Additive Manufacturing 16 (2017) 153–161

Contents lists available at ScienceDirect

Additive Manufacturing

journal homepage: www.elsevier.com/locate/addma

Full Length Article

A Tripropylene Glycol Diacrylate-based Polymeric Support Ink for Material Jetting

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ARTICLE INFO

Article history:
Received 6 September 2016
Received in revised form 3 May 2017
Accepted 11 June 2017
Available online 12 June 2017

Keywords:
Additive manufacturing
Inkjet printing
Material jetting
Support material
UV curing
TPGDA

ABSTRACT

Support structures and materials are indispensable components in many Additive Manufacturing (AM) systems in order to fabricate complex 3D structures. For inkjet-based AM techniques (known as Material Jetting), there is a paucity of studies on specific inks for fabricating such support structures. This limits the potential of fabricating complex 3D objects containing overhanging structures. In this paper, we investigate the use of Tripropylene Glycol Diacrylated (TPGDA) to prepare a thermally stable ink with reliable printability to produce removable support structures in an experimental Material Jetting system. The addition of TGME to the TPGDA was found to considerably reduce the modulus of the photocured structure from 575 MPa down to 27 MPa by forming micro-pores in the cured structure. The cured support structure was shown to be easily removed following the fabrication process. During TG-IR tests the $T_{5\%}$ temperature of the support structure was above 150 °C whilst the majority of decomposition happened around 400 °C. Specimens containing overhanging structures (gate-like structure, propeller structure) were successfully manufactured to highlight the viability of the ink as a support material.

1. Introduction

Additive Manufacturing (AM), colloquially known as 3D Printing (3DP), is a manufacturing approach that enables the fabrication of a 3D structure on a layer by layer basis, usually from a computer-generated file. The method has considerable advantages over traditional manufacturing, since it is free from the constraints of many subtractive or formative techniques. Over the last 25 years, it has moved from being used for prototyping purposes towards becoming an accepted manufacturing methodology [1–3]. The simplicity of the layer-by-layer approach, together with the freeform production methods that it offers, presents significant advantages in a wide range of fields, including biomedical, electronics and engineering structures [4–9]. Among the seven categories of AM techniques defined by the American Society for Testing and Materials (ASTM), Material Jetting (MJ) — '*an additive manufacturing process in which droplets of build materials are selectively deposited*' [10] — is particularly attractive due to its scalable production, potential for multi-material (and function) and high resolution [11–13]. Whilst there is much that is achievable with single material deposition, multi-material approaches can offer the opportunity for multifunctional components, combining for example, structural and biocompatible elements [14], electronics and diagnostics [15,16] and excipients and drugs [17].

Recent efforts in Material Jetting have demonstrated a widening vista of materials that can be processed [18–25]. However, several challenges present themselves. One of the most significant is the need for readily available materials that can support overhanging structures. Such supporting materials are needed since exploitation of the design freedoms afforded by AM often leads to the presence of cavities and voids. Material supports are an indispensable element, which work as a temporary base during fabrication and usually will be removed at the end of the process. Fahad et al. [25] suggested support materials need to support the layers of build material during the build process and be soft enough to be removed easily post fabrication. They hypothesised a methylcellulose-based ink, which could be used as a support material; [25]. Commercial 3DP inkjet companies have developed their own support structures, but their composition and use is usually protected. It is the aim of this paper to present alternative materials that are easy to

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http://dx.doi.org/10.1016/j.addma.2017.06.001

prepare, whilst also being inexpensive and effective, for the role of supports.

This paper focuses on the modification of Tripropylene Glycol Diacrylate (TPGDA) for the purposes of supporting structural materials during fabrication and post-manufacture removal. TPGDA is a commonly used material principally exploited for its balance of dielectric and structural properties [26], whilst also showing reliable jetting performance and good thermal stability. It is proposed that TPGDA can be mixed with Triethylene glycol methyl ether (TGME), a high boiling point solvent, in order to create a jettable support material. It will be demonstrated that the blending of TGME with TPGDA is akin to the formation of a hydrogel [27,28]; since the TGME solvent does not participate in the UV photochemistry that is used to crosslink TPGDA, this leads to the production of a soft gel-like structure. Evidence will be presented regarding the structural and thermal properties of the jetted materials and a demonstrator produced to illustrate that objects can be manufactured with this support.

2. Experimental

Formulations based on TPGDA with different proportions of TGME were prepared and their suitability for printing investigated. Rheological measurements were taken to determine printability and those formulations within the printable range were then printed using a Dimatix DMP-2830 in order to determine their behaviour during printing and after curing. Thermogravimetric Analysis coupled to Infrared Spectroscopy (TG-IR) and compression tests were used to evaluate their thermal and mechanical properties, respectively. Finally, demonstrators were built with a multi-head inkjet print system. These structures were used to illustrate that the use of the new support material enabled the fabrication of overhanging structures.

