-108 to Flex-113 resins, the D_P values are significantly larger, ranging in the area from 175 to 386 μm and are depending on the assigned photoinitiator concentration. The E_C values are now located in the range from 9.3 to 20.7 mJ/cm^2.

From this measurement it can be concluded, that the resin's process parameters cannot only be optimized for mechanical properties but also for either high build speed (e.g. 2.0 percent Irgacure 907 with $E_C = 9.3\,\mathrm{mJ/cm}^2$, $D_P = 175\,\mu$m) or high resolution (e.g. 1.0 percent Irgacure 369 with $E_C = 1.2\,\mathrm{mJ/cm2}$, $D_P = 35\,\mu$m). Further, optimization of the individual formulations led to stable resins that are suitable for the demands of commercial users.

Volume shrinkage of stereolithography resins is another problem that has to be taken into account, because its influence on the process stability as well as part precision is immense. The development of new resin materials always requires that the volume shrinkage is as low as possible.

For control of shrinkage during material screening tests in the early stages of development, a simple and fast method was used. The basic concept behind the chosen method is such that the weight of a specimen is measured in air m_{air} and under buoyancy of the liquid resin m_{buoy}.

The volume shrinkage S of a probe with the unknown volume V can hence be calculated using the following formula:

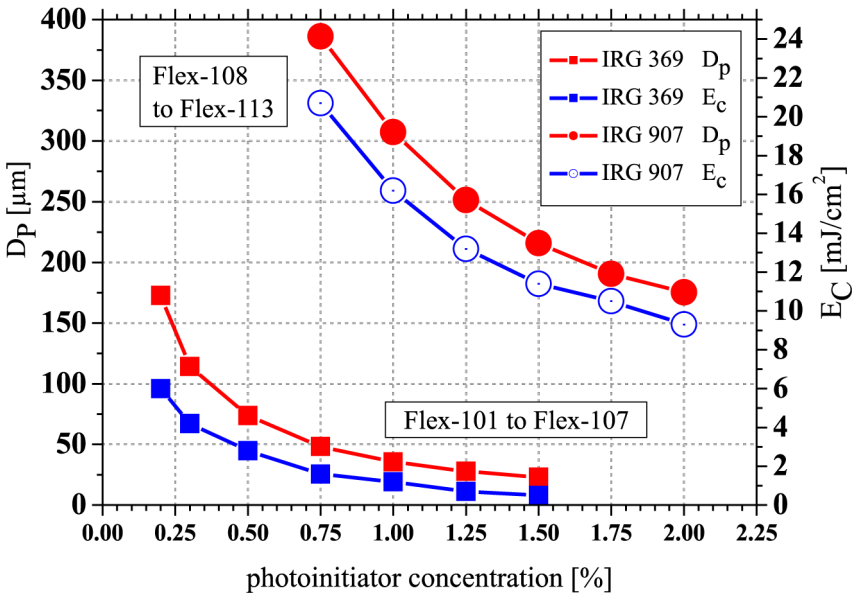
$$S = \frac{V_{\mathrm{start}} - V_{\mathrm{end}}}{V_{\mathrm{start}}} = 1 - \frac{V_{\mathrm{end}}}{V_{\mathrm{start}}} = 1 - \frac{m_{\mathrm{buoy}}}{m_{\mathrm{air}}} \qquad (2)$$

This measurement gives a very simple method to determine the polymerization shrinkage. Weight measurements were performed on a data-physics DCAT21 tensiometer system. Typical shrinkage values of the advanced FlexSL formulations are comparable to other commercial resins. SL 5510 (Huntsman), an epoxy-based material, shows volume shrinkage of nearly 5.2 percent with the above-described method. In contrast, for the resin formulations Flex-101 (5.4 percent), Flex-201 (3.4 percent) and Flex-202 (2.6 percent) similar or better results were measured.

