DOI: 10.31625/atnrs.778

Additive Manufacturing by Gel-in-Gel Printing

Yaman Boluk[1*], Xiaoyi Lan[1,2,], and Adetola Adesida[2]
[1]Department of Civil and Environmental Engineering, Faculty of Engineering, University of Alberta, Edmonton, AB, Canada
[2]Department of Surgery, Divisions of Orthopedic Surgery & Surgical Research, Faculty of Medicine & Dentistry, Li Ka Shing Centre for Health Research Innovation, University of Alberta, Edmonton, AB, Canada

ABSTRACT

Additive manufacturing by the 3D-printing processes enables solid free-form fabrication of three-dimensional objects directly from the digital images by melt prepolymers and gels following the post-curing of deposited polymers. Those processes have limitations due to long printing times, low-quality materials, and costs. The gel in gel printing by printing low viscosity materials in a support gel environment addresses those limitations. This process deposits a relatively low viscosity but curable liquids or gels into a medium of support gel. The support gel prevents the collapse or deformity of the printed object under its weight. Once the printing is completed, the object is cured, removed from the support bath, and rinsed off. The support gel can be reused. This sacrificial supporting gel has to be removed easily after 3D printing. There exists a very limited amount of materials suitable for printing and supporting the printed objects in a bath. Some of the support baths studied by different research groups are crosslinked polyacrylic copolymer microgels, granular gels, silica nanoparticle suspensions, and clay suspensions. The design of an appropriate supporting hydrogel bath poses several challenges. The supporting gel has to behave like Bingham plastic, not yielding until a threshold shear force is reached. In the meantime, its yield stress has to be low enough to accommodate nozzle movement. Besides supporting the deposited printing gel, the support bath must exhibit a high plateau shear elastic modulus, G'. In addition, those viscoelastic properties have been thermo-reversible. Here, we discussed the role of yield stress of printing and support gels on gelling, shape integrity, and interlayer fusion.

INTRODUCTION

Current 3D-printing processes enable computer-driven solid free-form fabrication of three-dimensional objects directly from the digital images by extrusion of thermoplastics, prepolymers, or hydrogels followed by various post-curing processes. Those processes have limitations such as long printing times, resulting in low-quality materials and costs. Rapid Liquid Printing (RLP) Process[1] has been developed to address those limitations by printing low-viscosity materials in a support gel environment (**Fig. 1**). This process deposits a relatively low viscosity but curable liquids or gels into a medium of support gel. The support gel prevents the collapse or deformation of the printed object under its weight. Once the printing is completed, the object is cured, removed from the support bath, and rinsed off. The support gel can be reused for printing other objects. There exists a very limited amount of materials suitable to be used in a bath for printing and supporting the printed objects. With this process, silicon structures are prepared by printing silicon elastomeric inks in support medium of granular micro-organogels in light mineral oil[2] and crosslinked polyacrylic copolymer (Carbopol^{TM}) suspensions[3] in water. In another study, the gelatin-alginate solution is extruded into nano clay suspension[4]. PDMS elastomer is printed in a hydrophilic support bath[5]. Proteins and polysaccharide hydrogels are printed into support gels prepared by gelatins for biomedical applications[6]. Our group has prepared and printed cell-laden collagens in gelatin support baths for engineered nasal cartilage applications which have the potential to replace and reduce donor-site morbidities associated with native cartilage grafts taken from other anatomical sites for reconstructive nasal surgeries[7]. In all of those studies, detailed objects are printed in support gels with fine structures. In this short communication, we discuss the required rheological properties of support gels using a model printing in a gel.

