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3D printing of cellulose by solvent on binder jetting

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Abstract

This project aims to 3D print wood by products. The printed parts are only made of cellulosic derivatives. The proposed process is powder based. Parts are made of semi-crystalline cellulose mixed with ethylcellulose (50/50). Similarly to binder jetting, successive layers of this mixture are spread out. Using an industrial inkjet print head from Fujifilm-Dimatix, isopropanol is selectively deposited on each of the powder layers. Isopropanol dissolve the ethyl cellulose, binding the cellulose particles together. The produced parts are brittle and require a post-treatment. A dedicated printer was built for this project. Ongoing research is done on optimizing of the layer formation and drying to increase mechanical properties.

Introduction and state of the art

The overall objective of this project is to 3D print wood materials. Wood is a sustainable resource. More and more additive manufacturing processes offer artificial wood as a printing material. Those processes - FDM [1], SLA [2], binder jetting [3], or SLS [4] - mostly use plastic wood composites, i.e. short wood fibers bonded in a polymer matrix.

Wood is a natural composite material constituted of cellulose fibers (35-50% w/w) within a matrix of lignin (15-25%)[5]. Cellulose is strong in tension and lignin in compression. The third wood component is hemicellulose, which accounts for 30-45% of wood. It constitutes an amorphous framework that binds cellulose fibers together. Cellulose forms a crystalline network with much higher strength than hemicellulose. Cellulose and lignin are standard industrial products available in bulk quantities, and both have an increasing economic importance [6], [7].

Cellulose itself is widely used for bioprinting as additive to increase hydrogel stiffness [8] or as a scaffold material [9]. Ethyl cellulose is a derivative of cellulose where hydroxyl groups on the repeating glucose units are chemically converted into ethyl ether groups. It does not occur naturally. Ethyl cellulose is widely used in food [10] and pharmaceutical industry [11] as a coating agent or thickener.

The additive manufacturing process used in this project is similar to binder jetting depicted in Figure 11.

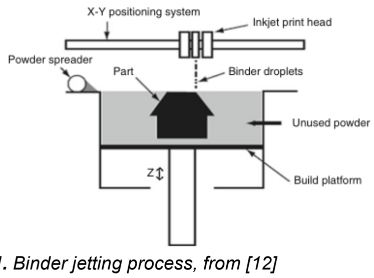

Figure 1. *Binder jetting process, from [12]*

Binder jetting is a powder based additive manufacturing process, where a binder is selectively deposited on a powder bed with an inkjet printhead to form cross sections of the part that is printed [12]. After each layer is printed, a new layer of powder is deposited on top of the previous one, and leveled by a blade or a rotating roller. Binder jetting is used to print a wide range of materials: metals, ceramics and polymers. In the case of metals and ceramics, green bodies are obtained.

Ideally, the powder should be bimodal or multimodal, the small particles filling the gaps between the large particles. A bimodal powder has higher packing density and flowability [13], and provides more junction points for sintering. In solvent jetting, the adhesive used in-bed is activated by an organic liquid that is in our case isopropanol. The solvent softens and partially dissolves the surface of the adhesive lignin or ethyl cellulose and bind the cellulose particles. The solvent is removed by evaporation.

Materials

First tests were conducted with cellulose powder and lignin as a binder. The idea was to mimic the wood structure. However, the tests failed to reach sufficient part quality as the produced parts remained very brittle despite of thermal-post processing. Tests were then conducted with cellulose derivatives to replace lignin as a binder: ethyl cellulose and methyl cellulose were investigated for this purpose. Ethyl cellulose is soluble in organic solvent such as alcohols and methyl cellulose is soluble in water. Both are thermoplastics. Pure solvent can be jetted with a piezo printhead while it is very difficult to jet pure water. Therefore, ethyl cellulose was selected to conduct this study.

The properties of the ethyl cellulose polymer change depending on molecular weight and the degree of ethoxyl group substitution. The ethyl cellulose used for the results presented here was Ethocel 20 (Dow Chemical). The molecular structure is shown in Figure 2.

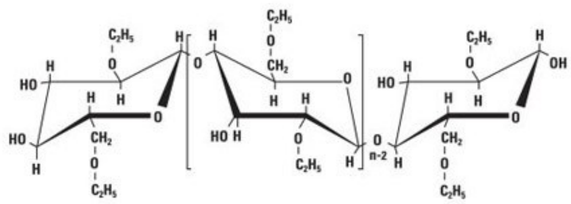

Figure 2. *Structure of ETHOCEL™ ethyl cellulose, from Dow Chemical*

The microcrystalline cellulose powder, Lattice NT100 was purchased from FMC BioPolymer. As for the ethyl cellulose, the cellulose powder is constituted of irregular grains and debris. The original size of these grains is between 50 and 150 µm. An electron-microscopy image of the cellulose powder is presented in Figure 3.

