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Reviewed Paper

Printability Assessment of Cellulose-Based Polymer Structures using Direct Ink Writing

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Abstract

In this paper, we demonstrate the preparation and printing of ethyl cellulose, a cellulose derivative, using a custom-modified direct ink writing (DIW) printer. Ethyl cellulose (EC) is widely used as a thin-film coating in controlled-release vitamins and medical pills as well as a thickener in the food, cosmetics, and other industries. It is, therefore, an attractive bio-mass derived polymer for 3D printing. Two types of ethyl cellulose, with different molecular weights (M_w), are dissolved in alpha-terpinol solvent to assess the feasibility of printing the polymer. In total, eleven different slurries are prepared at different solid weight percent. The stir time, stir temperature, and resting time are then varied. The results show that 10 wt. % ethyl cellulose slurry performs best for the initial printability assessment. Following printing, this slurry holds its shape, and shows uniform thickness in rectangular and snake patterns.

Keywords
Direct Ink Writing (DIW), Biopolymer, Ethyl Cellulose, Printability

1. Introduction

3D printing continues to generate an increased interest within the materials and manufacturing community due to its unique promise of fabricating complex multi-functional multi-material parts directly from a digital file [1]. Over the past few decades, 3D printing has been extensively used in processing several different types of materials from metals to ceramics and polymers. In particular, the ability to 3D-print biopolymers successfully is critical to a variety of fields, such as the medical and food industries [2]. 3D bioprinters frequently operate by either the extrusion of a bioink (in case of direct ink writing) [3] or jetting of droplets (in case of inkjet printing) [4]. Within the bioprinting community, direct ink writing (DIW) is of particular interest as it allows for a larger range of ink viscosities, therefore expanding the range of biopolymer choices [5]. In DIW, a shear-thinning ink or slurry is dispensed through a nozzle. Depending on the functional requirements of

the printed parts, multiple secondary print nozzles may be used during the printing process to fabricate multi-material graded components [6]. DIW has been successfully used for processing a range of different materials including ceramics and polymers. Existing research indicates that there are printability maps in DIW that describe the acceptable ranges of printing parameters (e.g., the extrusion flow rate, the distance between the nozzle tip and the build plate, and the print speed) for a slurry of a given viscosity [7].

Despite research progress in printing biopolymers using DIW, many challenges still exits, including determination of the optimal rheological properties and printing parameters for effective printing [7], limiting the widespread use of DIW for biopolymers [7]. Although there are commercially available DIW printers that seek to overcome such challenges [5], they are limited in their range of operation by virtue of their proprietary nature. In this paper, the preparation and printing of a biopolymer, namely ethyl cellulose, is demonstrated using a custom-modified direct ink writing (DIW) printer. The DIW printer is appropriately re-designed from a readily available thermoplastic 3D printer, where the gantry system of the original printer is repurposed to position a custom designed DIW print head assembly. This printer is an open-architecture one and, therefore, allows for any user specified modification e.g., sensor installation and feedback control. Once the printer was modified, it was interrogated to print slurries of ethyl cellulose dissolved in α-terpineol. The results demonstrate that 9-14 wt. % ethyl cellulose slurry performs best for the initial printability assessment.

2. Experimental

2.1. DIW Printer Development

A Creality Ender 5 Pro 3D printer (Creality 3D Technologies Co., Shenzhen, China) was used in this work. The printer is a fused deposition modeling (FDM) type and has a build volume of 200 mm × 200 mm × 300 mm. The gantry system can travel at a speed up to 80 mm/s. The thermoplastic print nozzle was removed (Fig. 1), and the printer was integrated with a syringe-plunger assembly. The 20 mL syringe consists of a Luer lock (McMaster-Carr 7510A807) that holds the biopolymer slurry as well as accommodates for various needle sizes. A 42 × 42 mm frame NEMA 17 non-captive stepper motor (OMC Corporation Limited, Nanjing City, China) was selected to apply the linear motion necessary to dispense the slurry (Fig. 1). Two ¼" guide rods made of 6061 Aluminum (McMaster-Carr 9062K26) were used to stabilize the non-captive motor travelling on a Tr8 × 8 lead screw (Amazon B079HQ386R). The stepper motor was then connected to a stepper motor driver (4A 40V SMAKN TB6600, Amazon B016ZJS1FA) and a control board (ELEGOO Uno R3 microcontroller, Amazon B01EWOE0UU) executing scripts written using the Arduino IDE software.