5. Bioanalytical characterization

The investigation of the biocompatibility of different photopolymeric materials has an increased importance in the field of custom-designed medical devices. The aim of this initial bioanalytical investigation was to test the biocompatibility of various materials on cellular basis. Therefore, we chose two different types of commercially available resins for comparison. On the one hand, this was SL 5510 (Huntsman Advanced Materials, 2006) as a technical epoxy-based resin. On the other hand SL Y-C 9300 ("Stereocol" Huntsman Advanced Materials, 2006), an acrylate-based resin for the medical field, and our compositions Flex-8, Flex-17 and Flex-201 (experimental

Figure 6 Material parameters E_c (mJ/cm^2) and D_r (μm) of Flex-1XX series (polyether based resin with bishenol-A-ethoxylated di(methacrylates)/polyetherdi(meth)acrylates/tri-and tetracrylates & stabilizers)



resin formulation) were chosen. At first, special test geometries were manufactured on a 3D Systems Viper Si^2 SLA (Flex-201) or by irradiating the photopolymers in silicon moulds (Flex-8, Flex-17). For a detailed overview of the used materials, look at the following Table II.

Stacked cylindrical geometries were designed using Magics RP 9.1 software (Materialise, Belgium) to achieve a maximized surface area and optimized solvent flow for the eluate experiments. Five discs, each 1.0 mm high and separated through 1.0 mm space are arranged in a cylindrical geometry with a diameter of 9 mm and a total height of 9 mm.

Each of the test parts were manufactured by common stereolithography equipment (3D Systems Viper Si^2, normal resolution, layer thickness of 0.1 mm, usage of individual default manufacturer resin parameters).

For the experimental materials Flex-8 and Flex-17 the test geometries (cylinders of 4.0 mm diameter and 2.0 mm height) were irradiated with a high-pressure mercury lamp (Lumatec SUV-DC-P with an energy dose of 1.8 J/cm^2 and an intensity of 30 mW UV radiation) in a silicone mould. All individual parts were washed twice with 2-propanol and then placed for 10 min in a solution of 2-propanol in an ultrasonic bath at 40°C. After the solvent was rinsed, the parts were dried with clean air. The individual test parts were then post-cured, with an additional irradiation with a 12-lamp setup of Philips UVA lamps (each six lamps of Philips "sunlamp" (20 W) and "aqua coral" (15 W); irradiation duration: 20 min with a recorded total UVA energy dose of 3.8 J/cm^2 in the spectrum range of 320-400 nm wavelength).

The rates of cytotoxicity was measured by determination of cell viability of the mouse embryonic cell line NIH/3T3 with crystal violet staining, using etoposide as positive control for cell death (Ishiyama *et al.*, 1996). The cells were treated with different concentrations of the test substance eluates, made by autoclaving the cured material in a PBS solution (0.2 g/ml, 15 min, 121°C and 150 kPa), and incubating for further 24 h at 37°C. Quadruplicates of each eluate concentration were performed in three independent experiments.

PBS eluates of all photopolymers proved to be cytotoxic to a different degree of their concentration of the eluate solution according to crystal violet staining procedure. These results were confirmed by morphology observation (Figure 7).

Table II Tested resin materials for biological characterization

Resin material	Material class	Base material composition	Eluate geometry
Huntsman renshape SL 5110	Technical material	Acrylate/epoxy-based formulation	5 × stacked SL manufactured
Huntsman renshape SL Y-C 9300	Medical material with color option	Acrylate-based formulation	5 × stacked SL manufactured
Flex-8	Experimental basic photopolymer formulation	Polyether(meth)-acrylate-based formulation	8 × 2 mm cylinder in silicone mould
Flex-17	Technical material	Polyether(meth)-acrylate-based formulation	8 × 2 mm cylinder in silicone mould
Flex-201	Experimental, advanced SL material for the intended medical usage (R&D material)	Polyether(meth)-acrylate-based formulation	5 × stacked SL manufactured

