ADDITIVE MANUFACTURING OF REGENERATED CELLULOSE (LYOCELL)

I.T. Garces[1,2], J. Goncalves[1,2], T.D. Ngo[3,4] , Y. Boluk[4] ,and C. Ayranci[1*]

[1] Mechanical Engineering, University of Alberta, Edmonton, Canada,[2] Mechanical and Aerospace Engineering, Carleton University, Ottawa, Canada,[3] Innotech Alberta, Edmonton, Canada, [4] Civil Engineering, University of Alberta, Edmonton, Canada
* Corresponding author (cayranci@ualberta.ca)

Keywords: *biomaterials, 3D printing, Lyocell, sustainable*

ABSTRACT

The 3D printing industry has shown concern about the environment, leading to a search for biodegradable and eco-friendly alternatives. Cellulose, the most abundant biodegradable polymer on earth, has become a focus of attention. Cellulosic pulp obtained from biomass can be dissolved in environmentally friendly solvents, such as N-methylmorpholine-N-oxide (NMMO), to create regenerated cellulose (Lyocell^{TM}). This material has been used in the textile industry for the past ten years. Lyocell offers the potential to produce high-quality cellulosic materials that are easily customizable and manufactured. We propose a detailed study of the use of Lyocell in 3D printing using an affordable desktop 3D printer modification. The 3D printing process for Lyocell is entirely circular because the solvent can be reclaimed from the printed parts, and the parts themselves are fully biodegradable. Further, lyocell dope can be easily customized and modified to produce multi-functional parts, such as magnetic, antibacterial, or moisturizing properties. This work describes the equipment developed, cellulosic dope preparation, dope manufacturing into parts, the extrusion process, and 3D printing.

1 INTRODUCTION

Considerable progress has been made in commercial desktop 3D printing of synthetic polymers in recent years, but this has also raised concerns about the environmental impact of conventional plastic materials. This has started to motivate researchers and engineers to look at alternative printing materials that are environmentally friendly. Cellulose is the most abundant polymer on the planet; however, processing difficulties to manufacture with this material limits its use for various applications. A solution that has been proposed, is the use of regenerated cellulose, which is a class of material obtained by the conversion of natural cellulose to a soluble cellulosic derivative (dope). A coagulation process then transforms the cellulosic dope into regenerated cellulose, and the solvent is recovered for reuse [1]. During the generation process, the dope can be transformed into a variety of useful materials, such as fibres and films. This process is commonly used in the textile industry for the manufacturing of regenerated fibres, for example rayon and viscose[2] . A similar process is used for the manufacturing of Lyocell, that is the focus of this study. During the processing of Lyocell the solvent N-methylmorpholine-N-oxide (NMMO)[3] is used to dissolve the cellulosic dope, converting it into an eco-friendlier solution to the mentioned alternatives since more than 99.5% of NMMO can be recovered after fibre regeneration[3], it is less harmful to the environment that other solvents used in the regeneration of cellulose. The schematic in Figure 1 represents the cyclic life of Lyocell, from the extraction of the cellulose source to the fibre regeneration, transformation into consumer products and their biodegradability.

Figure 1: Circular process for Lyocell

The dope produced in the Lyocell production can be malleable and easily melted and re-melted hence able to be used in a 3D printing process. Information about 3D printing with Lyocell is extremely limited in the literature [4], and this study is a first step in closing this gap. There are multiple challenges to produce and control the 3D printing parameters for Lyocell. Consequently, in this work, we explore the preparation of the dope material for the printing, the rheological characterization of the dope, feasibility printing and its challenges. Further, Lyocell dope can be used as a matrix for composites, particularly to also create biodegradable multi-functional parts. As such, this work is therefore, the first step geared towards printable magnetic regenerated cellulose parts.

2 MATERIALS AND METHODS

2.1 Dope Preparation

The cellulose used was Neucel V93 dissolving pulp grade bleached sulfite softwood. The pulp was dried at 60°C for 24 hours. The NMMO was added in 50% aqueous solution and antioxidant n-propyl gallate were obtained from Sigma Aldrich. The cellulose was ground and chopped into squares before being blended. Batches with 24g of pulp were manufactured at a time using a Huber brand reactor and a Caframo mixer. The NMMO solution was mixed with the thermal stabilizer n-propyl gallate and then with the pulp inside the reaction vessel. The dope was mixed at a rate of 150 rpm and changed according to the time and viscosity reached. The reaction took a total of 53 minutes, and the dope was collected immediately from the vessel and stored for further use. The resulting solution had a transparent deep caramel-yellowish colour, which indicates a complete reaction.