The final printer attachment housing (Fig. 1), consisting of the syringe-plunger assembly, the stepper motor, and the guide rods, were mounted on 3D printed parts made from white Polylactic Acid (PLA) using the same Creality Ender 5 Pro 3D printer. During the design and prototyping phase, the manufacturability of the housing via thermoplastic 3D printing was analyzed based on its complexity, tolerances, stress concentrations, and amount of thin or unsupported features. The CAD models were designed to avoid these criteria as well as to reduce the chances of part failure due to stringing and delamination of the printed filament layers. The final parts were lightweight

and sturdy. Minor post processing steps, including sanding and drilling, were required due to tolerance issues in the 3D printed parts. However, the post processing steps did not cause any detrimental effects on the overall design.

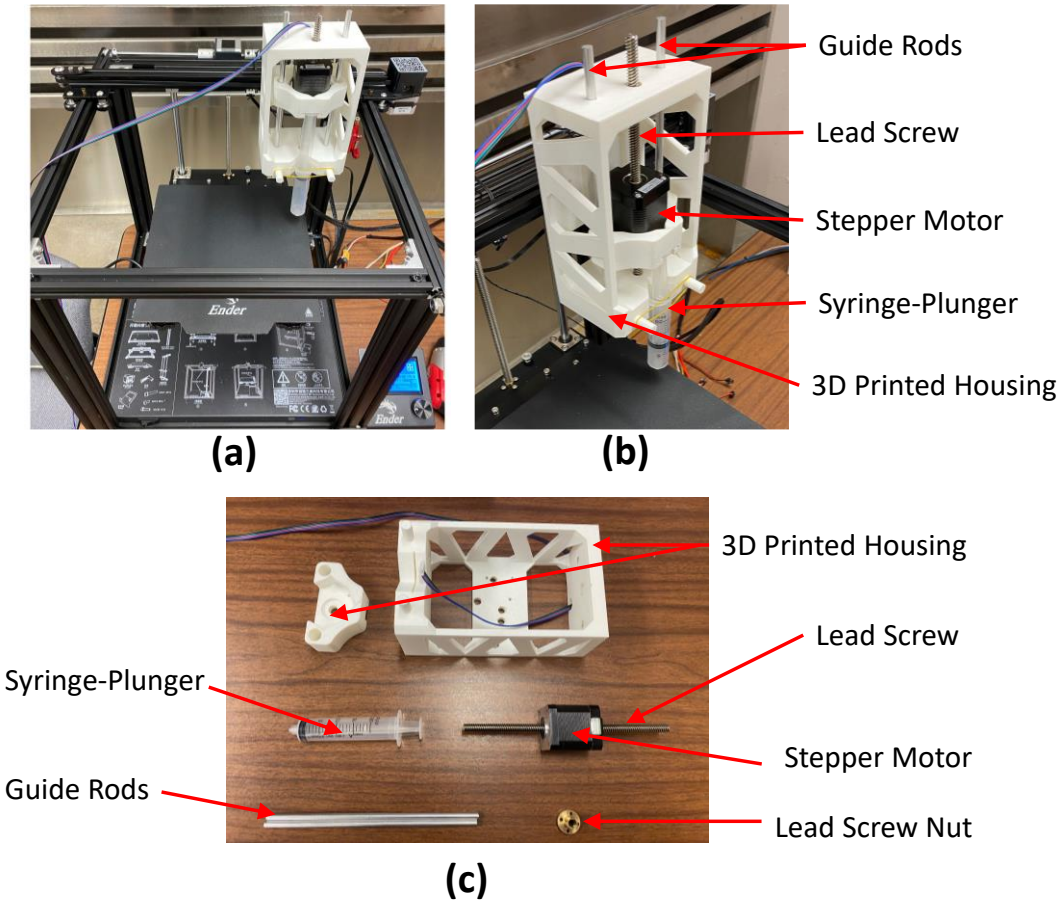

Figure 1: (a) DIW printer with syringe-plunger assembly. (b) Zoomed view of the 3D printed housing. (c) Different parts of the housing.

2.2. Slurry Development

Ethyl cellulose (TCI America, Portland OR, USA) was chosen due to its wide-spread application, and α-terpineol (TCI America, Portland OR, USA) was used as a solvent. Two types of precursor ethyl cellulose powders were used during the trial slurry tests, differentiated by their viscosity range, when a slurry was formulated: Type 1 [Product code: E0266, 45-55 mPa·s, 5% in Toluene + Ethanol (80:20) at 25 °C] and Type 2 [Product code: E0290, 90-110 mPa·s, 5% in Toluene + Ethanol (80:20) at 25 °C]. Due to the need for a more viscous slurry, Type 2 was used for most of the test batches. To prepare the slurry, the desired weight percent of ethyl cellulose was combined with α-terpineol in a beaker. Using a hot plate with a magnetic stirrer, the mixture was stirred at 120 RPM for at least twelve hours while the temperature of the heating plate is maintained at 95°C. The heat allowed the ethyl cellulose powder to dissolve more evenly as well as kept the viscosity in the appropriate range for mixing.