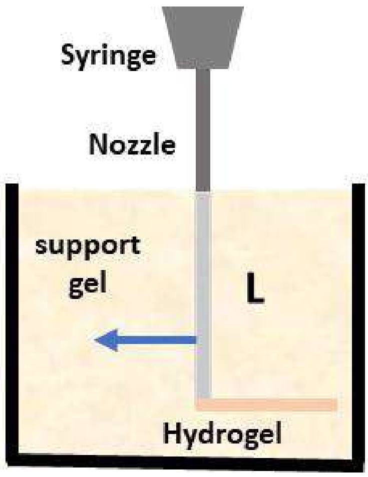

FIGURE 1a. 3D printing in a support gel environment

MODELLING GEL-GEL PRINTING

We model the gel in gel printing by selecting a non-Newtonian printing ink and Hershel Buckley yield stress gel in the bath. Modeling was prepared in two parts: 1) nozzle movement in the batch; 2) Drag in bath gel with filament moving axially.

1. Nozzle Movement in the Bath

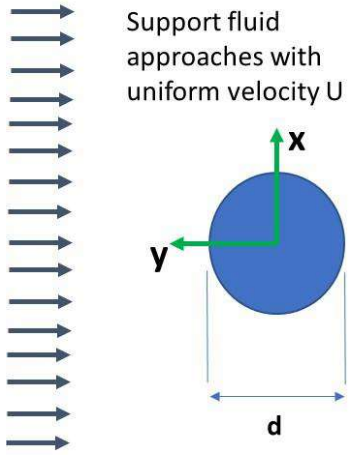

FIGURE 1b. Transverse Flow around nozzle (top view)

2. Drag in bath gel with filament moving axially

In a typical freeform printing in a gel process, a drop of filament extruded from the dispensing needle with a release speed of V_f and dragged to a horizontal distance which is equal to the step distance with a path speed of v_o. This step-by-step horizontal movement of filament extrudate in the support gel bath can be modeled as shown in Fig. 2.

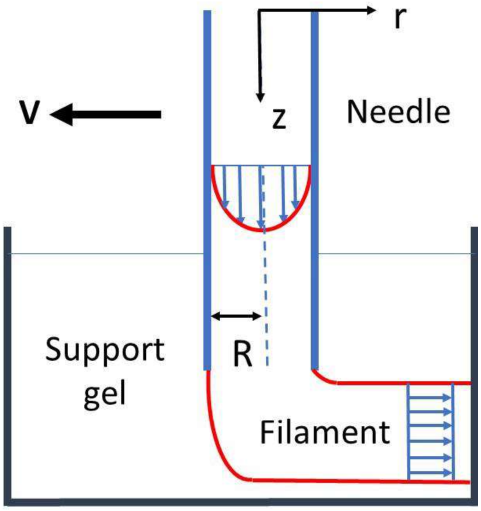

FIGURE 2. Ink gel flow from moving nozzle

This is not a steady-state process, nevertheless, for simplicity, the whole formation and movement of filament in the bath will be considered as a steady-state. With this flow, the extruded filament drags down the support bath gel while the needle moves in the bath with the velocity of v_o in the y direction. The equation of motion for this case can be reduced to:

$$\frac{1}{r}\frac{d}{dr}(r\tau_{rz}) = 0 \tag{1}$$

from which the integration follows:

$$\tau_{rz} = \frac{a\mu_f V_f}{r} \tag{2}$$

where a is a dimensionless constant of integration, μ_f is filament viscosity and V_f is the horizontal velocity at the needle exit.

Support bath fluid gel

Hershel-Buckley model

$$\tau_{rz} = \tau_y + k(\frac{dv_z}{dr})^n$$

Oldroyd Number, Od

$$Od = \frac{\tau_y}{k(U/d)^n}$$

SUMMARY OF DISCUSSION

Printing in a support bath: What do we need?

The hydrogel ink (body) and support gel (bath) have to meet several requirements:

The printing ink must be:

- Shear thinning yield stress fluid
- G' and τ_y of ink have to be the order of magnitude higher than G' of and τ_y of support gel, respectively.

Key printing parameters for gel in gel printng

- Movement of Nozzle in the Bath
    - Rheological properties of support gel
    - Nozzle movement speed (path speed)
    - Nozzle diameter
    - Nozzle length in the support gel
- Movement of Bioink Filament in the Bath
    - Rheological properties in bioink
    - Dispensing pressure
    - Nozzle diameter
    - Nozzle movement speed (path speed)

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