2.1. Ink preparation

Chemicals were all purchased from Sigma Aldrich and used as received. TPGDA (a mixture of isomers containing Mono Methyl Ether of Hydroquinone (MEHQ) and Hydroquinone (HQ) as inhibitors, technical grade) with 0 wt%, 10 wt%, 20 wt% and 30 wt% of TGME (95% purity) were mixed at room temperature with 2 wt% of 2, 4-diethylthioxanthone (DETX) and 2 wt% of Ethyl 4-(dimethylamino) benzoate (EDB), as photoinitiator and accelerator, respectively, in an amber vial. The mixture was then stirred at 800 rpm for 30 minutes to fully dissolve the initiators. The prepared inks were then degassed by bubbling nitrogen through them for 15 minutes to help minimize photoinhibition brought about by pre-dissolved oxygen.

2.2. Ejectability assessment

The viscosities of the ink candidates were measured in a Malvern Kinexus Pro equipped with a 40 mm parallel plate geometry and programmed with a shear rate table between $10\,\mathrm{s}^{-1}$ and $1000\,\mathrm{s}^{-1}$ at room temperature. The plate gap was set to 150 μm and each measurement was repeated three times. The surface tension of the droplet was measured by pendant droplet shape analysis (Kruss DSA 100S) [29], with each measurement repeated 5 times. The inverse Ohnesorge number or printing indicator, Z [30], was used to help judge the ejectability of the inks. Z is given by:

$$Z = \frac{\sqrt{\rho r \gamma}}{\mu} \tag{1}$$

where ρ is the density, r is the characteristic length (in this case the nozzle diameter), γ is the surface tension of the fluid and μ is the viscosity of ink at the printing temperature. A value of Z between 1 and 10 for a given ink suggests that it is ejectable by a drop-on-demand printhead.

2.3. Printing assessment

The ink candidates within the ejectable range were then printed with a Dimatix DMP-2830 material printer. The ink was injected into a print cartridge (DMC-11610) which was then fixed to a printhead consisting of 16 nozzles (21 μm in diameter). Stable droplets were obtained through adjustment of the pressure-generating waveform. A 365 nm UV LED unit was used to cure the deposited ink during printing through a free radical polymerization process.

2.4. SEM

The printed samples were put into liquid nitrogen and then fractured to expose the inner surfaces. The use of liquid nitrogen assists in minimising the potential polymer deformations induced by ductile fracturing. The sample was sputter coated with platinum at 2.2 kV for 90 seconds (Polaron SC7640) and then imaged using SEM (Hitachi TM3030).

2.5. TG-IR analysis

TG-IR analyses were carried out in an Evolved Gas Analyser TL 9000 (Perkin Elmer). A specimen of approximately 10 mg was cut from the printed sample for characterization while the heating rate was set to 40 °C per minute. The gas that was evolved during the temperature ramp was pumped from the TG into the IR module at a rate of 70 mL/min with a 150 °C tube temperature to prevent chemical condensation. Real-time infrared spectroscopy was performed to track the chemical species within the gas phase with a scanning interval of $2\,\mathrm{cm}^{-1}$ from $600\,\mathrm{cm}^{-1}$ to $4000\,\mathrm{cm}^{-1}$ and two scans per second.

2.6. Compression test

Cubic samples (5 mm edge length) were prepared for compression tests. The top and bottom sides of the samples were polished using SiC paper to ensure flat, parallel surfaces. An Instron Universal testing machine (Model 5969 Instron) was used with a load cell with a maximum available load of 5 kN. The compression tests were conducted in accordance with the ASTM standard D695. The crosshead speed during testing was 0.25 mm/min and the samples were loaded until fracture.

2.7. Demonstrator

A bespoke multi-material 3D Material Jetting system manufactured by Roth & Rau, encompassing six Spectra 128 SE print heads with Infrared and Ultra Violet (395 nm) processing methods was used to produce demonstrator components. In these experiments, one print assembly, which containing two printheads, was used and the inks was subsequently cured with the UV station (365 nm $1077 \pm 8\,\mathrm{mW/cm^2}$). One of the print heads was filled with a TPGDA based support ink and another with TPGDA-only ink as the structural material. Prior to multi-material fabrication, both the support ink and structural ink were printed independently and cured to measure their layer thickness after curing. These values were then used to inform the print strategy and calculate the number of layers required to achieve the designed dimensions. Gate-like and propeller structures were printed to demonstrate the feasibility of fabricating overhanging structures with the designed support ink.