The long stirring times were necessary to fully homogenize the slurry, and, in most cases, there was still a small amount of undissolved ethyl cellulose particles in the slurry (Fig. 2(a)). However, these particles dissolved after 1-2 weeks of resting time depending on ethyl cellulose content (see Fig. 2(b)). After the first 15 minutes of stirring, it was often necessary to scrape ethyl cellulose powders from the bottom and the side of the beaker. Slurries consisting of 8.58 wt.% or more ethyl cellulose became too viscous to stir well with the magnetic stirrer, therefore a stir rod was used. In total, eleven biopolymer slurries were created and tested. The composition of each batch, the stir times, and other relevant parameters are listed in Table 1. Images of the slurry batches after one to two weeks are provided in Fig. 3. It is noted that slurry K is not pictured as it solidified during stirring due to the high concentration of ethyl cellulose, while slurry J is not pictured due to an unfortunate book-keeping error. Overall, slurries with more than 24 wt. % of ethyl celluloses solidified during the stirring process as shown in Fig. 2(c).

Table 1: Details of the slurries.

Batch	*Ethyl cellulose type*	*Amount (g)*	*Solvent*	*Amount (ml)*	*Ethyl cellulose wt. %*	*Stir Time (hr.)*
A	Type 1	1.590	α-Terpineol	20	7.84%	0.25
B	Type 1	0.980	α-Terpineol	20	4.98%	0.25
C	Type 1	0.472	α-Terpineol	20	2.46%	0.25
D	Type 2	1.570	α-Terpineol	20	7.75%	0.50
E	Type 2	0.979	α-Terpineol	20	4.98%	0.25
F	Type 2	0.465	α-Terpineol	20	2.43%	0.25
G	Type 2	1.550	α-Terpineol	20	7.66%	17
H	Type 2	1.943	α-Terpineol	20	9.42%	8
I	Type 2	1.753	α-Terpineol	20	8.58%	13
J	Type 2	4.151	α-Terpineol	30	13.84%	14
K	Type 2	7.293	α-Terpineol	30	24.31%	14

Slurries A through C, where low molecular weight ethyl cellulose was used, were not investigated further because of their very low viscosity. Slurries D through F, using high molecular weight ethyl cellulose, had comparable stir times (0.25-0.5 hrs.); however, in slurry E and F, no undissolved particles were observed after 1 to 2 weeks due to low weight percentage of ethyl

cellulose in these slurries (4.98 wt. % and 2.43 wt. %, respectively). Slurry D had 7.75 wt. % of ethyl cellulose and showed undissolved particles. Slurries G, H, and I had >8 hrs. of stir time; however, they all showed considerable amount of undissolved ethyl cellulose particles after two weeks. In the future, the resting time will be further increased with weekly stirring to ascertain that the final slurry does not have any undissolved powders in it.