2.2 Rheology

Rheological measurements were conducted using an AR-G2 rheometer to perform steady shear mode tests. Test samples were prepared by cold pressing the dope into 1mm thickness moulds and punching 1-inch disk. samples. Tests were conducted with a gap of 1 mm using a 25mm parallel plate.

2.3 3D printing

The Creality CR-10 printer was modified in-house to enable 3D printing of cellulose-NMMO (dope) samples using a piston-driven system, as portrayed by the picture shown in Figure 2. A stainless-steel syringe with chemical-resistant O-rings and a lead screw plunger was used to push the dope at controlled speeds. A calibrated force-sensing resistor was placed on top of the plunger to detect clogging during extrusion. The dope was loaded into cartridges and inserted into the piston carefully to prevent bubble formation. The extrusion flow rate, head pressure, and the diameter of the extrudate at the nozzle tip were measured during extrusion. Samples were 3D printed at 0 and 90° degrees and tested for layer bonding strength. Once printed, samples were immersed in a water bath to remove NMMO and regenerate the cellulose.

Samples were 3D printed with a 0.6mm nozzle and tested for layer bonding strength in both vertical and horizontal orientations. After printing, samples were immersed in distilled water to remove the solvent. Samples were kept immersed in water until their mechanical properties were tested. The printing temperatures were 90 and 130°C at a controlled flow of 0.22g/min. The G-code flow was tested for good bonding, and the adhesion properties were examined under the microscope.

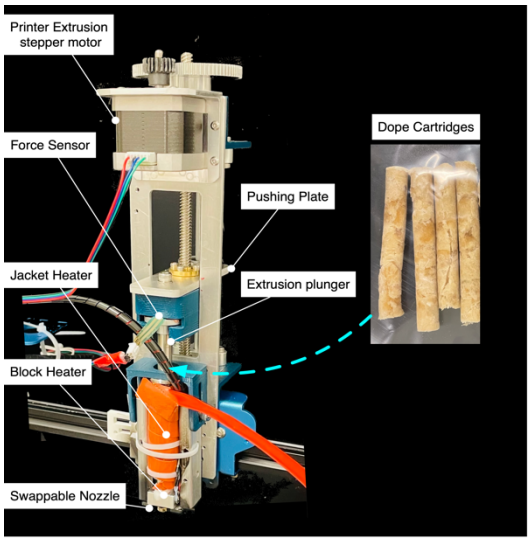


Figure 2: Picture of the 3D printing head prototype for Lyocell

2.4 Mechanical testing of a single printed layer

Layer bonding strength was tested by printing samples with respect to the vertical axis at 0 and 90° degrees. Vertical samples (those printed at 0°) were designed in size to 10x60 mm^2 and horizontal samples, 20x120 mm^2. Horizontal samples (those printed at 90°) were designed to have a larger horizontal surface for mechanical testing purposes. Mechanical Testing was performed in an Instron tensile testing machine equipped with a pneumatic gripper. A load cell of 5N was used for samples that were very weak and a 50N load cell for all the rest. Samples were tested at a strain rate of 0.1mm/min with five repetitions. Samples were placed in between paper windows to allow for easy placement in between grips. A rupture at the middle of the samples was consistently verified.

As reference for the obtained mechanical strength, each sample was patted dried and weighed on a high-precision scale before mechanical testing.

2.5 Sample regeneration and freeze drying

Sample cellulose regeneration is carried out at room temperature on distilled water. Samples were left in a water solution for over 24 hours to ensure complete solvent release. A freeze-drying procedure at -80°C was briefly looked at as a technique to achieve shape fixing of the samples.

4 RESULTS

4.1 Dope Preparation

The preparation of the Lyocell dope is rather a difficult and complex chemical process, which involves the degradation of the NMMO with the cellulose pulp and the interaction with the other substances, such as the added stabilizer (Propyl Gallate) and the transition metals in the cellulose dope [5]. NMMO disrupts the hydrogen-bond network of the cellulose and forms new hydrogen bonds between the macromolecules and the solvent. Dope preparation works best at approximately 0.7 NMMO to 0.2 cellulose to 0.1 water ratios[6]. To accomplish this ratio at higher volumes requires a finetuning of the evaporation process and the mixing speeds. A standardized process was accomplished to obtain a see-through dope. Changes in the dope during the reaction from opaque to glossy can be observed in

Figure 3.

