MECHANICAL PROPERTIES AND BIOANALYTICAL CHARACTERIZATION FOR A NOVEL NON-TOXIC FLEXIBLE PHOTOPOLYMER FORMULATION CLASS

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Abstract

We present herein a new class of resin formulations for stereolithography, named FlexSL, with a broad bandwidth of tunable mechanical properties. The novel polyether(meth)acrylate based material class has outstanding material characteristics in combination with the advantages of being a biocompatible (meth)acrylate based processing material. FlexSL shows very promising results in several initial biocompatibility tests. This emphasizes its non-toxic behavior in a biomedical environment, caused mainly by the (meth)acrylate based core components. The FlexSL materials are less cytotoxic than other commercial available and tested resin materials. This novel resin material could then be one of the engineering materials of choice for very complex three-dimensional structures in the medical technologies area. A short overview of mechanical and processing properties will be given in the end.

Introduction

One of the 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. So the mechanical properties of the used photopolymeric resin materials are optimized to mimic stiff technical polymers like PP, PE or ABS. Nowadays, standard stereolithographic resins consist mainly of epoxy based oligomeric compounds due to the given high accuracy and low shrinkage of these materials. On the other hand there is a special demand for softer stereolithographic materials to cover new fields of applications, which cannot be fulfilled sufficiently yet.

The technique of stereolithography uses a liquid photopolymer that is locally cured by a UV laser. In the last years, there has been a growing need from customers for resins with novel material characteristics in order to enter new application fields. Our focus of interest 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 [7, 8, 12 and 13]. Furthermore, 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 epoxy monomers in the cured polymer models. The resin class is named FlexSL [1] because of its outstanding material properties and its adjustable characteristics (e.g. adjustable hardness and strength) for stereolithography and other photolithographic applications (see figure 1). Depending on the individual formulation, the cured resins show an adjustable Young's modulus in the range from 10 MPa up to 2000 MPa. Other mechanical parameters (e.g. tensile modulus and soft/hardness) are also customizable in a very broad range.

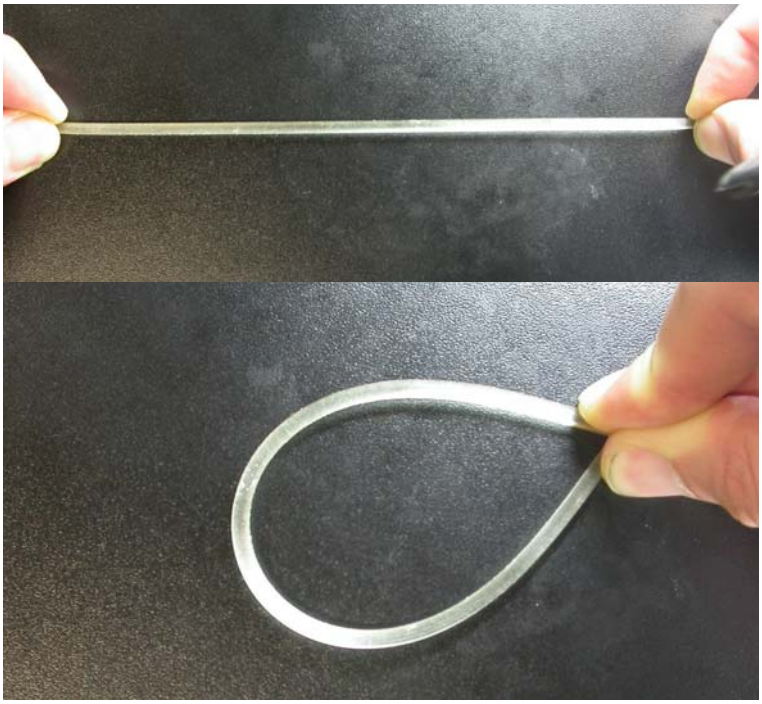

Figure 1: Sample parts demonstrating the high flexibility of FlexSL resin materials

Usage of these new resins for medical rapid prototyping (e.g. presurgical planning models, tools for drilling and sawing guides for intra-operation surgical techniques) requires the biocompatibility of non-cytotoxic materials that should be sterilizable for a direct application on human body contact. The production of non-toxic, biocompatible design and functional prototypes for medical instruments and devices is also a field of interest. We started to investigate and understand the detailed pathways of cytotoxic agents from commercially available raw materials to three-dimensional products in the end. For the biological characterization of a new non-toxic material, cell toxicity and biocompatibility has been tested according to ISO 10993 procedures. These initial tests show how promising the results in several biocompatibility tests are, which will be also presented in a chapter hereafter.

Materials Preparation and Composition

The single compounds for a basic FlexSL resin formulation are listed hereafter. A typical formulation consists of mainly these components:

- Very flexible oligomeric, polyether(meth)acrylate monomers with a high molecular weight of more than 1000 g/mol,
- Short and therefore hard-segment polyfunctional polyether(meth)acrylate monomers with a lower molecular weight of less than 1000 g/mol,
- Polyfunctional cross linking (meth)acrylates,
- Special selection of additives (photoinitiators, stabilizers, fillers and other processing chemicals).

