Towards Micro Rapid Manufacturing (μ RM) with functionalized materials: material properties and process accuracy during stereo lithography

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Abstract:

The suitability of stereo lithography for the rapid manufacturing of micro components is presented. Since Rapid Manufacturing requires a higher-order diversity of materials than available for current Rapid Prototyping machines, our research aims towards the fabrication of new rapid manufacturing materials.Ormocer[®]s offer various material properties that can be adjusted by the internal nano-structure of the organic-inorganic parts. In order to attract micro system technology product designers, the process precision has been investigated by means of micro computer tomography (μ CT) and the generated parts have further been mechanically characterized. The resulting process accuracy is in the order of a few tens of μ m, the mechanical strength of the Ormocer[®] is above several hundreds of MPa. The combination of micro stereo lithography and Ormocer[®] offers new possibilities for the Rapid Manufacturing of micro components with adjustable properties for end-user applications.

Keywords: Laser Micro Stereo Lithography (μ SLA), Rapid Manufacturing, Ormocer[®], Hybrid polymer

1. Introduction

Rapid Prototyping (RP) is gaining increased interest for the cost-effective production of functional parts for end-user purpose in the field of medicine or aeronautics [1]. The main field of application is the prototype fabrication in order to study product properties like design and the ease of use (e.g. computer peripherals, mobile phone housings). Parts are redesigned if required and subsequently mass produced by die casting or injection moulding with materials that fulfill the customer's demands. Since it is an effort to change or modify the tools, the flexibility of such ways of mass production is very limited. In many cases, inevitable design changes at the tools can lead to high additional costs and a reduction of the process economy. In contrast to tool based fabrication, rapid production technology uses CAD data only to form three dimensional solid objects from a liquid polymer, powder or thin foils. This leads to a very high flexibility, low costs and the option to directly change the CAD parameters if required. Due to the high processing time, rapid technologies are not applicable for mass production, but they are useful for individually designed parts (e.g. medical applications) or low to medium batch sizes for niche markets. Recent developments have faced towards the fabrication of end-user parts for technological sectors like tool production or medical application systems [2]. However, the properties of rapid manufactured parts (e.g. mechanical properties, ageing) need to be well known and the functionality has to be verified in industrial applications, before establishing Rapid Manufacturing in the industrial environment as an accepted production method (e.g. for fluidic devices, optical elements, MEMS). Additionally, a broad catalog of materials has to be developed, that can be processed with Rapid Prototyping machinery. However, for

achieving process resolutions on the micron scale, commercially available Rapid Prototyping systems are not applicable. Within this work, the authors present a combined machine and material system that faces towards the Rapid Manufacturing of three dimensional objects with a process resolution on the micron level. As one important issue, the work focuses on the characterization of both the machining capabilities (process resolution) and the part properties (mechanical properties, form accuracy).

2. Three dimensional Micro Rapid Manufacturing

2.1 Principle of operation

The setup uses the principle of laser induced photo polymerization of a liquid polymer in a layer based production fashion, technically known as stereo lithography. The machining system (Fig. 1) has been reported in detail elsewhere [3].

Figure 1: Picture of the machining setup for micro stereo lithography (a) with laser source (b) and beam guidance (c).

During the stereo lithographic processing, the photo sensitive polymer is cured by the controlled scanning of a focussed laser beam on the polymer's surface. In a subsequent procedure, a substrate is positioned into a polymer filled processing chamber, coated and irradiated.

Consequently, the three dimensional part is formed in a step and repeat fashion of individually cured single layers. The geometrical information of the layers is generated by a software tool that slices a three dimensional CAD model at constant increments among the stereo lithographic building direction. The ready-built part will be chemically cleaned to remove residua of liquid resin and partly polymerized features.

2.2 Material preparation and properties

For stereo lithography micro production, a specially designed inorganic-organic UV-curable resin from the typeOrmocer b59 (Ormocore) has been applied. Ormocers are hybrid polymers that are synthesized by the sol-gel process [4], where Diphenylsilanediol reacts with Methacryloxypropyltrimethoxysilane (Fig. 2). By controlled hydrolysis and condensation of the organically modified Si alkoxides, the sol-gel processing is initiated. A radical initiator from the type Irgacure 369 is added after the removal of solvents at the end of the synthesis process.

Figure 2: Chemical structure of Diphenylsilanediol (a) and Methacryloxypropyltrimethoxysilane (MEMO) (b).

The material characteristics like mechanical or optical properties can be widely adjusted by the internal structure of the Ormocer. Additives can further lead to enhanced possibilities for modifying the curing properties (curing resolution) and viscosity of the material.