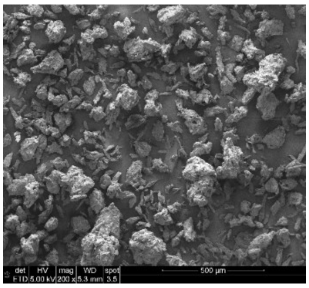

Figure 3. SEM *image of Lattice NT100*

The powder bed is constituted of a 50/50 blend of microcrystalline cellulose and ethyl cellulose. It was sieved at 50 µm. Isopropanol as solvent for the solvent jetting process was purchased from Carl Roth.

Binder jetting printer

A research and development binder jetting printer was especially developed for the project (Figure 4). The printer has a small build volume of 80x58x50mm. The architecture of the printer is modular and open. It gives the possibility of future improvements and an easy access to the printhead and powder trays.

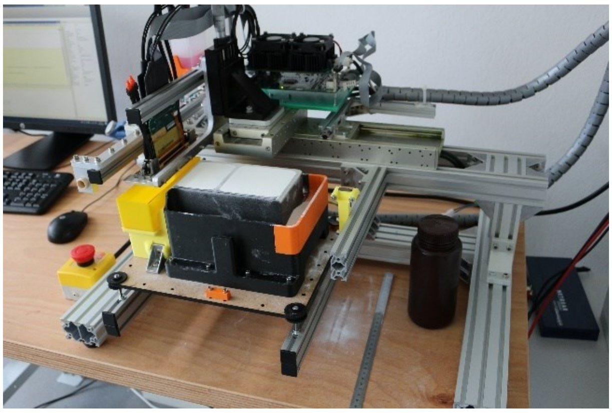

Figure 4. *Picture of the printer while printing*

The printer can be divided into different subassemblies. The two preponderant ones are the axis system supporting the printhead and the powder trays. The axis system, shown in Figure 5, is moving the printhead and the powder spreading system. It is constituted of two linear motors from Jenny Science.

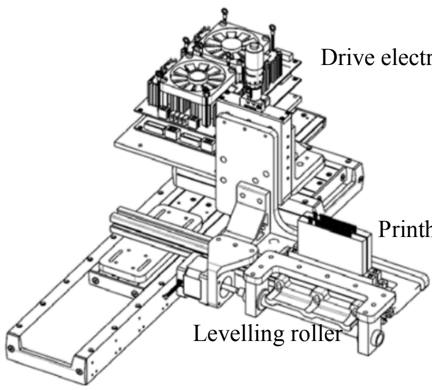

Figure 1. *Axis system constituted of two linear motors supporting the printhead, its drive electronics and the powder levelling system.*

The industrial printhead used for the solvent deposition is a Polaris PQ-512-35/AAA from Fujifilm-Dimatix. This printhead has a nominal drop size of 35 pL, 512 individually addressable nozzles with a native resolution of 200 dpi for a total print width of 64.9 mm. The drive electronics for the printhead were purchased from Global Inkjet Systems. The ink supply system was simple and consisted of a manual pressure regulation of the meniscus pressure and a single reservoir for the ink. For the printhead maintenance, a cleaning station with a wipe is mounted on one side of the x-axis. Purging and spitting, the other maintenance operations are done on top of a collecting tray.

The powder spreading system consists of a counter rotating levelling roller. A piece of felt pressing against the top of the roller was used to remove any powder sticking to it due to electrostatic charges. The roller was moved using a NEMA 13 stepper motor. The powder spreading system was fixed in front of the printhead. It was not in contact with the powder trays while the printhead is printing.

The printer has two moving powder trays, one feed tray and one for the build platform. All the powder trays (Figure 6) were 3D printed using an FDM 3D printer. They are clipped on a support plate. Like so they can be easily removed for cleaning. The support plate was connected to the chassis via a levelling system. The fresh powder was moved from the powder feed supply to the build platform by the levelling roller. The excessive powder was discharged on a collecting tray. Collecting trays were also present on the side of the two moving powder trays.

Figure 6. *Powder trays removed from their support, from left to right, collecting tray, build platform, feeding unit*

The printer was controlled through the MATLAB software. Scripts were written for the different printing operations.