All (meth)acrylates, purchased from Sigma-Aldrich, were weighed into glassware equipment according to their percentage and then additionally the photoinitiator summed up to its weight percentage of this (meth)acrylates mixture was added. Then the formulations were mixed in complete darkness at room temperature and normal atmosphere for additional 24 hours. For the more advanced FlexSL resin formulations (e.g. Flex-BA-01) the single compounds (bishenol-A-ethoxylated di(methacrylates), polyetherdi(meth)acrylates, tri-and tetracrylates, photoinitiators, stabilizers, UV-filters, fillers and other processing chemicals) were weighed into a stainless steel tank (3-12 liter volume) and were stirred with a laboratory dissolver Ivory Line 2100 (ATP Engineering, The Netherlands) at 2000 to 4000 rpm for 30 to 90 minutes. Then the resins are kept for 24 hours in the dark before processing them on a Viper si^2 (3D Systems, USA) SLA equipment.

Bioanalytical Characterization

The investigation of the biocompatibility [2] of different photopolymeric materials as outlined before has special importance in the field of custom-designed medical products. The aim of the bioanalytical investigations was to test the biocompatibility of various commercially available resin materials and the initial FlexSL formulations on a cellular base. Therefore we have chosen two different types of commercial available resins for comparison, SL 5510 (Huntsman, USA) as a technical epoxy-based resin, and YC-9300R (Huntsman, USA), also known as “Stereocol” material, as a biocompatible acrylate based resin with applications in the medical area, and the formulations Flex-AE-07 (70 % bisphenol-A-ethoxylate- (15EO/phenol)-di(meth)acrylate, 30% bisphenol-A-ethoxyylate-(4EO/phenol)-diacrylate, plus additional 1% Irgacure 184 photoinitiator), Flex-AF-08 (80 % bisphenol-A-ethoxylate-(15EO/phenol)-di(meth)acrylate, 20 % Trimethylolpropan-triacrylate, plus additional 1% Irgacure 184 photoinitiator) and FlexSL-BA-01 (bishenol-A-ethoxylated di(methacrylates), polyetherdi(meth)acrylates, tetra- and triacrylates, photoiniators, UV-stabilizer and 4-methoxyphenol).

Table 1: Tested resin materials.

RESIN MATERIAL	MATERIAL CLASS	BASE MATERIAL COMPOSITION	ELUATE / GEOMETRY
Huntsman renshape SL 5110	technical material	acrylate/epoxy based formulation	5x stacked SL manufactured
Huntsman renshape SL YC-9300R	medical material with possible medical usage (with color option)	acrylate based formulation	5x stacked SL manufactured
Flex-AE-07 (equals Flex-17)	experimental basic photopolymer formulation	basic (meth)acrylate formulation	8 x 2mm cylinder (irradiated in silicone mould)
Flex-AF-08 (equals Flex-8)	experimental basic photopolymer formulation	basic (meth)acrylate formulation	8 x 2mm cylinder (irradiated in silicone mould)
Flex-BA-01	experimental, technical SL material for the intended medical usage (R&D material)	polyether(meth)acrylate based formulation	5x stacked SL manufactured

Special test geometries (see figure 2) have been generated by a classic stereolithography machine, the Viper si^2 (3D Systems, USA), or were irradiated in silicon moulds. For the experimental materials Flex-AE-07 and Flex-AF-08 the test geometries (cylinders of 8.0 mm diameter and 2.0 mm height) were irradiated with a high-pressure mercury lamp SUV-DC-P (Lumatec, Germany) with an energy dose of 1.8 J/cm^2 and an intensity of 30 mW/cm^2) in a silicone mould. Each of the test parts originated from commercial material and Flex-BA-01 were manufactured by common stereolithography process equipment. The detailed building parameters were: normal resolution, layer thickness of 0.1 mm, usage of individual default manufacturer resin parameters, e.g. hatch spacing, hatch overcure values, and part precision of +/- 0.05 mm.