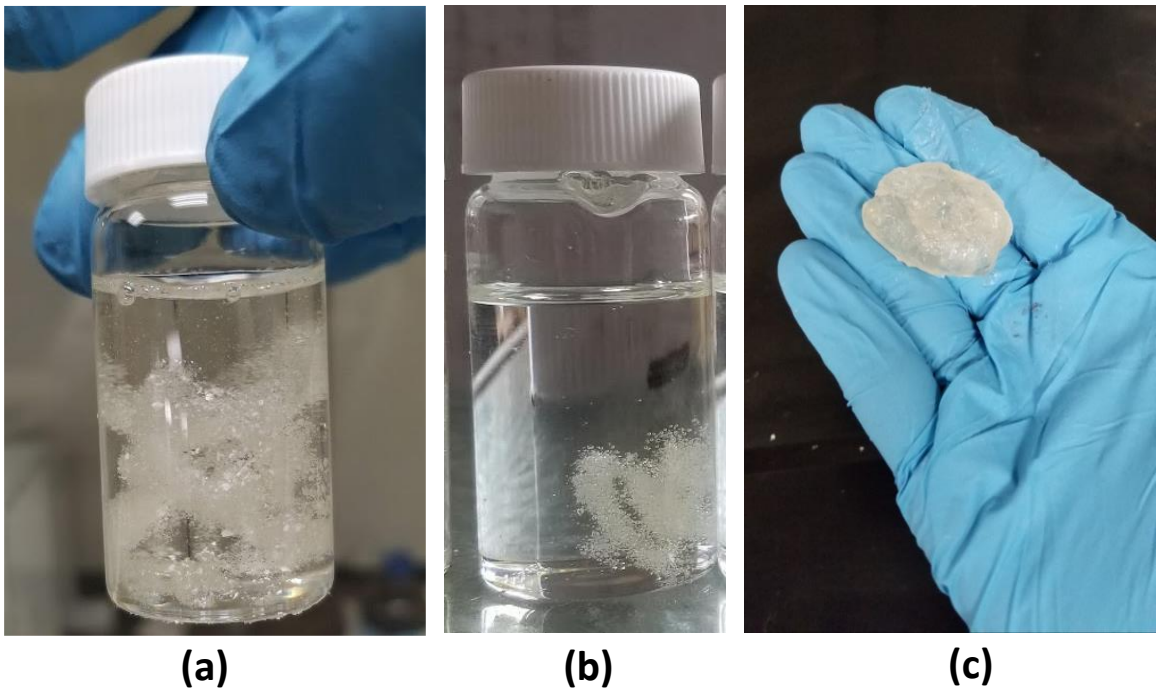

Figure 2: (b) Slurry B after 15 mins of stir time. (b) Slurry B after one week. (c) Solidified slurry.

