Digital light processing of ceramic components from polysiloxanes

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Johanna Schmidt[a], Paolo Colombo[a,b,*]

[a] Department of Industrial Engineering, University of Padova, Italy
[b] Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16801, United States

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ABSTRACT

Additive manufacturing using photocurable polymers is one method to answer the increased demand of ceramic structures with complicated morphology by fabricating ceramic parts with high resolution and good surface quality. We introduce here a new method to fabricate SiOC ceramic structures by utilizing a simple physical blend between two different preceramic polysiloxanes, one providing photosensitive acrylate groups while the other one a high ceramic yield. Different blend ratios have been realized and respectively optimized concerning the printing additives and setting times to fabricate exact replications of highly complex polysiloxane structures by Digital Light Processing. After pyrolysis, a uniform, homogenous shrinkage was observed yielding dense, pore- as well as crack-free SiOC ceramics. By adjusting the ratio between the different polysiloxanes, parameters such as the ceramic yield, shrinkage, chemical composition and resolution after pyrolysis could be tailored in a wide range of values.

1. Introduction

Standard techniques for ceramic processing such as powder pressing, tape or slurry casting do not easily allow for the production of complicated structures with undercuts or designed, non-stochastic porosity. Hard machining, that becomes necessary in order to achieve the level of details required for many ceramic parts used in engineering nowadays [1], is time as well as cost consuming [2]. Additive manufacturing (AM) provides a suitable approach for fulfilling the need for near net-shape three dimensional ceramic parts with a complicated morphology [2].

Stereolithography (SLA) is an indirect additive manufacturing technique that was first proposed in 1968 with the release of the first stereolithography machine by 3DSystems [3]. It is a laser-based technology that typically uses a liquid photosensitive resin containing vinyl or acrylate moieties [1]. A laser beam scans the surface of the resin and selectively hardens the material corresponding to a cross section of the product, building the 3D part layer by layer, enabling the fabrication of components with high resolution and a good surface quality [1,4]. Digital light processing (DLP) is a variant of this technique in which a projector is used to selectively expose and cure an entire cross-sectional slice of the photopolymerizable resin at each given time. Because an entire layer is exposed with a single pattern, faster build speeds are achieved independent of layer complexity [1].

For printing ceramics, the photosensitive resin is typically filled up to 40–60 vol% of ceramic particles [2]. After light exposure and

hardening of the photosensitive material, the photopolymerized green samples are subsequently sintered [1,5–8]. Difficulties in printing ceramic structures using SLA or DLP include the need for special dispersants [7,9] to maximize the ceramic solid loading while keeping a suitable viscosity for printing [9,10], as well as light absorbance and scattering due to the interaction of the incoming light with the ceramic particles [2,6,7].

By using preceramic polymers these problems can be avoided, as no ceramic particles are added to the solution, but the preceramic polymers themselves are converted by pyrolysis into ceramics [11,12], with decomposition of organic moieties and associated shrinkage. Furthermore SiC, Si_3N_4, BN, SiOC, SiCN, SiBCN ceramics or other ceramic compositions can be manufactured, some of which cannot be otherwise realizable but via the molecular route [12–14]. They are converted into ceramics at rather low temperatures, of around 1000–1300 °C, compared to powder-based ceramic technologies [4,11–13,15].

Preceramic polymers have been successfully employed as feedstock for a variety of different AM techniques [16]. Obviously, in order to process preceramic polymers by SLA/DLP, they need to possess photocurable moieties (usually, SLA operates with radiation in the UV region, while DLP in the visible range). There exists a small number of commercially available silicon-containing polymers possessing photoreactive groups (produced by companies such as Merck, Bluestar Silicones, Evonik and Starfire Systems). However, they often display very low ceramic yields, due to the decomposition of their photocurable acrylic side groups [17,18] and the fact that they possess a linear

polymeric chain which generates volatile low molecular weight fragments during pyrolysis [19,20]. Some of them, on the other hand, have a suitable ceramic yield (around 60–80 wt% [21]) and have been used in soft lithography for the production of microreactors [22] or other micro components [23,24]. Although they exhibit good soft lithography characteristics, the necessary UV exposure time [22–24] excludes them for the use in 3D Stereolithography since in the available printing time frame no crosslinking between the preceramic chains on their own takes place using a SLA/DLP printer [18,25].

Three different approaches can be followed in order to process preceramic polymers via SLA/DLP, maintaining a suitably high ceramic yield:

1. Chemical modification of a commercially available, high ceramic yield preceramic polymer by grafting of photocurable moieties;
2. Building up of a preceramic polymeric structure starting from the photoinduced reaction of two distinct (often oligomeric) precursors;
3. Blending of a photocurable preceramic polymer with a non-photocurable, high ceramic yield preceramic polymer. In this case, no crosslinking reaction between the two different polymer occurs upon light illumination, and the high ceramic yield preceramic polymer does not need to have specific functional groups.

In the first approach, a single source material is used for generating the 3D network upon light illumination. This has been successfully pursued in a few cases, but it requires a long chemical synthesis and the presence of suitable reactive groups in the preceramic polymer [4,17,26,27]. In the second approach, two components are needed (either two silicon-containing oligomers/polymers [12] or a silicon-containing oligomer/polymer and an organic one [18,28]) possessing different functional groups which crosslink together upon light illumination. Both components are participating during the photoinduced crosslinking reaction via a thiol-vinyl [12,28] or an acrylate-vinyl [18] copolymerization, therefore requiring specific functional groups (e.g. vinyl, acrylate, thiol) which limits the selection of the components [12,18,28].