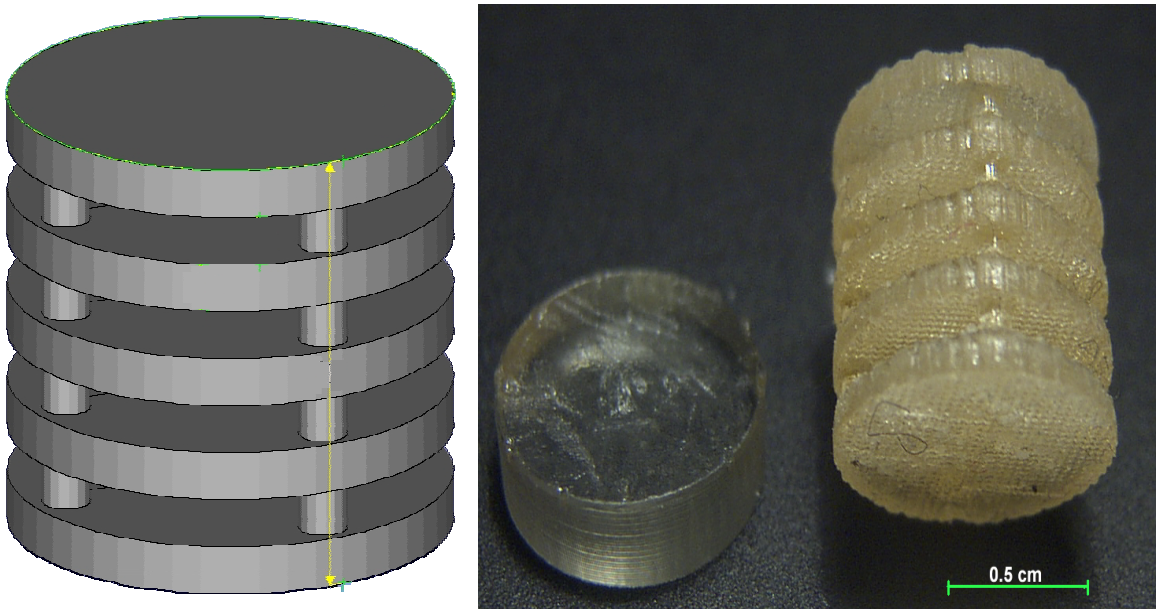

Figure 2: Left picture: CAD stl-model of the test geometry (diameter 9.0 mm; complete height 9.0 mm; height of one disc 1.0 mm); right picture: test geometry for Flex-AE-07 (left) and FlexSL-BA-01 (right) before the eluate experiments in PBS puffer.

The special stacked cylindrical geometries were designed with the standard 3D-design software Magics 9.1 (Materialise, Belgium) for an optimized solvent flow characteristic in 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. The surface of this individual test part is with 807 mm^2 (volume 333 mm^3) tripled in contrast to the calculated area of 269 mm^2 (volume 318 mm^3) of a solid cylinder of 9.0 mm diameter and 5.0 mm height. The size and dimensions of these test parts are also chosen to fit perfectly in standard 48-well plates for biological experiments for further cell-growth test experiments. The test parts have been also optimized for an easy building process, as there is no need for internal supports between the individual discs.

All individual parts were then washed twice with 2-propanol and then placed for 10 minutes 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 finished with an additional irradiation with a 12-lamp setup, consisting of Philips UVA lamps, each 6 lamps of Philips sunlamp (20 W)

and Philips aqua coral (15 W); irradiation duration: 20 minutes with a recorded total UVA energy dose of 3.8 J/cm^2 in the spectrum range of 320 to 400 nm wavelength.

To investigate the reaction of the tested photopolymers on the mammalian fibroblast cells, eluates of each cured substance were prepared by autoclaving in PBS. All eluates were made from a defined net weight of cured material by autoclaving them in 2 ml PBS solution for 20 min, at 121°C and 1,2 bar, followed by an incubation for 24h at 37°C. For biocompatibility analysis, NIH/3T3 cells were seeded on 24 well plates and quadruplicates of each eluate concentration have been performed. The mouse embryonic cell line NIH/3T3 was treated with different volumes of each eluate. To determine the rates of cytotoxicity, cell viability was measured by crystal violet staining using etoposide as positive control for cell death and non-treated cells as negative control. PBS Eluates of all photopolymers proved to be cytotoxic to a different degree depending on the volume of eluate solutions on the cells according to crystal violet staining procedure and by morphology observation (see figure 3). For the Scanning Electron Microscopy (SEM) results, depicted in figure 3, the used NIH/3T3 cells were first treated with the corresponding eluates and were then fixed in glutardialdehyde (2.5 % in cacodylate buffer), and then dehydrated in a series of ethanol (30, 50, 70, 80, 90, 96, and 3 x 100 %) and finally infiltrated with HMDS. Various types of cytopathic effects were visible in the SEM pictures, showing different morphology such as normal shape, apoptotic cell blebbing, swollen necrotic cells, and skeletized cells in different variations of the eluates.

The results obtained for cytotoxic effect of SL 5510 (see figure 4) confirmed previous studies [9-11] and showed the highest cytotoxicity for this photopolymer material, representing classical, technical epoxy based resins. The photopolymer YC-9300R showed a significant lower cytotoxicity than SL 5510. YC-9300R had a more cytotoxic effect on the cells than the examined FlexSL (Flex-AE-07, Flex-AF-08 and Flex-BA-01) photopolymers.