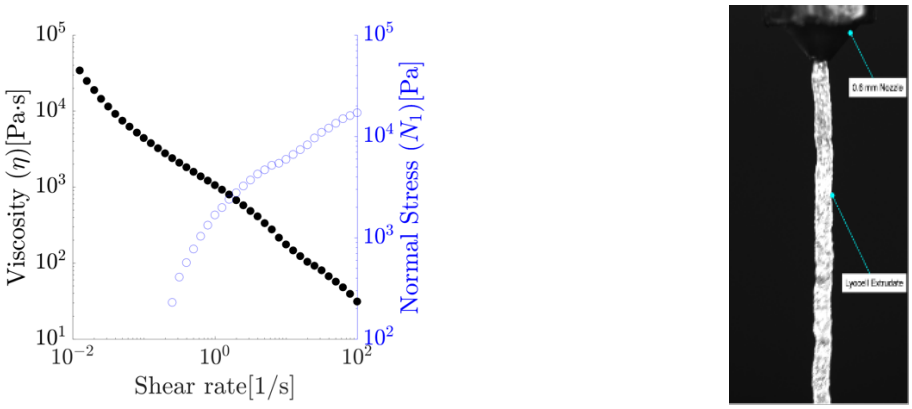
Figure 3: Consistency and reaction of the dope.

4.2 Rheology

During the printing process the dope is forced through the nozzle under an applied stress. The rheology properties of the dope are of immense importance as they determine the behaviour during extrusion, swelling after extrusion and the deposition of the material. The main goal of this test was to determine a preliminary printing temperature to and understand the printability of the material. The first aspect of determining printability was to determine if the viscosity was within the limits for our equipment to be able to apply a force for extrusion to occur. The second is, whether there is a good shape fidelity post extrusion.

On Figure 3a. we can see a nonlinear plastic behaviour with respect to shear rate, having a much higher viscosity at rest than during the extrusion process. This is caused by the change in arrangement of the molecules from a disordered state at rest to an ordered flow state. A shear thinning behaviour is desired during the printing process as it implies a decrease in applied force during the printing process.

To determine post extrusion shape fidelity, a qualitative analysis was performed as seen in the image on Figure 3.b, where the extrusion process of the Lyocell is shown including the swelling post extrusion. This particularly is important for the printing process as it determines the printing parameters. As expected, we found that an increase in nozzle diameter translates into lower dope swelling, where a smaller diameter means higher swelling values. A middle ground with a nozzle of 0.6mm was chosen as to control the swelling during the printing process. The shape fidelity post extrusion is an aspect that must be fine-tuned when using Lyocell. Although the shape of the filament was maintained, an uneven surface was observed during the extrusion process which can translate to a rough printing surface.

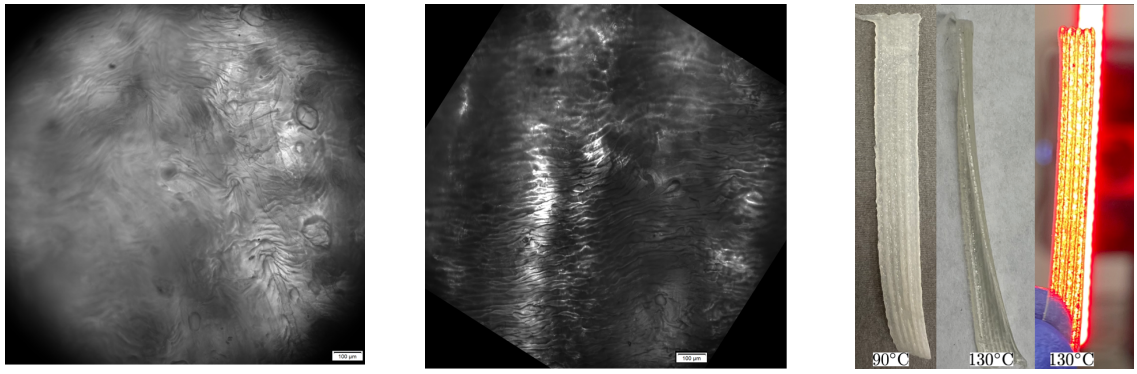


(a) (b)

Figure 3: (a) Rheology values at 90°C and (b) the extruded dope using a 0.6mm Nozzle

5 MECHANICAL TESTING AND LAYER BONDING

Micrographic pictures of samples are shown in Figure 4, where (a) is the micrograph of samples printed at 90°C and (b) at 130°C. A complete bonding and lack of holes in the structure was confirmed with the micrographs. At first glance, we could see a homogenous printed material at higher temperature. Further, a curious effect that occurred when increasing the printing temperature is the increase in transparency as can be observed in Figure 4 (c), which suggests a complete reaction of the solvent on the cellulose fibers post 3D printing.