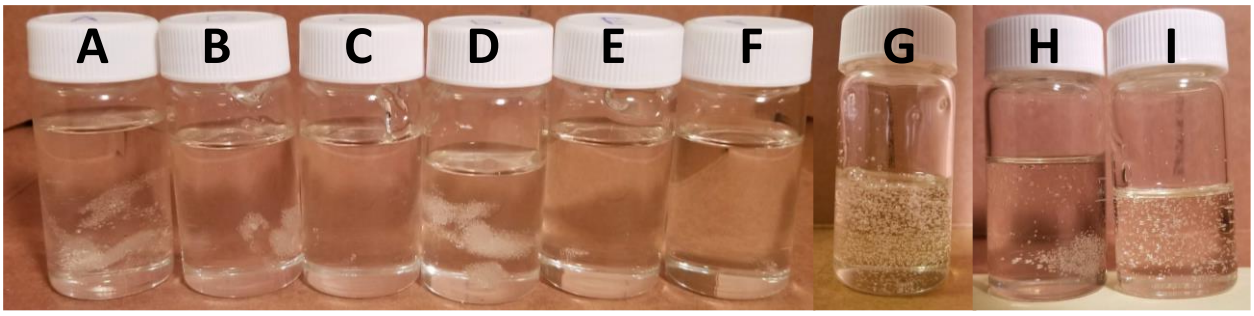

Figure 3: Images of slurries A through I after 1 to 2 weeks.

3. Results and Discussion

Manual printing using the syringe-plunger assembly was carried out to investigate whether the slurry can be extruded and whether it can hold its shape once it is successfully extruded; the advantage of this process is that it is a quick and inexpensive way to evaluate the slurries without loading them in the DIW printer. Fig. 4 shows the snapshots of manual printing with slurries G, H, and I. The biopolymer slurries, with 7.66 wt.% or more ethyl cellulose, were found to be the most promising ones during the manual testing as they held their shapes reasonably well for at

least fifteen minutes following manual printing tests. Since the initial G through I slurries had undissolved particles in them, the printed layer also showed these undissolved particles as seen in Fig. 4. Slurry J is not pictured due to an unfortunate book-keeping error as mentioned earlier.

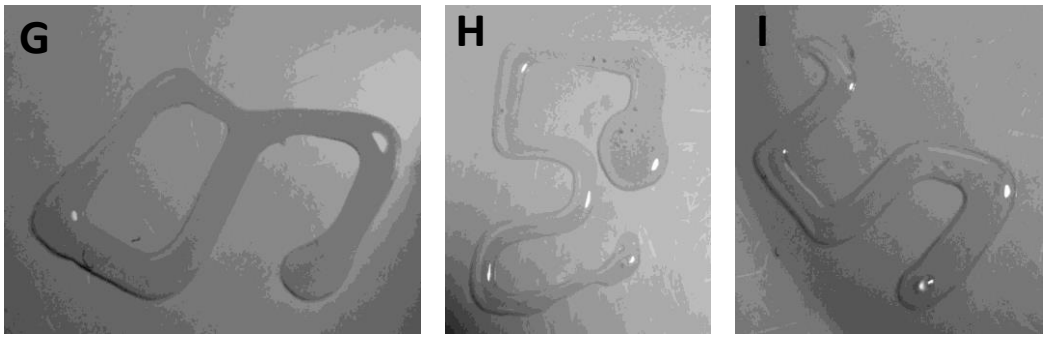

Figure 4: Manual printing results with slurries G-I. Images are not to scale.

From the four slurries that were successfully 'printed' using the manual test, i.e., G-J, once the DIW printer was used, only slurries I and J showed good results (Fig 5). Slurries G and I showed excessive spread during the printing process. All printing experiments were carried out at 20 mm/s. This difference in results between the manual printing and printing with the DIW printer is likely due to medium on which the slurries were printed. While glass petri dishes were used during manual printing, the actual (DIW) printing was carried out on plastic ruler papers to facilitate measurements. The build-plate medium (plastic vs. glass) is expected to affect the wettability of the slurries [8]. Hence the difference between manual and DIW printing in terms of wettability of the slurries is justified. In the future, investigations will be carried out on the effects of build-plate medium on the wettability of different slurries.