To analyze if the induced cell death is due to apoptosis a Western Blot Analysis for PARP-cleavage (poly-(ADP)-ribose polymerase) has been performed. For this, the cells were synchronized by serum starvation (0,5% FCS). SL 5510 eluates were added 24 hours to the cells and protein extracts were analyzed by Western blotting. DMSO served as negative and etoposide as positive controls. Proteins were analyzed for the presence of poly-(ADP)-ribose polymerase (PARP) - in a cleaved or uncleaved state - using a polyclonal PARP antibody. Western blot analysis of PARP (116 kD) and its cleavage products (89 and 24 kD) excluded apoptosis as type of cell death, with the exception of YC-9300R (Fig. 6). The obtained data indicates that apoptosis is not the main cause for cell death with exception of the photopolymer YC-9300R. These data are confirmed by electron microscopy. Further investigations are necessary to investigate the different causes of cell death.
Additional GPC measurements of the tested photopolymers showed no detection of polymers (data not shown). Gel Permeation Chromatography (GPC) measurements were performed with a GPC system (Waters Corporation, USA), using RI-detection and showdex columns for aqueous solutions (MW range: 5000–1000000 g/mol; PEG/PEO standard). The aqueous extracts of the autoclaved photopolymers in PBS were investigated. However, all water-based extracts contain significant amounts of low molecular substances (MW<970 g/mol) that must be verified in future experiments. First results of GPC show a reasonable amount (< 5000 g/mol) of a low molecular weight fraction. In order to analyze the detailed structure of theses low molecular compounds GC-MS further studies must be performed.