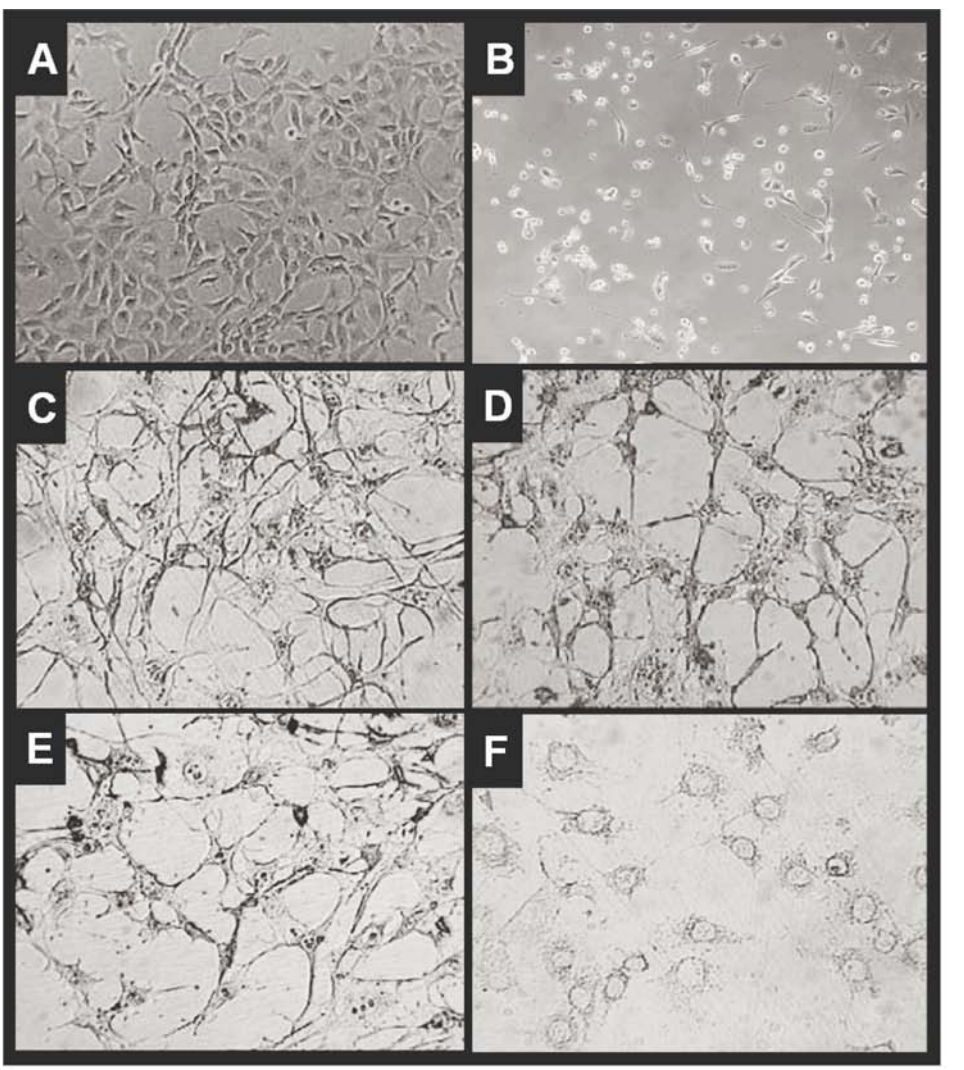
Figure 8 shows the cytotoxic experiments, showing that SL 5510 reveals the highest cytotoxicity, representing classical technical epoxy-based resins. In comparison, the photopolymer SL Y-C 9300 shows a significantly lower cytotoxicity than SL 5510. The cytotoxic effect of the tested FlexSL formulations is even lower than that of SL Y-C 9300.

Western blot analysis results of poly-(ADP-ribose) polymerase (PARP) cleavage (116 kDa) and its cleavage products (89 and 24 kDa) excluded apoptosis as type of cell death, with the exception of SL Y-C 9300 (data not shown). The obtained data indicated that apoptosis might not be the main cause for cell death with exception of the photopolymer SL Y-C 9300. These data are confirmed by electron microscopy (data not shown). Further, investigations are necessary to investigate the different causes of cell death.

Additional GPC measurements of aqueous extracts of the autoclaved photopolymers in PBS showed no detection of polymers (data not shown). However, all water-based extracts contain significant amounts of low molecular substances (MW $<$ 970 g/mol) that must be verified in future experiments.