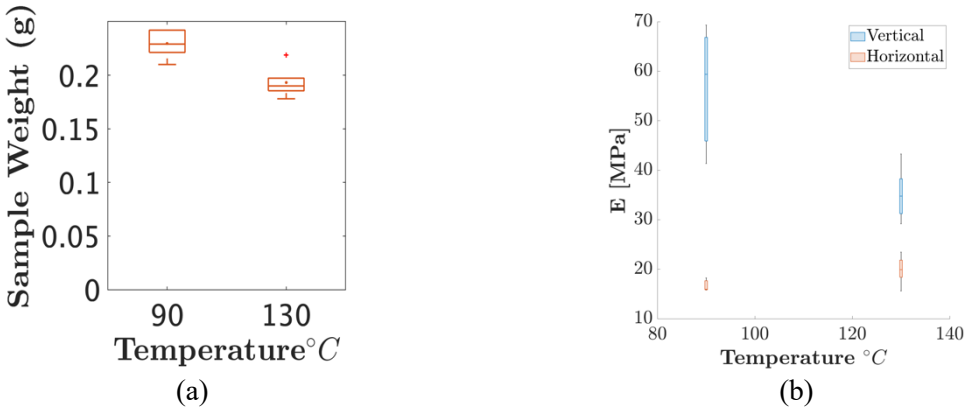


(a) (b) (c)

Figure 4: (a) Micrograph of Lyocell printed sample at 90°C and (b) Micrograph of sample printed at 130°C, both at 0.22g/min (c) Picture depicting opacity of samples

The weight of samples decreased slightly at an increased temperature. This is correlated to the increased viscosity observed at high temperatures. Evaporation when printing at higher temperatures also directly contributed to the change in viscosity. The difference is only slightly statistically significant as there was an outlier within the sample weight range of 90°C.

Elastic properties of the printed samples were significantly less when printed in the vertical direction at higher temperatures. The authors believe this is attributed to the remainder fibers in the dope observed by an incomplete reaction. The horizontal layer bonding, however, was much better when printed at higher temperatures, which correlated to a better dope bonding during printing.



(a) (b)

Figure 5: (a) Sample weights at different temperatures for vertical samples (b) Elastic modulus obtained from vertical and horizontal samples at 90°C and 130°C

Functionally, the 3D printed parts can benefit from an incomplete reaction favoring embedded small fibers within the printed batch, but poor layer bonding can potentially hurt different printing angle orientations and multi-layer printing.

5 PRINTING CAPABILITY AND REGENERATION

Different types of parts specifically with the aim for tissue templates were investigated including honeycomb printed structures as observed on Figure 6 a-c and grid like structures as observed in Figure d-f. The following pictures were not taken at scale, and this is a mere proof of concept of the 3D printed part structures. An observation being investigated is the large shrinkage after cellulose regeneration and the post-shaped deformation after freeze drying.