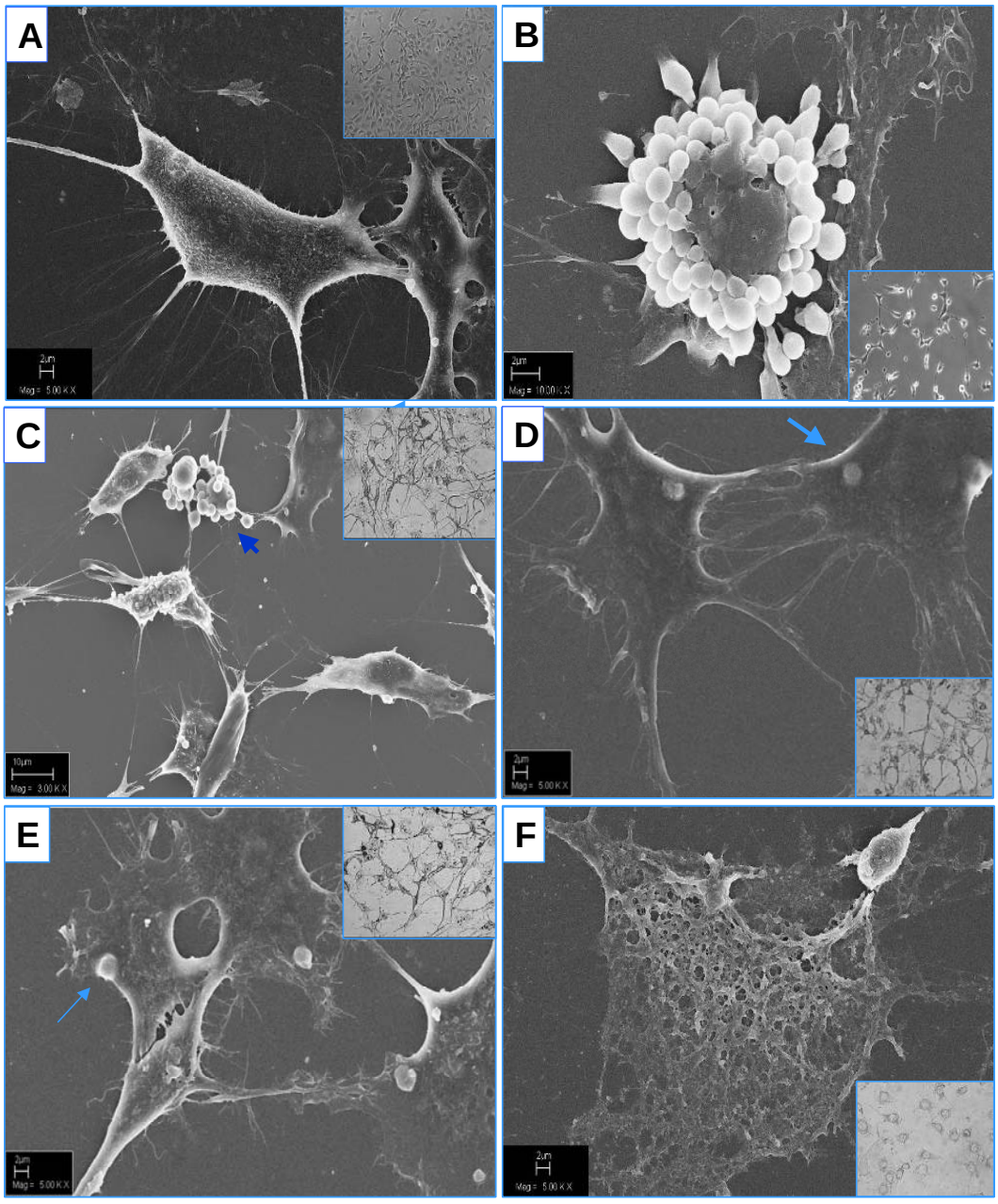

Figure 3: SEM images of NIH/3T3 cells treated with photopolymer eluates.
(Inlays show corresponding microscopic images at 100 x magnification)
(A) Negative control – vital cells
(B) Positive control treated with etoposide showing a blebbing apoptotic cell
(C) Cells treated with 250 µl/ml of FlexSL-BA-01 eluate – cells showing different cytopathic effects
(D) Swollen cell compartments due to necrosis in cells treated with 250 µl/ml Flex-AE-07 eluate
(E) Cells treated with 250 µl/ml Flex-AF-08 eluate –
necrotic cells are flat, partly skeletized and have swollen cell compartments
(F) Cells skeletized by the effects of 250 µl/ml YC-9300R eluate

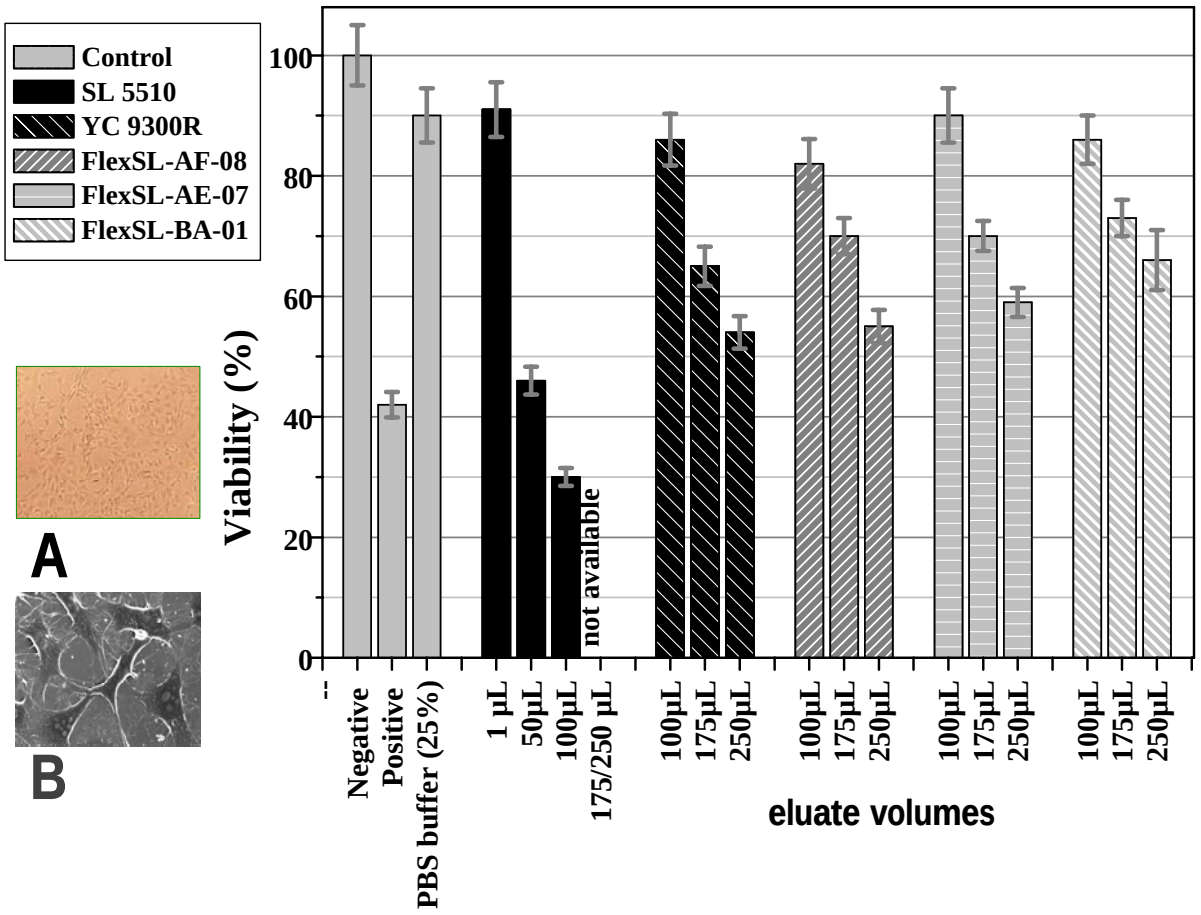

Figure 4: Cytotoxicity of photopolymers SL 5510, YC-9300R, FlexSL-AE-07, FlexSL-AF-08 and FlexSL-BA-01 on NIH/3T3 cells; neg. control: untreated cells, pos. control: cells treated with 200 µM etoposide. The results shown are the mean from quadruplet wells taken from one representative experiment out of three independent experiments; insert pictures: natural shapes of mouse embryonic fibroblasts NIH/3T3 cells monitored with (A) Inverse Light Microscope (10 x) and (B) Electron Micrograph (SEM 100 x).