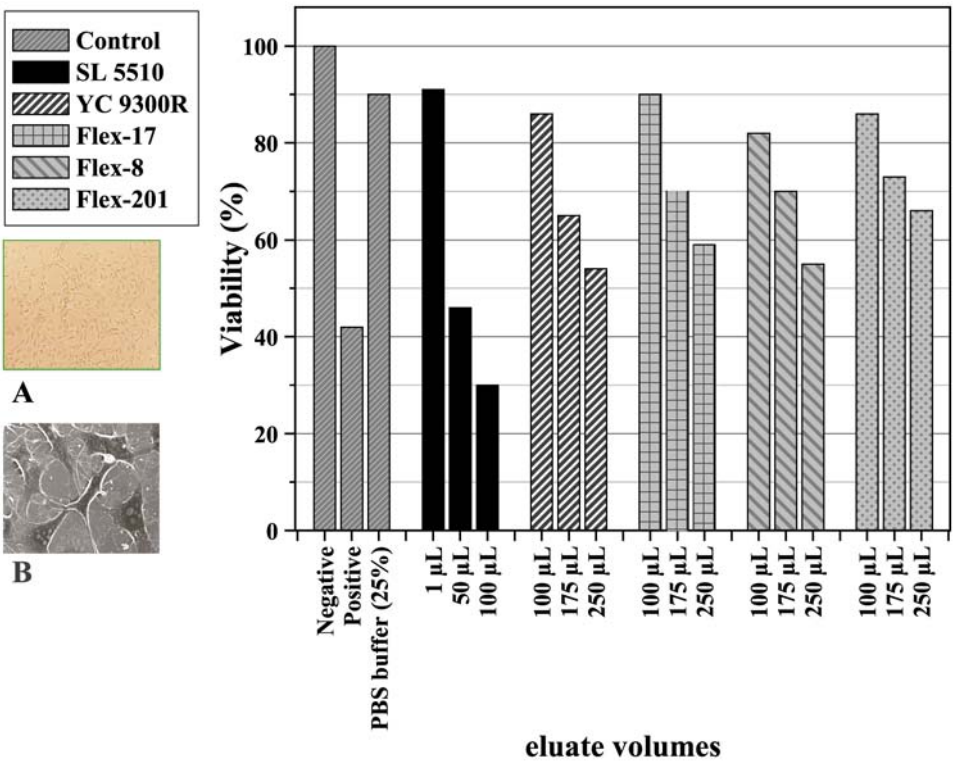
The resin material SL 5510 indicates a high cytotoxic effect during the test series. Low concentrations of this substance already designate cytotoxic effects. As an acrylate-based material with substantial usage in medical prototyping, SL Y-C 9300 shows a lower grade of cytotoxicity. The results lead to the conclusion that SL 5510 and SL Y-C 9300 cannot be considered as generally biocompatible for short or long-term implant usage, since SL Y-C 9300 induces apoptosis and SL 5510 has cytotoxic and genotoxic effects (Huxoll *et al.*, 2005; Nickel *et al.*, 2004; Paulmann *et al.*, 2005).

Figure 7 Microscopic images of NIH/3T3 cells treated with photopolymer eluates at 100 × magnifications



Notes: (A) Negative control – vital cells; (B) Positive control treated with etoposide showing approx. 50 % survival rate; (C) Cells treated with 200 µl/ml of FlexSL-201 eluate – cells showing high number of cytoplasmic extrusions; (D) Increased occurrence of cytoplasmic extrusions and partly skeletized cells due to necrosis in cells treated with 200 µl/ml Flex-17 eluate; (E) Cells treated with 200 µl/ml Flex-8 eluate – necrotic cells are flat, part ly skeletized and have swollen cell compartments; (F) Cells skeletized by the effects of 200 µl/ml SL Y-C 9300 eluate

Figure 8 Cytotoxicity of the photopolymers SL 5510, SL Y-C 9300, Flex-8, Flex-17 and Flex-201 on NIH/3T3 cells



Notes: neg. control: untreated cells, pos. control: cells treated with 200 µM etoposide. The results shown are the mean from quadruplet wells taken from one representative experiment out of three independent experiments.; insert pictures: natural shapes of mouse embryonic fibroblasts NIH/3T3 cells monitored with (A) Inverse Light Microscope (100 x) and (B) Electron Micrograph (SEM 100 x)

The three tested FlexSL material formulations are less cytotoxic in comparison. Higher eluate amounts are needed to achieve equally strong cytopathic effects as SL Y-C 9300.

Therefore, these resins will probably show positive behavior for applications with short-term contact to human body.

After these results, a special non-toxic branch of the novel FlexSL material was optimized. For all release candidates of the FlexSL material biocompatibility tests according to EN ISO 10993-5 protocol have been performed (e.g. FlexSL® SM-25 and FlexSL® SM-1500) (Bens *et al.*, 2006; Tille, 2006).