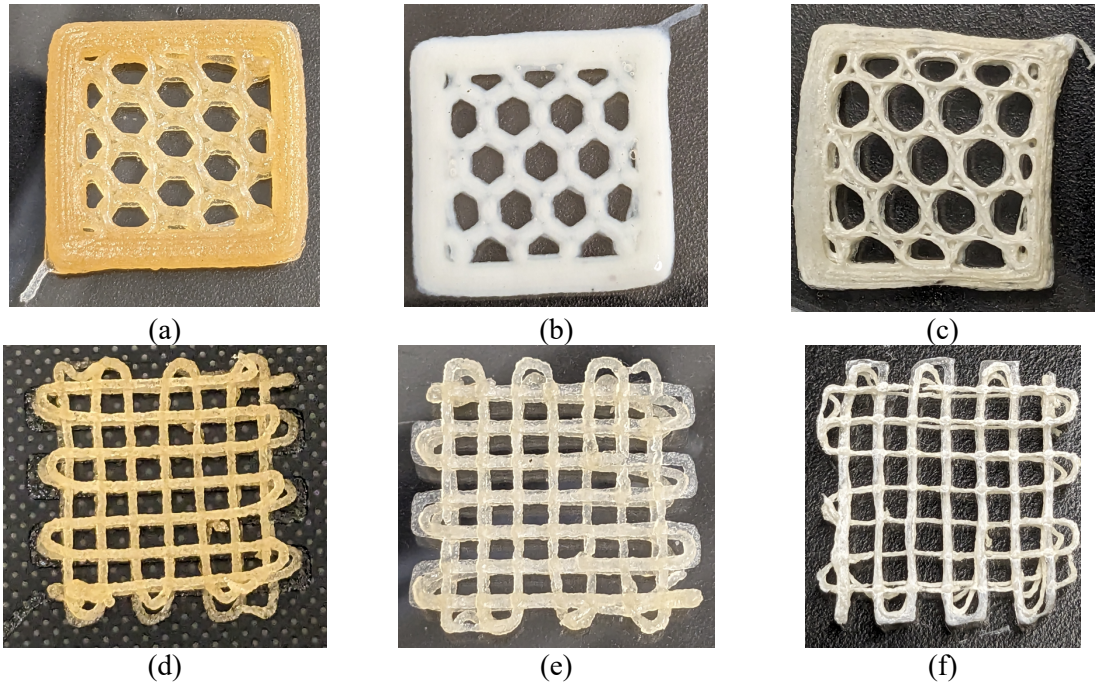


Figure 6: (a) Honeycomb 3D printed sample (b) Honeycomb sample after regeneration, (c) Honeycomb sample after freeze drying, (d) Grid 3D printed sample, (e) Grid sample after regeneration and (f) Grid sample after freeze drying.

6 CONCLUSIONS AND FUTURE WORK

This work is still on-going, and this is the beginning of very thorough research on the applications of 3D printable Lyocell. We have looked at a preliminary work on the methodology for manufacturing 3D printed Lyocell, including the dope synthesis, equipment manufacturing, 3D printing of Lyocell dope and a characterization of the printed parts after regeneration. This paper briefly covers some of these aspects as it is part of a larger on-going investigation on affordable eco-friendly 3D printed cellulosic parts.

Lyocell 3D printing has great potential as an eco-friendly and sustainable manufacturing method. However, there are still many challenges to overcome to be able to print larger structures and reliable geometries. Adding particles to the dope may be a solution to improve the material's thermal conductivity, strength, and shape retention properties. Future research will also focus on the rheological properties of the material to improve material bonding and polymer chain diffusion, ultimately leading to higher geometric fidelity and material properties in 3D printed parts.

Moreover, because of the flexibility and consistency of the dope, we envision being able to change the dope properties by particle and additive addition, to not only improve the shape fidelity of the 3D printed

parts and dope properties but also to obtain multifunctional properties such as magnetic cellulosic parts. Overall, lyocell 3d printing is an exciting area of research that could revolutionize the field of sustainable manufacturing.

ACKNOWLEDGEMENTS

This work was funded by Innotech Alberta and MITACS Elevate. We would additionally like to thank Mr. Juan Segura and Mr. Marco Paez for their support during the project.

REFERENCES

[1] A. Sharma, S. Nagarkar, S. Thakre, and G. Kumaraswamy, "Structure–property relations in regenerated cellulose fibers: comparison of fibers manufactured using viscose and lyocell processes," *Cellulose*, 2019, doi: 10.1007/s10570-019-02352-w.

[2] T. Rosenau, A. Potthast, H. Sixta, and P. Kosma, "The chemistry of side reactions and byproduct formation in the system NMMO/cellulose (Lyocell process)," *Progress in Polymer Science (Oxford)*, vol. 26, no. 9, pp. 1763–1837, 2001, doi: 10.1016/S0079-6700(01)00023-5.

[3] H.-P. Fink, P. Weigel, H. J. Purz, and J. Ganster, "Structure formation of regenerated cellulose materials from NMMO-solutions," *Progress in Polymer Science (Oxford)*, vol. 26, no. 9, pp. 1473–1524, 2001, doi: 10.1016/S0079-6700(01)00025-9.

[4] L. Li, Y. Zhu, and J. Yang, "3D bioprinting of cellulose with controlled porous structures from NMMO," *Mater Lett*, vol. 210, pp. 136–138, 2018, doi: 10.1016/j.matlet.2017.09.015.

[5] T. Rosenau, A. Potthast, H. Sixta, and P. Kosma, "The chemistry of side reactions and byproduct formation in the system NMMO/cellulose (Lyocell process)," *Progress in Polymer Science (Oxford)*, vol. 26, no. 9, pp. 1763–1837, 2001, doi: 10.1016/S0079-6700(01)00023-5.

[6] J. Eckelt, T. Eich, T. Röder, H. Rüf, H. Sixta, and B. A. Wolf, "Phase diagram of the ternary system NMMO/water/cellulose," *Cellulose*, vol. 16, no. 3, pp. 373–379, 2009, doi: 10.1007/s10570-009-9276-2.