The resin material SL 5510 indicates a severe and high cytotoxic effect during the test series. The concentration to give a positive test result is very low in comparison to the other acrylate-based materials. Even low concentrations (50–100µL) of this substance eluate clearly designate cytotoxic effects. Higher concentrations (172-250µL) were not tested then. YC-9300R shows as an acrylate based material with substantial usage in medical prototyping a less grade of cytotoxicity. In comparison, the three tested initial FlexSL material formulations are even less cytotoxic. Higher eluate amounts are needed to achieve equally strong cytopathic effects than in YC-9300R. The FlexSL material formulations are optimized for a less toxic behavior compared to the tested commercial resins. In addition, a detailed investigation of the cellular effects caused by the photopolymers is underway to evaluate if the low molecular weight chemical compounds cause structural damages in cells. Furthermore possible mutagenic effects of the photopolymers on chromosomes could be tested by demonstration of sister chromatid exchanges (SCE's) and Micronucleus detection. SCE's are the result of breakage and reunion of the two sister chromatids of one chromosome.

Mechanical & Processing Characteristics

Viscosity

Because of the sensitivity of the recoating process to viscosity, resulting in insufficient part quality at higher viscosity rates, it was necessary to monitor the viscosity of each formulation and to limit the target value for the dynamic viscosity to approx. 1.5 Pas. For special applications (e.g. polymer and ceramic filled FlexSL resin formulations) this limit can be infringed only by adopting special building style modifications. Dynamic viscosity measurements were performed on a RS 600 rheometer (Thermo-Haake, Germany). The dynamic viscosity of tested FlexSL resins is located in the range of 200 mPas (FlexSL-1) to 1000 mPas (FlexSL-BJ-02).

Mechanical Properties

Five tensile samples of each material formulation (S3a probe geometry, taken from DIN 53504) were finally measured in a universal testing machine Z020 (Zwick-Roell, Germany). Results included tensile strength, Young's modulus, and elongation at break for all formulations according to ISO 527-1 [3,4].

For example, the Young's modulus for FlexSL-1 to FlexSL-20 is depicted in figure 5. On the left part of the diagram, the formulations FlexSL-01 to FlexSL-10 show the measured bandwidth of achievable Young's modulus. Whereas the right diagram part represents the soft formulations FlexSL-11 to FlexAL-20 with a very low Young's modulus. Due to the amount and nature of the second compound B it is possible to fine-tune the mechanical properties of the polymeric resin for stereolithography.

Table 2: Typical mechanical properties of the FlexSL material class

	FlexSL FAMILY	**TYPICAL SL RESIN**
Young's modulus	15 – 1800 MPa	1400 – 2800 MPa
Tensile strength	2 – 50 MPa	30 – 110 MPa
Elongation at break	2% –15%	5% – 10%
Shore A/D hardness	Shore A 30 - 95	Shore D 75 - 95