In this work we propose and demonstrate, for the first time, the third approach, that is a novel way to produce ceramic structures using DLP by generating a blend between two preceramic polymers. The primary polymer contains the acrylic groups necessary to form a polymerized network upon light illumination, while the secondary preceramic polymer, although non-photosensitive, possesses a high ceramic yield, but otherwise leaves a high degree of freedom in selection as no specific functional groups are required. This is a fast and reproducible approach that benefits from the use of commercially available preceramic polymers, requiring no special chemical expertise besides the selection of a suitable co-solvent.

Moreover, it should be pointed out that this innovative method has a significant additional benefit. Specifically, the ceramic yield, and therefore the shrinkage upon pyrolysis, can be varied by simply changing the ratio between the two polymers in the blend. This, in turn, controls the dimension of the structural details of the printed body after pyrolysis. This means that it is possible to achieve a variable, higher resolution with respect to the one achievable in the green state and limited by the equipment employed for the fabrication.

2. Experimental procedure

The preceramic polymers used in this work were a liquid photocurable siloxane of proprietary composition (TEGO RC 711, Evonik Industries, Germany) and two high ceramic yield silicone resins (Silres 601 and H44, Wacker Chemie A.G., Germany). Toluene was employed as a solvent for the preparation of the blends, and diphenylether for the cleaning of the printed parts (both from Sigma Aldrich). A photo-initiator (Irgacure 819, Ciba Specialty Chemicals, Switzerland) and a photoabsorber (E133, Squires Kitchen, England) were also added to the

system. No catalyst was added for promoting the crosslinking of the preceramic polymers.

The solid polysiloxanes Silres 601 and H44 were dissolved in toluene in a constant weight ratio of polysiloxane/solvent of 3/1 with a magnetic stirrer at 60 °C within 2 h. TEGO RC 711 was then added to the dissolved preceramic polymer solutions in the desired amount. After the addition of photoinitiator Irgacure 819 and photoabsorber E133, the bottles containing the photosensitive blends were wrapped in aluminium foil to prevent light illumination and homogenized at 60 °C overnight.

The homogeneous blends were printed using a DLP printer (3DLPrinter-HD 2.0, Robofactory, Italy) operating in the visible light range (the wavelength was limited to 400–500 nm by applying an optical filter). The structures were cleaned after printing using diphenylether in an ultrasonic bath for 6 min and blow dried using compressed air. After the removal of the uncured liquid, the partially cured structures were illuminated for 15 min in an UV furnace (365 nm, Robofactory, Italy), to complete the formation of the acrylic network. The fully cured structures were dried at 60 °C in a drying furnace overnight, to remove all traces of cleaning solvent from the surface of the parts, and were then pyrolyzed in an alumina tube furnace (Lindberg, Riverside, MI) at 1000 °C for 1 h in nitrogen (99.99%) with a heating rate of 2 °C/min.

Morphological characterization of printed model cube structures, employed to determine the optimal printing time, the necessary amount of photoabsorber to prevent overexposure and the shrinkage of the different blends, was performed by stereo-microscopy (STEMI 2000-C, Zeiss, USA). Higher resolution investigations were conducted by scanning electron microscopy (SEM, Quanta 450, FEI, USA) on metal-coated samples. Thermo-gravimetric analyses (TGA, STA 409/429 Netzsch, Verona, Italy) were carried out at a heating rate of 5 °C/min in flowing nitrogen. The optical absorbance of the constituent parts of the printable blends was investigated by UV–vis spectrometry (V-650, JASCO International Co., Japan).

3. Results and discussion

3.1. Blending of the polymers

The synthesis of the photocurable preceramic blends was based on a physical mixture of two commercial available polysiloxanes, one providing the photocurability and the other the high ceramic yield. Several combinations of the RC 711 siloxane with different high ceramic yield silicone resins (e.g. MK, H62C, Silres 610, all from Wacker Chemie, Germany) and solvents were tested (e.g. Phenoxyethanol, Dowanol, Benzyl alcohol, Cyclohexanone, all from Sigma Aldrich), in order to select a combination that would provide the formation of a homogenous system, without separation of a second phase. At the end of this preliminary work, two silicone resins (Silres 601 and H44), containing phenyl and phenyl-methyl side groups, and toluene as the solvent, were selected as they enabled the formation of a homogeneous mixture with RC 711, providing not only compatibility but also long-term stability without precipitation of any secondary phase in the course of several months. It should be noted that the investigation of the specific reasons for the phase separation with some combination of materials was beyond the scope of this work, which mainly aimed at validating the general processing approach of printing using a mixture of two different preceramic polymers.

During the printing, the highly acrylated, photosensitive RC 711 provided the reactive end groups capable of forming a continuous polymer network acting as a partially frame incorporating the silicone resin chains. While Silres 601 and H44 on its own are photoinsensitive, they became entrapped by the polymerized network during printing, decreasing the weight loss of the blends upon pyrolysis, due to their high ceramic yield. After heating, a continuous pore-free ceramic SiOC structure was generated. Its chemical composition, and especially the