6. Applications

Today, important applications of commercially available, biocompatible stereolithography materials can be found in the sector of hearing aid shells (Dreve, 2006) and surgical guides and anatomical models (SurgiGuides Materialise, 2006).

The FlexSL® SM resin class is designed for a short-term contact to human body usage.

According to ISO 10993-1 there are different biological tests necessary depending on the application area and duration of the application (ISO 10993-1, 2003). An essential requirement for all medical device applications is the execution of cytotoxity tests according to ISO 10993-5. This requirement can be fulfilled by FlexSL® (Bens *et al.*, 2006; Tille, 2006). Owing to these qualities the material is suitable for applications:

- in contact with the body surface (skin, mucous membrane, hurt or endangered surfaces) up to a maximum contact time of 30 days (so-called short-term contact)
- from the outside penetrating into the body or implantable medical devices only in contact to bones, dentin and tissue, not in contact with blood vessels, up to a maximum duration of 24 h.

For long-term implants or for medical devices with direct blood contacts further extensive tests are necessary. Independently from the results of the tests, which describe the fundamental suitability only as some preliminary tests, the manufacturer of the medical device has the sole responsibility for the concrete application. For this reason clinical studies are only possible for a concrete medical device, not however for a raw material.

Examples for potential applications of the FlexSL® in the field of medical rapid manufacturing – besides hearing aid shells and drill guides – are surgical guides and templates for bone and reconstructive surgery, anatomical models and templates and other functional prototypes with direct human body contact, e.g. breathing masks, hearing aid shells or functional medical housing prototypes.

The aspect of fabricating soft parts with improved biocompatibility forms a significant basis for the extension to future applications in this area. Applications are the small series production of medical devices with a special need for a soft material, e.g. anatomical soft tissue models for intra-OR usage (e.g. models of ear, nose, skin, vessels, inner organs like heart

valves). In addition, the usage for short-term intra-operative planning services and tools like intra-op cutting templates and sawing guides is very attractive (Figures 9 and 10).

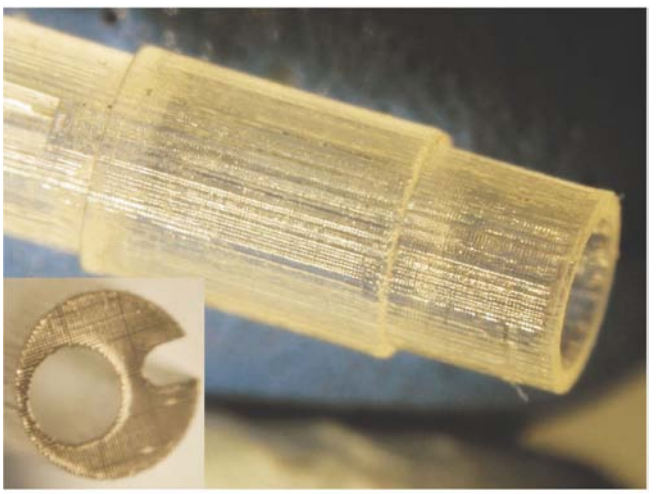
Even general technical applications are of interest for the FlexSL resins. Typical parts are flaps, tubes, hoses, cables, sealing parts, connectors and other technical rubber-like applications (Figure 11).

7. Discussion and outlook

Herein we have presented a completely new class of stereolithography resins. We introduced the FlexSL® resin materials, showing significant advantages, such as the possibility to mimic soft or stiff technical plastics depending on the formulation, a sufficient low dynamic viscosity, high process speed and good accuracy. FlexSL® materials show a lower toxicity in contrast to other acrylic resin materials. Beside the technical usage of this material class, there is a broad field of potential biomedical applications in which the FlexSL® material class can be beneficial.

These resin formulations are applicable and adjustable to different stereolithographic equipment available on the market. Currently, a group of different resin materials for technical (FlexSL® SE-25, SE-50, SE-1500) and medical (FlexSL® SM-25, SM-1500) applications undergo first application tests at our customer's stereolithography systems.