Printing process

The process started with an STL file of the part to be printed. The STL was sliced into an image per layer in the Z direction. As an entry parameter, the printing resolution in X and Y was used to control the quantity of solvent that will be deposited on the powder bed per mm^2.

The image to be printed can be larger than the printhead width or the printing resolution can be higher than the native resolution of the printhead (200 dpi). In both cases, the image to be printed is sliced in the printing direction in different passes. For a graphical inkjet printer, this is the key difference between a single pass printer, usually fed by a continuous system and a scanning printer typically the large format printer. This step was done by the print engine of Global Inkjet System.

After homing all axis, the powder trays are filled. A thicker first layer of powder is levelled on the build platform.

The printing procedure started with a printhead maintenance cycle of purging and spitting. Purging is the action to push solvent through the nozzle plate with positive pressure while spitting is printing continuously at a high frequency. The goal of this procedure is to ensure that there will be solvent in the nozzle channels during printing. Without this step, the ink channels can be dry due to solvent evaporation. This maintenance step was repeated between each layer.

The printing step consisted in the back and forth movements of the printhead along the X axis until all swathes are done. The Y axis moves only in between the different passes to change the position of the printhead. The different passes were randomized to account for missing nozzles.

A printing strategy allows to define how the solvent is deposited. Deposition patterns are used for this purpose. In Figure7, an example of a simple deposition pattern is shown. The image pixels are divided into many subsets depending on the level of complexity of the pattern. Then each subset is printed individually. Patterns can be geometrical pattern or purely random. Deposition patterns were used to avoid drop coalescence before ink absorption. The use of deposition pattern increases the printing time.

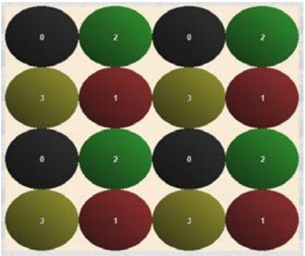

Figure 7. *Illustration of a deposition pattern, image pixels are divided in 4 subsets according to this pattern.*

After all layers have been printed, the powder trays are unmounted from the printer. The printed part is extracted from the powder bed of the build platform and cleaned with compressed air. Post processing by soaking in solvent or heat is done.

Experimental

The waveform created used the second acoustic optimum of the printhead to drive the printhead for depositing isopropanol. The drop formation was optimized using a drop watching station developed at the institute iPrint. The average measured drop volume was 22.67 pL for a drop speed of 4.3 $m \cdot s^{-1}$. The drops had a formation distance under 1 mm which is the printing distance. The waveform is not perfect as a small satellite that do not collide with the main drop was visible. A stitch image of a drop in flight is given in Figure 8.

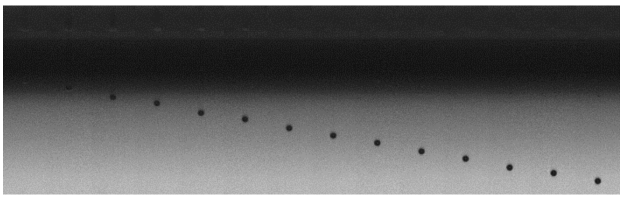

Figure 8. *Isopropanol drops generated with a Polaris 35 pL with the waveform used for the project*

Despite the low printing speed, the presence of a satellite is known to decrease the print quality. For printed parts, this results is the absence of sharp edges as shown in Figure 9.

Layer thicknesses above 200 µm were chosen. The precision of the moving powder trays was measured to be close to 50 µm. In addition, this dimension was equal to the maximum particle size after sieving. Smaller layer thicknesses than 100 µm leaded to the formation of aggregates during bed leveling.

For the printing tests, multiple printing resolutions and printing strategies were investigated. It was observed that for the

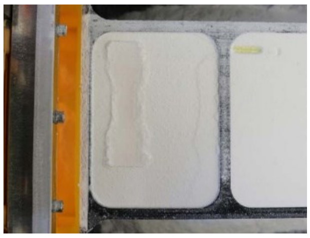

Figure 9. *Dog bone being printed, resolution of 2500 dpi in X and 600 dpi in Y, no deposition pattern, 10th layer*

same printing resolution, the parts printed without using a printing pattern presented more warping. Warping is normally due to internal stresses. It is supposed that drop coalescence increased the internal stresses appearing upon the evaporation of the solvent.

Delamination between the layers was noticed when the volume of solvent was too low as in Figure 10.

Figure 3. *Dog bone presenting delamination, resolution of 2500 dpi in X and 400 dpi in Y, layer thickness of 250 µm, deposition pattern x4*

An example of a part being successfully printed is presented in Figure 11.