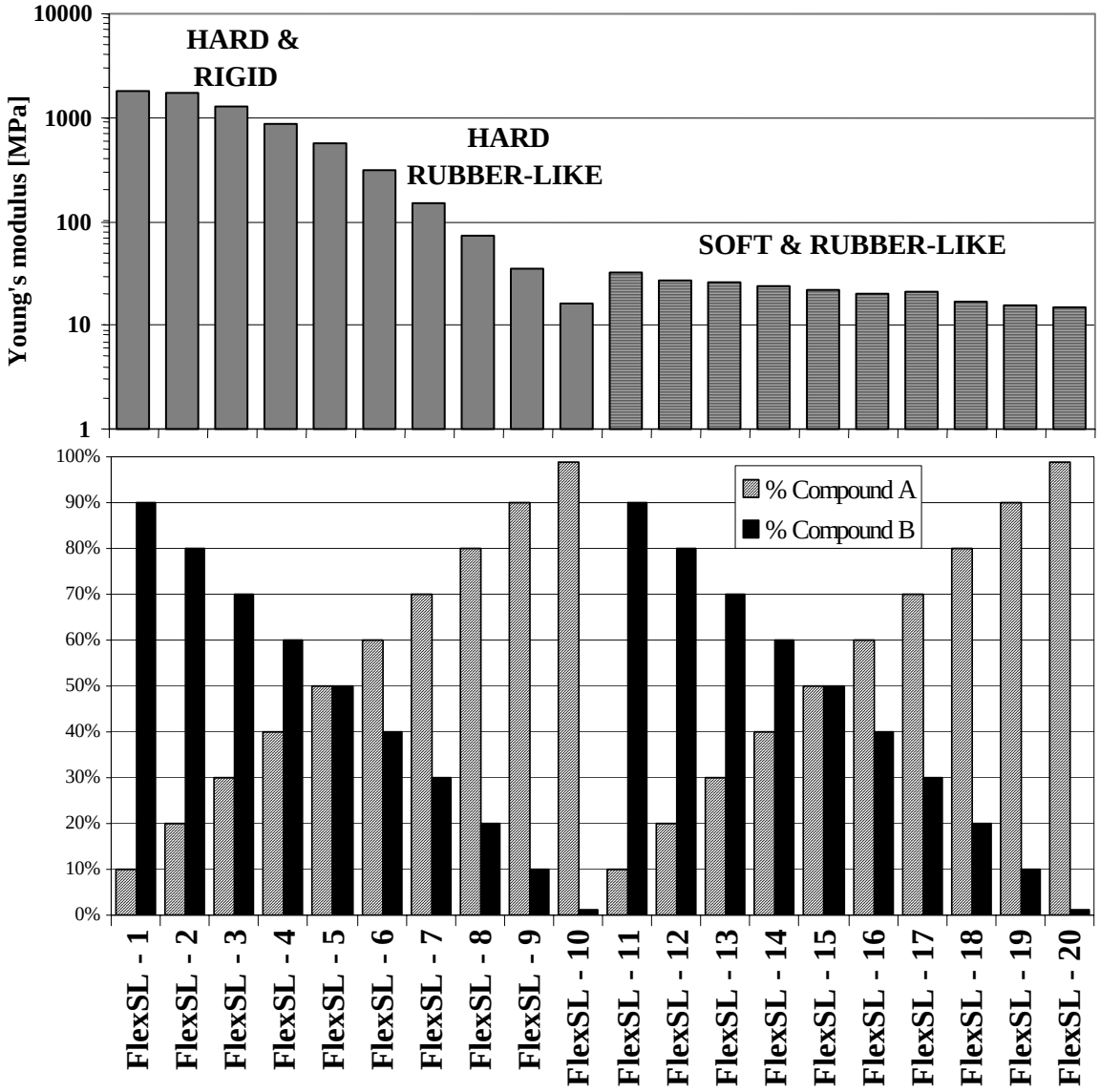

Figure 5: Upper diagram: mechanical properties (Young's modulus) for different flexible FlexSL specimens according to ISO 527-1 of all cast specimen of Flex-1 to Flex-20; lower diagram: Composition in % (weight) of the initial formulations FlexSL-01 to FlexSL-20 with compound A: bisphenol-A-ethoxylate-(15EO/phenol)-dimethacrylate, compound B: trimethylolpropane-triacrylate (in the series of FlexSL-1-10) and bisphenol-A-ethoxyylate–(4EO/phenol)-diacrylate (in the series of FlexSL-11-20); additionally the compound C: 1.0 weight-% Irgacure 184 photoinitiator was added each.

E_C and D_P Measurements

Starting from the FlexSL-1 to FlexSL-20 formulations, the advanced resin material formulations FlexSL-21 to FlexSL-33 have been developed. The optimization of critical processing parameters (E_C and D_P) for the stereolithography process was the focus. To describe a resin's photolithographic behavior, the well-known Windowpane technique [6] is widely used to capture the working curve of a new material. 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 (1) leads to the characteristic resin values of polymerization energy dose (E_C) and penetration depth (D_P) of a stereolithography resin.

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

Especially the free-floating geometry of a windowpane that is exposed by the laser leads to a high distortion and thus a high statistical error has to be accepted. 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. Therefore, we have recently developed a new protocol that uses a 120 x 120 mm optical quality quartz-glass window [12, 13]. This method allows a significantly higher precision (approx. ±5 µm) in comparison to the standard Windowpane method and allows now also making very fast, cost-effective, and reliable measurements to control the quality of stereolithography resins regularly.

