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Influence of irradiation parameters on the polymerization of ceramic reactive suspensions for stereolithography

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ABSTRACT

Stereolithography is an additive manufacturing process which makes it possible to fabricate useful complex 3D ceramic parts, with a high dimensional resolution and a good surface finish. Stereolithography is based on the selective UV polymerization of a reactive system consisting in a dispersion of ceramic particles in a curable monomer/oligomer resin. In order to reach a homogeneous polymerization in the green part, and to limit the risk of cracking and/or deformation during subsequent stages of debinding and sintering due to internal stresses, the influence of various fabrication parameters (laser power, scanning speed, number of irradiations) on the degree of polymerization was investigated. In addition, the impact of the irradiation of the subsequent upper layers onto the previously deposited and irradiated layers was evaluated. The degree of conversion was determined by Fourier Transform Infrared Spectroscopy (FTIR). Raman spectroscopy was also used and a brief comparison between these two methods is given.

1. Introduction

Conventional ceramic processing routes are limited to the creation of complex shapes and are costly thanks to tooling and/or machining for the fabrication of prototypes or short-range production. Previously called Solid Freeform Fabrication (SFF) or Rapid Prototyping, additive manufacturing (AM) techniques, that open the possibility to produce parts of nearly any shape, are becoming more and more accessible.

AM technologies have shown a growing interest these past few years. At first, simple tools to build polymer prototypes, with the main objective to help for designing parts, AM technologies have become nowadays real production tools, able to shape different materials (polymer, metal, and ceramics) into complex parts. Used in a wide range of industries, AM allows companies to turn innovative ideas into successful end products rapidly and efficiently. In the domain of ceramics, AM technologies constitute an attractive answer to the need of shaping techniques to produce useful complex parts and specific architectures without costly tooling and/or machining. Additive processes are likely going to transform the field of ceramic manufacturing and will open new ways of thinking about the design and fabrication of objects [1–3].

Among the AM techniques used to fabricate ceramic parts, stereolithography (SLA) is an efficient way to fabricate useful complex 3D objects, with a high dimensional resolution and a good surface finish. Stereolithography is based on the selective UV polymerization of a reactive system consisting of a dispersion of ceramic particles in a curable monomer/oligomer resin with the addition of a photoinitiator [4–7]. Using the three dimensional CAD file of the part to be built, the UV laser beam, focused onto the surface, is deflected in the X-Y plane to polymerize each cross sectional patterns of successive layers of the part to build the 3D green object. The green part is cleaned to remove the remaining non polymerized suspension/paste, then debinded and sintered.

Polymerization is a critical step to control in the stereolithography process. Submitted to UV light, the photoinitiator releases reactive radicals, initiating the polymerization which transforms the liquid monomer/oligomer into solid polymer. In this respect, the manufacture, using stereolithography, of useful complex 3D parts with a high dimensional accuracy and properties similar to those obtained by classical routes requires the understanding of the main process parameters which influence the polymerization. For instance, the higher the degree of conversion of the curable system, the higher the mechanical strength of the green part [8].

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It is then critical to determine not only the degree of conversion of the monomer/oligomer system, but also the kinetics of the polymerization, i) to have a pertinent choice of the organic system in terms of kinetics and reactivity, ii) to evaluate the effects of additives such as dispersant and diluent and, iii) to determine the best fabrication parameters such as the layer thickness, the density of energy, the power of the laser, the scanning speed or the number of scans to build a cohesive ceramic green part, without deformation or cracking, in a reasonable time [9,10].

This study considers the last point, based on the determination of the degree of polymerization, with the objective to reach a homogeneous polymerization in the volume of the green sample in order to minimize internal stresses, then the risk of cracking and/or deformation during subsequent stages of debinding and sintering.

Fourier Transform Infrared Spectroscopy (FTIR) is a common method used to determine the final degree of conversion of monomers and oligomers in the polymer industry [11]. Thanks to the absorption band (e.g. acrylate double bond stretching in acrylate resins) area being proportional to the bond concentration, it is possible to follow the evolution of the polymerization, also allowing kinetic studies using Real-Time Infra-Red spectroscopy (RTIR). Several studies of ceramic loaded systems have been performed by FTIR, RTIR [12,13]. Raman spectroscopy has been mainly used to characterize the structural evolution of monomer/oligomer. Nevertheless, Raman spectroscopy is an attractive method to follow the polymerization of a reactive system directly during the fabrication by stereolithography and makes it possible to adjust the manufacturing parameters in real time [14–16].