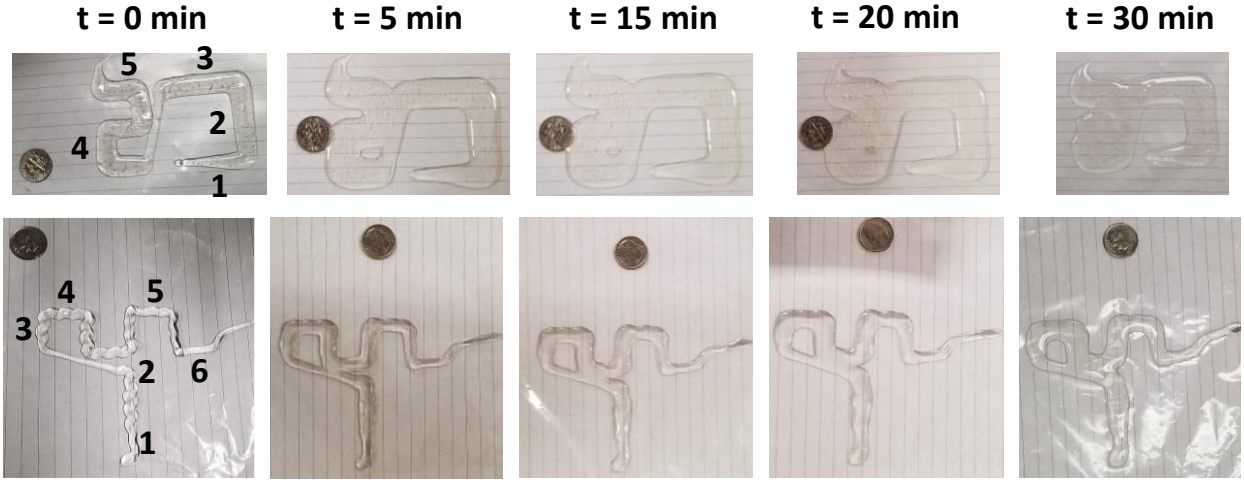

Figure 5: Results from DIW printing. Top row: Slurry H at 0 minutes, 5 minutes, 15 minutes, 20 minutes, and 30 minutes. Bottom row: Slurry J at 0 minutes, 5 minutes, 15 minutes, 20 minutes, and 30 minutes. Locations where the width measurements were performed are marked on the left images.

The uniformity of the printed layers was characterized by comparing the dimensions (e.g., layer width) of the layer using ImageJ software [9]. The results for slurries H and J are shown in Fig. 5. Slurry J held the shape the most over a period of half an hour as illustrated in the bottom panel of Fig. 5 while slurry H spread out after half an hour as shown in the top panel of Fig. 5. However, slurry J showed balling behavior during printing. It is anticipated that such a behavior could be easily mitigated by optimizing the printing parameters such as the print speed and the nozzle relative position. The width of each printed layer was measured at several different locations initially, and then again at five, fifteen, twenty, and thirty minutes. Fig. 6(a) shows the evolution of layer width at several different locations for slurry J. Fig. 6(b) shows that the spreading rate decreases with time. Similar observations were obtained for slurry H as well. Using Slurry J, a rectangular shaped single-layer deposit was printed and let to air dry for about four weeks. The fully dried deposit was optically transparent (Fig. 7(a) and flexible (Fig. 7(b)). More quantitative characterization is required to fully understand the properties of the printed layers.

