Supporting Information:

Effect of Polymer Binder on the Synthesis and Properties of 3D-Printable Particle-Based Liquid Materials and Resulting Structures

Nicholas R. Geisendorfer\textsuperscript{1,2}, Ramille N. Shah\textsuperscript{2,3,4,*}

Affiliations:

\textsuperscript{1}Department of Materials Science and Engineering, \textsuperscript{2}Simpson Querrey Institute, \textsuperscript{3}Department of Biomedical Engineering, Northwestern University, Evanston, Illinois, 60208, USA
\textsuperscript{4}Department of Bioengineering, University of Illinois at Chicago, Chicago, Illinois 60607, USA

*Correspondence to: ramille@uic.edu

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Abstract:

Recent advances have demonstrated the ability to 3D-print, via extrusion, solvent-based liquid materials (previously named 3D-Paints) which solidify nearly instantaneously upon deposition and contain a majority by volume of solid particulate material. In prior work, the dissolved polymer binder which enables this process is a high molecular weight biocompatible elastomer, poly(lactic-co-glycolic) acid (PLGA). We demonstrate in this study an expansion of this solvent-based 3D-Paint system to two additional, less-expensive and less-specialized polymers, polystyrene (PS) and polyethylene oxide (PEO). The polymer binder used within the 3D-Paint was shown to significantly affect the as-printed and thermal post-processing behavior of printed structures. This development enables users to select one of several polymers to impart the most desirable properties for a given application. Additionally, 3D-Paints based on these new binders are not adversely affected by classes of particles that can chemically degrade PLGA, notably particles containing large quantities of alkali ions. This study demonstrates the ability to successfully use of PS and PEO as binders in the 3D-Paint system, and compares the rheological, mechanical, microstructural, and thermal properties of the modified 3D-Paints and resulting as-printed and thermally post-processed objects. These objects include, for the first time, structures resulting from 3D-Painting which contain a majority soda-lime glass and 45S5 bioactive glass.
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Supporting Experimental Section

**Figure S1:** Images of 3D-printed samples used in this study

**Figure S2:** Schematic showing 3D-printing parameter space for inks used in this study

**Figure S3:** Compressive properties of 3D-printed cylinders produced for this study

**Figure S4:** Calculated polymer crystallinities in 3D-printed/dried inks based on DSC melting endotherms

**Figure S5:** Nitrogen and carbon content of metallic Fe specimens produced for the study, determined by combustion fusion analysis

Other Supporting Information for this manuscript:

**Video S1:** Video shows inks at appropriate viscosities for 3D-printing. 45S5:PLGA is degraded and therefore does not thicken appropriately.

**Video S2:** Video shows the 3D-printing of compression cylinders from PLGA-based inks.

**Video S3:** Video shows the 3D-printing of compression cylinders from PS-based inks.

**Video S4:** Video shows the 3D-printing of compression cylinders from PEO-based inks.

**Video S5:** Video shows the compression of 3D-printed cylinders. Qualitative differences in the mechanical behavior between cylinders containing different polymer binders are readily visible.
Supporting Experimental Section:

3D-Printing: Tensile dogbones with a gauge length 20 mm, gauge width of 3 mm, and thickness of 1 mm were printed with a fully dense inner pattern printed parallel to the length of the gauge. Compression cylinders were 3D-printed with an outer contour of 1 cm diameter and a height of 2 cm, with an internal strut space of 1.2 mm (center-to-center) alternating 90° in each subsequent layer. Shrinkage cylinders were printed with an outer contour of 1.5 cm diameter, with an internal strut spacing of 1.5 mm (center to center) alternating 90° in each subsequent layer. Substrate for 3D-printing was 320 grit sandpaper for all tensile specimens and shrinkage cylinders, and a polystyrene petri dish for compression cylinders.

Mechanical Testing: A compression cage was employed for every test. Sample dimensions were measured individually for each sample using a caliper (rather than relying on nominal 3D-printed dimensions). Six samples of each material were tested, except SLG:PS, where five samples were tested.