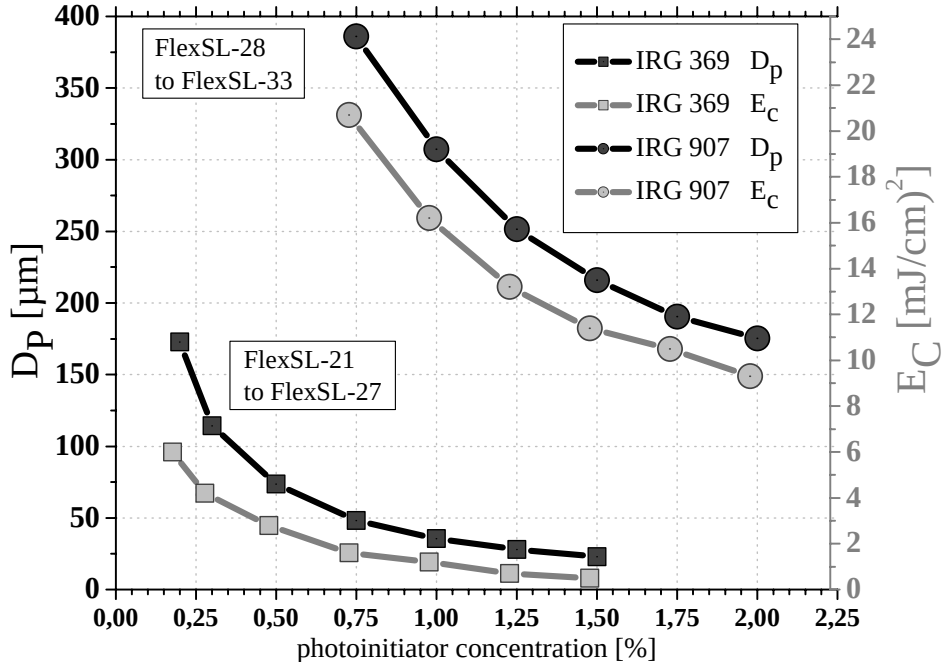

Figure 6: Process parameters E_C [mJ/cm^2] and D_P [µm] of the FlexSL-21 to FlexSL-33 series (polyether based resins with bishenol-A-ethoxylated di(methacrylates) / polyetherdi(meth)acrylates / tri-and tetracrylates / photoinitiators and stabilizers)

Using the described quartz-glass window protocol, the photolithographic parameters of a set of advanced FlexSL resins (see figure 6) were characterized. For the chosen Irgacure 369 photoinitiator, the resins (FlexSL-21 to FlexSL-27) show that the values for D_P can be easily adjusted from 23 µm (FlexSL-27) to 173 µm (FlexSL-21) by changing the photoinitiator concentration. This results in a high-resolution resin for high accuracy applications. In this case, the appropriate E_C values range from 0.5 mJ/cm^2 (FlexSL-27) to 6.0 mJ/cm^2 (FlexSL-21). Using a different photoinitiator (Irgacure 907) for the FlexSL-28 to FlexSL-33 resins, the D_P values are

significantly larger, ranging in the area from 175 µm (FlexSL-33) to 386 µm (FlexSL-28) and are depending on the assigned photoinitiator concentration (see figure 6). The E_C values are now located in the range from 9.3 mJ/cm^2 (FlexSL-33) to 20.7 mJ/cm^2 (FlexSL-28). From this measurement it could be concluded, that the resin process parameters of this material class cannot only be optimized for mechanical properties. It is possible to achieve either high building speed (2.0 % Irgacure 907 with E_C = 9.3 mJ/cm^2, D_P = 175 µm) or a potential high resolution (1.0 % Irgacure 369 with E_C = 1.2 mJ/cm2, D_P = 35 µm) material. Further optimization was then necessary to find a more exact formulation.

Volume Shrinkage

The volume shrinkage of stereolithography resins is also a big problem. The influences on the process stability as well as on parts precision are immense. Especially curling is the main topic in this context. The development of new resin materials always requires that the volume shrinkage is as low as possible. For the control of shrinkage during material screening tests in the early stages of development, a simple and fast method was found. 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:

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

This measurement gives a very simple and very cost-effective method to determine the polymerization shrinkage. Volume shrinkage measurements were performed on a DCAT21 tensiometer (Data-Physics, Germany). Typical values for the advanced FlexSL formulations are significantly lower than commercially available resins. SL 5510 (Huntsman), a high precision epoxy based material, shows volume shrinkage of nearly 5.2% in the tests with the above-described method. In contrast, the resin formulations FlexSL-21 (5.4%), FlexSL-BA-01 (3.4%) and FlexSL-BJ-02 (2.6%) show at least similar or even better results. Linear Shrinkage should not be mistaken with the herein described volumetric shrinkage in a three-dimensional system. The measured volume shrinkage is roughly three orders of magnitude larger than the normally considered linear shrinkage of a geometric dimension.

Conclusion & Outlook

The herein presented novel FlexSL materials show a significant lower cytotoxicity in contrast to commercial applied acrylic stereolithography resins. Further biocompatibility tests according to ISO 10993 protocols are planned. On the one hand, there are technical applications for this material (e.g. flaps, tubes, hoses, cables, sealing parts, connectors and other technical rubber-like applications), and on the other hand, broad fields of potential biomedical applications in which the FlexSL materials can be beneficial are obvious. Especially these could be small series production of medical products with special flexible material requirements. In addition, the usage for individual soft hearing aid shells, intra-operative planning services and tools like intra-op cutting templates and sawing guides is very attractive.

The possibility to modify the FlexSL resins also for high-resolution applications makes it possible to manufacture now very flexible micro-prototypes with outstanding material characteristics and very fine structures with a minimum resolution of 20 µm and a layer thickness of minimal 5 µm. These resin formulations are applicable and adjustable to other stereolithographic equipment available on the market. A group of different soft resin materials has passed first application tests and will be soon made commercially available.

Acknowledgements

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