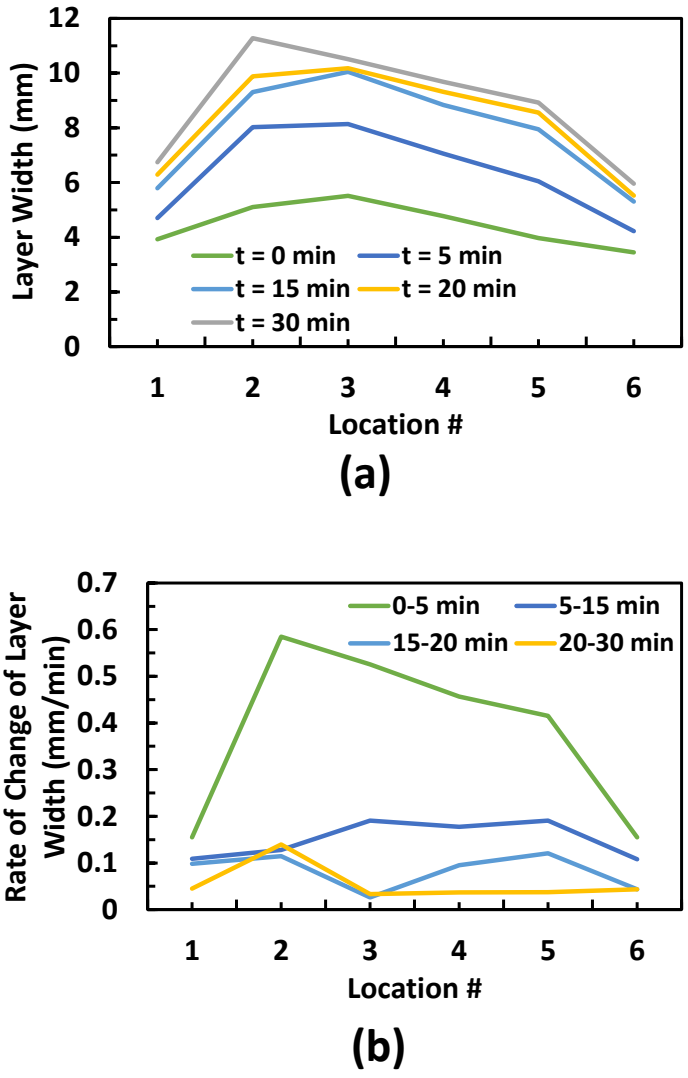

Figure 6: Results from DIW printing of slurry J (a) evolution of layer width at different locations as marked on Figure 5 and (b) rate of change of layer width with time.

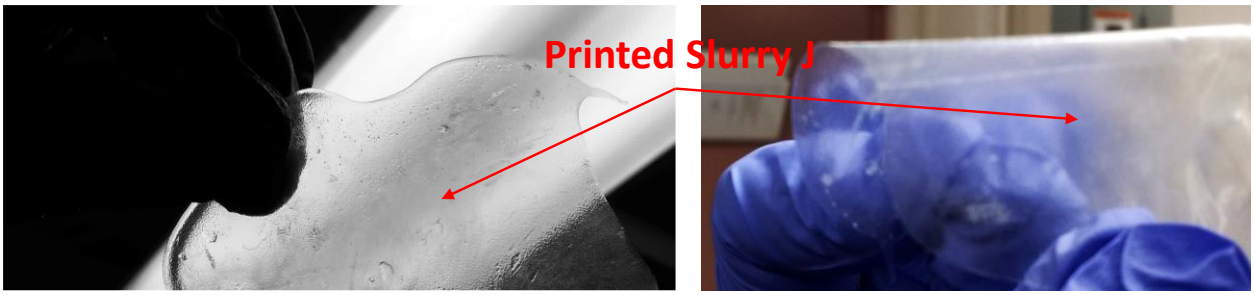

Figure 7: Properties of the air-dried Slurry J – (a) transparent and (b) flexible.

4. Conclusion and Future Work

Ethyl cellulose slurries were successfully prepared by dissolving in α-terpineol. Two different molecular weight powders were used, and it was found that the higher molecular weight powder was more suitable due to its higher viscosity. Results indicated that solid content in the range of 9-14 wt. % ethyl cellulose slurry led to better printability. Following printing, these slurries held their shapes and showed uniform thickness in rectangular and snake patterns. The present work also indicates that post-processing methods are required to solidify the printer layers. In the future, the effects of printing parameters such as print speed, nozzle relative height, and build plate temperature will be evaluated. Gradually drying the layers *in-situ* is also expected to improve the structural integrity of the printed layers. The findings reported in this paper open opportunities for the 3D printing of bio-mass derived polymers.

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6. References

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