Figure 9 Medical micro application sample (material: FlexSL micro): functional prototype as a carrier tube with a total length of 7.2 mm

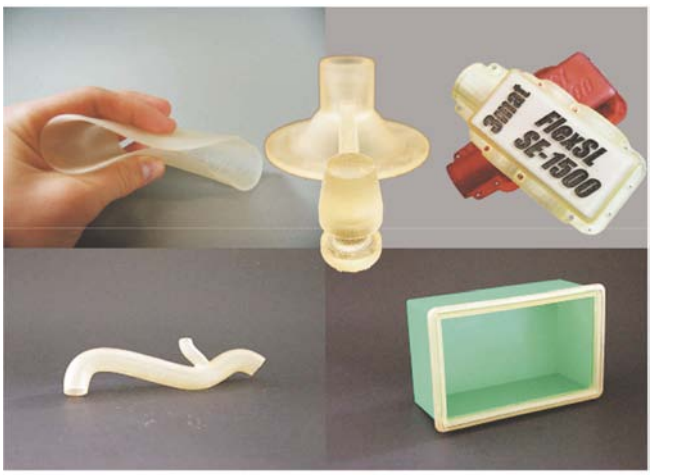


Note: The inset pictures the part's diameter of 1.1 mm
Source: Authorization/courtesy of St. Jude Medical AB, Sweden

Figure 10 Anatomical models examples

Notes: Soft tissue model, realized using FlexSL SM-25 (left picture & insert) and an skull model for intra-OR use (FlexSL SM-1500 material, lower right picture)

Figure 11 Technical samples



Notes: (left to right): breathing mask model (bended), elastic closure unit (both FlexSL SE-25), housing (FlexSL SE-1500), tube and sealing ring (FlexSL SE-50)

References

3D Systems Corp. (2006), "Technical datasheets for accua stereolithography resins, 2006", available at: www.3dsystems.com/products/solidimaging/accura/datasheets.asp

Bens, A.T., Seitz, H. and Tille, C. (2005a), "Liquid radiation-curing compositions", International PCT Patent Application WO 2006/005772 A1, Germany.

Bens, A.T., Tille, C. and Seitz, H. (2006), "Advances in product design for medical applications with the help of a novel fully customizable photopolymer material-class for 3-dimensional applications – materials, properties and examples", Medical Polymers 2006, International Conference, Cologne, June 6-7.

Bens, A.T., Irsen, S., Bermes, G., Seitz, H. and Tille, C. (2004), "Biomedical rapid prototyping for medical applications", paper presented at Medical Plastics 2004 – 18th Annual International Conference November 1-4 2004, Seminar and Exhibition, Copenhagen.

Bens, A.T., Tille, C., Bermes, G., Emons, M. and Seitz, H. (2005b), "Novel biocompatible polyether(meth)acrylate-based formula-tions for stereolithography – a new flexible material class for three-dimensional applications", e-Polymers, no. 037, available at: www.e-polymers.org

Bens, A.T., Tille, C., Leukers, B., Bermes, G., Emons, M., Sobe, R., Roitzheim, B., Schulze, M., Tobiasch, E. and Seitz, H. (2005c), "Mechanical properties and bioanalytical characterization for a novel non-toxic flexible photopolymer

formulation class", paper presented at SFF2005: 16th Solid Freefrom Fabrication Symposium, Austin, August 1-3, 2005.

DSM Somos Corp. (2006), "Technical Datasheet for Somos ULM™ 17220", available at: www.dsm.com/en_US/downloads/dsms

D'Urso, P.S. (2006), *Advanced Manufacturing Technology for Medical Applications*, Professional Engineering Publishing Pty Ltd., London.

D'Urso, P.S., Barker, T.M., Earwalker, W.J., Bruce, I.J., Atkinson, R.L, Lanigan, M.W., Arvier, J.F. and Effeney, D.J. (1999), "Stereolithographic (SL) biomodelling in cranio-maxillofacial surgery: a prospective trial", *The Journal of Cranio-maxillofacial Surgery*, Vol. 27, pp. 30-7.

D'Urso, P.S., Earwalker, W.J., Barker, T.M., Redmond, M.J., Thomson, R.G., Effeney, D.J., and Tomlinson, F.H. (2000), "Custom cranioplasty using stereolithography and acrylic", *British Journal of Plastic Surgery*, Vol. 53 No. 3, pp. 200-4.