In this work, the degree of conversion of stereolithography reactive suspensions containing 50 vol% alumina particles submitted to UV laser beam was measured by FTIR and Raman spectroscopies. Then, a comparison of the degree of polymerisation of curable suspensions measured by FTIR and Raman spectroscopies is also presented in this paper. The Raman spectroscopy presents the advantage of being able to be used *in operando*, whereas it is not possible for FTIR for technical constraints. Indeed, the Raman head can be offset by a distance of 15 cm or more from the working plan, which leaves room for the spreading and insolation systems.

2. Experimental procedure

2.1. Preparation of the alumina reactive system

Stereolithography suspensions are basically composed of a curable oligomer/monomer, a photoinitiator, a ceramic powder and a dispersant. The main requirements for this reactive system are: i) a high powder loading (i.e. >50 vol.%) to ensure suitable mechanical properties to the green part during debinding and a sufficient densification during sintering, ii) a rheological behavior adapted to the spreading of thin layers, i.e. shear thinning and, iii) a sufficient reactivity to UV, even for a concentrated suspension, in order to reduce the time of fabrication with a sufficient cure depth.

The organic media is a mixture of two different reactive resins chosen in the family of acrylates: 1,6-hexanediol diacrylate (HDDA) which is a di-functional monomer (viscosity 25 °C: 7 mPa s) and a tetra-acrylate (PPTTA) with a functionality of 4 (viscosity 25 °C: 190 mPa s). The ratio between the two resins is 10% PPTTA/90% HDDA. The combination of these two resins constitutes a good compromise between high reactivity and low viscosity. The photoinitiator is a 2,2-dimethoxy-1,2-phenylethan-1-one (DMPA) (BASF, Germany), which absorbs in the range of 220–380 nm. Alumina powder P172SB (Alteo, France) has been used (mean particle size: 0.5 μm, specific surface area: 7.6 m^2/g, density: 3.96 $g\,cm^{-3}$).

The alumina powder was mixed with the organic media to reach a 50%vol powder loading, with the help of a dispersant, and ball milled for 4 h. The final suspension is homogeneous and presents a shear-thinning behaviour. The viscosity at 100 s^{-1} (25 °C) is 3 Pa s which is in agreement with the layer spreading requirements. A critical energy of 491 mJ cm^{-2} has been experimentally determined thanks to the Jacobs equation [4]. The critical energy represents the minimum of energy for which polymerization occurs, and thus describes for the reactivity of the system.

2.2. Manufacturing

Thin layers of suspension were spread by means of a moving blade, similar to tape-casting. The thickness of the layers was fixed at 50 μm according to the reactivity of the suspension and in order to reach a good dimensional resolution of the future 3D objects manufactured.

Three types of samples were prepared in order to evaluate, i) the number of layers with a given thickness influenced by the irradiation (A samples), ii) the respective contribution of the scanning speed and of the laser power, at constant density of energy, on the degree of polymerization (B samples) and, iii) the influence of the number of irradiations maintaining a constant density of energy (C samples).

The optical system of the stereolithography machine consists of different elements (Fig. 1):

- a UV laser source with a 355 nm wavelength,
- a laser beam expander which maximises the use of the scan system aperture and reduces the power density on the mirrors,
- a scan head composed of two galvanometer movable mirrors which deflect the laser beam with a high precision and repeatability,
- a F-Theta objective that focuses the laser beam at the focal point. This objective ensures that the focal point is always positioned in the working plane, perpendicular to the optical axis of the objective. The spot size of the laser beam, focused onto the surface, has a diameter of 21,6 μm.

A-samples

A first objective was to determine the number of layers, with a typical thickness of 50 μm, influenced by the laser irradiation. The upper side of the multilayer object will only be submitted to one irradiation at a given density of energy. Depending on the depth of penetration of the UV light, the layers below can be affected with an increase of their degree of polymerization. In this respect, multilayered samples containing from 2 to 12 layers with a thickness of 50 μm were fabricated. A first 50 μm thick layer was deposited on the working platform and a rectangle zone of 12 × 5 mm^2 was irradiated with an UV laser beam (355 nm), at a constant energy dose (DE = 1.02 J cm^{-2}). After moving down the working platform of the layer thickness, a second 50 μm thick layer was deposited on the first one and a same rectangle was irradiated with the same energy dose and so on. The degree of polymerization of the two accessible sides (bottom side and upper side, the upper side being the irradiated side submitted to only one irradiation) was measured.

B-samples

The degree of polymerization is directly related to the density of energy DE (J cm^{-2}) delivered. We have considered the average density of energy which depends on the spot size of the laser beam radius ω_0 (cm), the scanning speed v_s (cm/s) and the power of the laser P_0 (W) according to Eq. (1).

$$DE = \frac{2P_0}{\pi\omega_0 v_s} \quad (1)$$

This equation considers the Gaussian distribution of the energy of the laser beam with a radius ω_0 corresponding to a decrease of power of $1/e^2$. The generally named spot size is equal to $2\omega_0$ [4].

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