Figure 3: The curing depth c_d versus the laser fluence H_0 of modified Ormocer b59 with varying parts of a dye material (ADM3)

The preparation and characterization of a specially adapted Ormocer[®] for micro stereo lithography has been shown detailed in other reports [3]. The main improvement of the material has been the adaptation towards the micro stereo lithography process by decreasing the optical penetration depth of the laser radiation inside the resin (Fig. 3). The measurements on the non-modified Ormocer[®] revealed that no suitability for micro stereo lithography was given, while the modified resin with 0,5 % of ADM3 enabled an adjustable vertical process resolution in the range from $\sim 20 < c_d < 80 \mu\text{m}$ below a cumulative laser fluence of $F_L = 1000 \text{ J/cm}^2$.

2.3 Experimental investigations

The fabrication of complex three dimensional objects by means of micro stereo lithography has already been shown by various groups [3, 5]. In order to further characterize the process accuracy and the properties of the generated parts, a reference structure according to Fig. 4 has been developed.

Figure 4: CAD design of a reference structure for process accuracy measurement purpose, with related feature sizes listed in Table 1 (1-12).

The size of the structure has been 1.5 mm in all three directions. Basic cylindrical specimens have been generated for the characterization of the mechanical properties (two identical samples, height of $50 \mu\text{m}$, diameter 2 mm).

Table 1: Dimension of circular and rectangular features inside the reference structure

#	diameter/ edge length (μm)	#	diameter/ edge length (μm)
1	50	7	100
2	100	8	100
3	150	9	150
4	200	10	300
5	300	11	200
6	300	12	200

The reference structure has been fabricated with suitable fabrication parameters that have been distinguished in recent investigations [3]. The characterization of the process accuracy has been made via scanning electron microscopy (SEM), optical microscopy and micro computer tomography (μCT , Fig. 5), respectively. The SEM has been applied to perform high resolution imaging

to analyze the quality of the external geometry of the reference structure. Especially, the feature entrances have been investigated, to what extend residua of the liquid polymer remained within the channels or on the surface. The dimensions of the generated features have been measured via optical microscopy (feature #1-4 using 50x objective, feature #5-12 using 20x objective) and μ CT, respectively. The optical microscopy measurements have been compared in order to evaluate their accordance and the data confidentiality of the μ CT. In order to have a full three dimensional access to the internal geometry of the reference structure, the μ CT has been additionally used to generate vertical cross sections, providing further data of the form accuracy (e.g. parallelism of hidden features, clarity of internal features).

Figure 5: (a) Phoenix x-ray 180 kV Nanotom for micro computer tomography (μ CT), (b) Hysitron Triboscope® for mechanical characterization

The mechanical properties have been measured with nanoindentation and nanoscratch tests by applying a Hysitron Triboscope®, which was integrated in a Digital Instruments NanoScope 2® atomic force microscope. In order to detect the hardness and Young's modulus of the samples, a Berkovich tip with a triangular diamond pyramid is mounted on the nanoindenter. For the indentation a load is applied to the tip and the penetration depth is measured. By dividing the load by the area of the contact, the hardness is calculated. A force of 5 mN was used. Tests with lower forces showed that the material close to the surface is very soft and insufficiently cross-linked. Therefore at lower forces the tip does not create an indent.

The indentation result does not only allow the determination of the hardness but also of the Young's modulus which can be determined by the unloading curve. Nanoscratch tests have been carried out using a spherical cone tip to determine the adhesive wear and friction of the polymer. For the test, the tip moved across the surface while the load increased with the travel distance. The scratch length was 10 μ m, the final force 1 mN. To characterize the elastic and plastic behavior of the system, the surface profile before the scratch test, the tip penetration depth during the scratch test, and the final scratch profile after the scratch test were recorded.

During the indentation test, material is piled up at the edge of the indent. During the scratch test, displaced material accumulates in front of the tip and next to it.

3. Results

3.1 SEM and optical microscopy

The SEM images (Fig. 5) show a well-cleaned and clearly defined surface and outline of the fabricated reference structure. The entrances of the features are clean and no residua of liquid polymer or partly polymerized features are detected.

Figure 6: SEM images of the reference structure, fabricated with a cumulative laser fluence of $F_L = 208 \text{ Jcm}^{-2}$

Table 2: Optical microscope measurement of through holes

#	diameter, (deviation)		#	edge length, (dev.)	
	μm			μm	
	(x-dir.)	(y-dir.)		(x-dir.)	(y-dir.)
1	38 (-12)	38 (-12)	7	44 (-6)	50 (0)
2	89 (-11)	89 (-11)	8	93 (-7)	94 (-6)
3	136 (-14)	136 (-14)	9	139 (-11)	140 (-10)
4	184 (-16)	184 (-16)	10	187 (-13)	194 (-6)
	(x-dir.)	(z-dir.)		(x-dir.)	(z-dir.)
7	90 (-10)	67 (-33)	8	91 (-9)	51 (-49)
9	137 (-13)	108 (-42)			
12	191 (-9)	166 (-34)	11	191 (-9)	166 (-34)
10	278 (-22)	265 (-35)	6	279 (-31)	279 (-32)