Thermal Measurements: During all measurements, the furnace was held at 30°C for three minutes following sample insertion, in order for the sample to thermally equilibrate prior to the beginning of the measurement.

Imaging: SEM samples were coated in 12 nm Os metal using an Os plasma coater (SPI Supplies). Photographs and supplementary videos were captured either with a Canon EOS Rebel SL1 or with a Google Pixel 2 cell phone camera.

Sintering and Shrinkage/Porosity Analysis: Sintered samples for metallography were sectioned (diamond-blade saw), embedded in epoxy (EpoThin 2, Buehler) and polished using a Ecomet/Automet 250 (Buehler) with 320 grit sandpaper for leveling (240 rpm) followed by 6, 3, and 0.05 µm polishing suspensions (120 rpm), followed by 200 proof ethanol wash and 30 seconds of sonication to remove debris. See imaging section for microscopy details; porosity was measured using image analysis software ImageJ on polished sample cross sections.
Supporting Figures:

**Figure S1**: 3D-printed samples used in this study. A) Overview of all samples, 45S5-containing samples (foreground), SLG-containing samples (middle ground), Fe-containing samples (background) with PLGA-based samples on the left, PS-based in the center, and PEO-based on the right. 45S5:PLGA and SLG:PLGA were not printable, hence the empty space on the left in the fore- and middle ground. B) Single sample group containing compression cylinders (left), shrinkage cylinders (center), and tensile specimens (right), C) Close-up of a shrinkage cylinder, D) Close-up of a compression cylinder, E) Close-up of a tensile specimen.
Figure S2: Schematic chart showing 3D-printing parameter space with respect to extrusion pressure (bar) and the linear speed of the nozzle (mm/s) for inks containing each of the three polymer binders used in this study. For PLGA-based inks, extrusion pressures range between approximately 1.0-3.5 bar, at linear speeds between 7.5-20 mm/s. PS-based inks are generally extruded at lower pressures than PLGA-based inks, between 0.5-1.5 bar at linear speeds between 10-15 mm/s. PEO-based inks require higher pressures, from 4.0-5.0 bar and slower speeds 1.0-6.0 mm/s. All ranges are general and approximate, and ideal parameters for a given ink will depend on exact viscosity of the ink, particle size and shape, etc.
Figure S3: A) Representative compressive load vs. strain curves on 3D-printed 1 cm diameter compression cylinders. PLGA and PEO-based cylinders barrel and then densify, but PLGA-based cylinders yield at much higher loads than PEO-based cylinders. PS-based cylinders fail catastrophically and pulverize by sections. B) Images of the fully-compressed cylinders. Compressive PLGA and PEO-based cylinders leave behind a densified disc, whereas PS-based cylinders leave only a pulverized powder.
Figure S4: Calculated crystallinities based on melting endotherms measured from DSC. In all cases, dissolution of the polymer in DCM followed by reprecipitation and/or 3D-printing leads to a lower crystallinity than the as-received polymer, as would generally be expected.
Figure S5: Nitrogen and carbon content in metallic Fe after thermal processing of Fe:PLGA, Fe:PS, and Fe:PEO. A) Similar levels of dissolved N indicate that N is likely not responsible for differences in sintering between measured samples, and the relatively low levels of measured nitrogen generally indicate that samples are minimally affected by sintering in N$_2$ / H$_2$ mixed atmosphere. B) Carbon content is consistent with that in an engineered medium-carbon steel. Carbon content in the Fe trends qualitatively with the contribution by weight of carbon to the molecular weight of the polymer, (92.3%, 54.5%, and 48.5% C for PS, PEO, and PLGA respectively).
Supporting Videos:

**Video S1**: Video shows inks at appropriate viscosities for 3D-printing. 45S5:PLGA is degraded and therefore does not thicken appropriately.

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