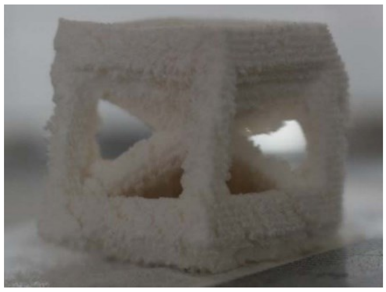

Figure 2. *Lattice cube, resolution of 2500 dpi in X and 600 dpi in Y, layer thickness of 0.25 mm, deposition pattern x4*

Conclusion

The results presented here are a first step in the development of an additive manufacturing process based on binder jetting to print wood derivatives. The printer built for this project allows to test various inks or powders. It is shown that the controlled deposition of isopropanol on a powder bed of a mixture of cellulose and ethyl cellulose can be used to produce 3D parts. The produced parts remained brittle and showed printing flaws. A potential application of this technology is the production of biodegradable implants.

References

[1] W. Xu, A. Pranovich, P. Uppstu, X. Wang, D. Kronlund, J. Hemming, H. Öblom, N. Moritz, M. Preis, N. Sandler, S. Willför, and C. Xu, "Novel biorenewable composite of wood polysaccharide and polylactic acid for three dimensional printing," *Carbohydr. Polym.*, vol. 187, pp. 51–58 (2018).

[2] X. Feng, Z. Yang, S. Chmely, Q. Wang, S. Wang, and Y. Xie, "Lignin-coated cellulose nanocrystal filled methacrylate composites prepared via 3D stereolithography printing: Mechanical reinforcement and thermal stabilization," *Carbohydr. Polym.*, vol. 169, pp. 272–281 (2017).

[3] S. Holland, T. Foster, W. MacNaughtan, and C. Tuck, "Design and characterisation of food grade powders and inks for microstructure control using 3D printing," *J. Food Eng.*, vol. 220, pp. 12–19, (2018)

[4] K. Jiang, Y. Guo, D. L. Bourell, W. Zeng, and Z. Li, "Study on Selective Laser Sintering of Eucalyptus/PES Blend and Investment Casting Technology," *Procedia CIRP*, vol. 6, pp. 510–514, (2013)

[5] W. A. Côté, "Chemical Composition of Wood," in *Principles of Wood Science and Technology*, Berlin, Heidelberg: Springer Berlin Heidelberg, , pp. 55–78 (1968).

[6] E. R. P. Keijsers, G. Yılmaz, and J. E. G. van Dam, "The cellulose resource matrix," *Carbohydr. Polym.*, vol. 93, no. 1, pp. 9–21 (2013)

[7] M. Norgren and H. Edlund, "Lignin: Recent advances and emerging applications," *Curr. Opin. Colloid Interface Sci.*, vol. 19, no. 5, pp. 409–416 (2014).

[8] D. Choe, Y. M. Kim, J. E. Nam, K. Nam, C. S. Shin, and Y. H. Roh, "Synthesis of high-strength microcrystalline cellulose hydrogel by viscosity adjustment," *Carbohydr. Polym.*, vol. 180, pp. 231–237 (2018).

[9] K. Rodríguez, J. Sundberg, P. Gatenholm, and S. Renneckar, "Electrospun nanofibrous cellulose scaffolds with controlled microarchitecture," *Carbohydr. Polym.*, vol. 100, pp. 143–149, (2014)

[10] T. Wüstenberg, *Cellulose and cellulose derivatives in the food industry : fundamentals and applications*. .

[11] T. L. Rogers and D. Wallick, "Reviewing the use of ethylcellulose, methylcellulose and hypromellose in microencapsulation. Part 1: materials used to formulate microcapsules," *Drug Dev. Ind. Pharm.*, vol. 38, no. 2, pp. 129–157 (2012)

[12] I. Gibson, D. W. Rosen, and B. Stucker, *Additive Manufacturing Technologies*. Boston, MA: Springer US (2010)

[13] Y. Bai, G. Wagner, and C. B. Williams, "Effect of Particle Size Distribution on Powder Packing and Sintering in Binder Jetting Additive Manufacturing of Metals," *J. Manuf. Sci. Eng.*, vol. 139, no. 8, p. 081019 (2017).

Author Biography

Mathieu Soutrenon is an engineer from IMT Mines Alès (2008). He did a PhD. in materials science at EPFL (2013) on composite materials for the European Space Agency. After his graduation, he worked in startups developing medical devices, heart implants then injectors. He joined iPrint to work on 3D printing. His areas of expertise are additive manufacturing of polymers and rheology

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