The dimensions of the features have been measured with optical microscopy. According to the results (Table 2), it has been found that the contour accuracy of the through holes #1 - #4 is not depending on the size and shape of the holes or the measurement direction. The average of the error has been calculated to 13 μ m, which is in the range of the curing width at the deployed fabrication parameters [3]. Due to the regularity of the error, it is estimated to achieve an error correction by the addition of a beam size compensation function inside the process control software. In contrast to the measurements of the laterally arranged features, the error of the vertical features #6–12 has shown a distinctive difference between the x- and z-direction. While the error in the x-direction is exactly in the order of the previously measured through holes #1–4, the one in the z-direction is in the range between 32 and 49 μ m. The difference is caused by the optical penetration of the laser radiation into the liquid resin with subsequently initiated polymerization. According to Figure 3, the process parameters (cumulative fluence $F_L = 208 \text{ Jcm}^{-2}$ [10.4 mJcm^{-2} at a hatch distance $d_h = 0.001 \text{ mm}$]) lead to a curing depth of around $c_d = 45 \mu\text{m}$ which is in agreement with the detected deviation. Since the penetration of the optical radiation inside the material is required for layer bonding and sufficient cohesion between individual layers, a further reduction of the penetration depth may result in an unstable micro structure.

3.2 Micro computer tomography

The results of the μ CT measurements of the features #1–12 are listed within table 3.

Table 3: μ CT measurement of through holes

#	diameter, (deviation)		#	edge length, (dev.)	
	μm			μm	
	(x-dir.)	(y-dir.)		(x-dir.)	(y-dir.)
<i>1</i>	38 (-12)	38 (-12)	<i>7</i>	39 (-11))	44 (-6)
<i>2</i>	88 (-11)	88 (-12)	<i>8</i>	91 (-9)	93 (-7)
<i>3</i>	136 (-14)	136 (-14)	<i>9</i>	139 (-11)	140 (-10)
<i>4</i>	184 (-16)	184 (-16)	<i>10</i>	186 (-14)	190 (-10)
	(x-dir.)	(z-dir.)		(x-dir.)	(z-dir.)
<i>7</i>	82 (-18)	66 (-34)	<i>8</i>	84 (-16)	43 (-57)
<i>9</i>	-	-			
<i>12</i>	185 (-15)	153 (-47)	<i>11</i>	185 (-15)	153 (-47)
<i>10</i>	-	-

Figure 7: Virtual cross sections of the reference structure

The results show a great accordance compared to the data generated by optical microscopy, especially for the features #1–4. Here, the maximum absolute error between both methods is 6 μm . The image analysis of the vertical cross sections have shown up, that the internal channels are cylindrically shaped and the walls of the rectangular features are highly parallel.

3.3 Mechanical characterization

The laser polymerized cylindrical test specimens have been post cured at 200 °C for 1 hour. In order to determine the hardness and Young's modulus, scratch tests have been performed at a maximum force of $F_S = 1000 \mu\text{N}$ (Fig. 8 (a)) and nanoindentation tests have been done at $F_N = 1000 \mu\text{N}$ and 5000 μN , respectively (Fig. 8 (b),(c)).

Figure 8 (a)-(c): Results of scratch tests on Ormocer test specimen (a) and nanoindentation tests (b,c)

During scratch test measurements, a maximum penetration depth of 600 nm has occurred at the applied test force of $F_S = 1000 \mu\text{N}$. It has been investigated that the friction coefficient has drastically increased during the scratch test. The surface near region of the substrate is less hard, showing only limited resistance against the penetration of

the examination tip. The more the tip enters into the cured material, the more resistance against penetration has been detected. After testing, a permanent plastic deformation of around 100 nm has been measured. Similar observations have been made during nanoindentation tests (Figure 8; b,c). The tests performed with $F_N = 1000 \mu\text{N}$ have shown up the soft, elastic character of the sample (hardness around 0.1 GPa, Fig. 8 (b)), while at $F_N = 5000 \mu\text{N}$ a hardness of the material could be measured around 1.6 GPa (Fig.8 (c)).

4. Conclusion

The micro stereo lithography technique for the fabrication of complex shaped structures has been presented and found to be well suited for precise additive machining. In combination with an innovative, specially adapted material of the Ormocer® class, the production of parts with hardness and Young's modulus in the GPa regime could be demonstrated. The future work will closer focus on the fabrication and characterization of functional parts (e.g. micro fluidic systems, MEMS) in order to attract product designers for using micro stereo lithography as Rapid Manufacturing method suitable for micro system technology.

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