Dreve, Germany (2006), "Information homepage about stereolithography and otoplastics", available at: www.dreve.de/dreve_neu/otoplastik_gb/industrie_stereolitho_oto_gb.htm

Huntsman Advanced Materials (UK) (2006), "Technical datasheets for huntsman renshape® SL Stereolithography resins, 2006", available at: www.renshape.com

Huxoll, R., Hergert, M., Kautz, C., Nickel, A-C., Wagner, N., Tille, C., Pansky, A., Roitzheim, B., Jakoby, K., Bens, A.T., Leukers, B., Baal, A., Schroeder-Obst, D., Kamm, B., Schulze, M. and Tobiasch, E. (2005), "Determination of the biocompatibility of photopolymeric materials designed for medical rapid prototyping applications", paper presented at the XVIIIth Aachen Colloquium on Biomaterials, Aachen.

ISO 10993-1 (2003), "Biological evaluation of medical devices – part 1: evaluation and testing", International standard.

Irsen, S., Seitz, H., Tille, C., Bermes, G., Wolfinger, E., Sader, R. and Zeilhofer, H-F. (2004), "Anatomical rapid prototyping models with soft and hard tissue representation for surgical planning", paper presented at 7th Conference of the European Society for Engineering and Medicine, Halle, September 18-21, 2003.

Ishiyama, M., Tominaga, H., Shiga, M., Sasamoto, K., Ohkura, Y. and Ueno, K. (1996), "A combined assay of cell viability and in vitro cytotoxicity with a highly water-soluble tetrazolium salt, neutral red and crystal violet", *Biol. Pharm. Bull.*, Vol. 19 No. 11, pp. 1518-20.

Jacobs, P.F. (1993), *Rapid Prototyping & Manufacturing: Fundamentals of Stereolithography*, McGraw-Hill, New York, NY.

Materialise, Belgium (2006), "Information homepage about SurgiGuides", available at: www.materialise.be/surgiguides/main_ENG.html

Nickel, A-C., Wagner, N., Gennaro-Selvaggio, P., Weißenberger, K., Kleinfeld, C., Pansky, A., Roitzheim, B., Jakoby, K., Bens, A.T., Leukers, B., Irsen, S., Tille, C., Seitz, H., Schulze, M. and Tobiasch, E. (2004), "Chemical and bioanalytical characterization of commercial photopolymer based products used for medical rapid prototyping applications", paper presented at 5th caesarium on Advances in Biomedicine, Bonn.

Paulmann, C., Holzhauer, C., Maiworm, A., Specht, A., Pansky, A., Roitzheim, B., Leukers, B., Schulze, M. and Tobiasch, E. (2005), "Analysis of genotoxic effects of photopolymer SL-5510 on human cells", paper presented at the XVIIIth Aachen Colloquium on Biomaterials, Aachen.

Seitz, H., Tille, C., Irsen, S., Bermes, G., Sader, R. and Zeilhofer, H-F. (2004), "Rapid prototyping models for surgical planning with hard and soft tissue representation", paper presented at Computer Assisted Radiology and Surgery Conference June 23-26, 2004, Chicago, IL, International Congress Series 1268, pp. 567-72.

Tille, C. (2006), "Neuartige Photopolymere und weitere Kunststoffe für das Rapid Manufacturing in der Medizintechnik", *Conference Proceedings Kunststoffe in der Medizintechnik VDI-Verlag, Friedrichhafen, Germany*, pp. 175-87.

Tille, C., Bens, A.T. and Seitz, H. (2005b), "Processing characteristics and mechanical behavior of a novel stereolithographic resin system for engineering and biomedicine", paper presented at 2nd International Conference on Advanced Research in Virtual and Rapid Prototyping, Leiria, September 28-October 1.

Tille, C., Bens, A.T., Bermes, G. and Seitz, H. (2005a), "A new flexible stereolithographic resin class for engineering and biomedical applications – material properties and use", Euro-uRapid'05 May 10-12, 2005, Leipzig.

Wohlers, T. (2005), "Wohlers report 2005: rapid prototyping and tooling, state of the industry, annual worldwide progress report", available at: www.wohlersassociates.com

Further reading

3mat (2006), available at: www.3mat.de

ISO 10993-5 (2003), *Biological Evaluation of Medical Devices – Part 5: Tests for Cytotoxicity: In Vitro-Methods*, International standard, Geneva.

Corresponding author

Arthur Bens can be contacted at: bens@caesar.de