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REVIEW PAPER

3D printing with cellulose materials

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Abstract With the development of cellulose chemistry and processing technology, the applications of cellulose materials were not limited to traditional fields as engineering materials in forest originated products, paper, and textile industries, but also used for advanced functional applications in the field of biomedical and smart health care, printed electronics, and responsive wearable textiles. With the advantage of sophisticated geometry fabrication and low cost production, 3D printing technologies have been employed with many materials for a variety of applications. This critical review focuses specifically on the development and assessment of cellulose materials for 3D printing. A special focus was paid on extrusion based 3D printing. Detailed examinations of cellulose hydrogel rheology, fiber entanglement, fiber alignment, gelation, printability, shape fidelity, cell viability and processing parameters in extrusion based 3D printing are explored. Other 3D printing techniques such as inkjet 3D printing, 3D spinning, stereolithography, laminated object manufacturing and selective laser sintering are also introduced. The functionality of 3D printed constructs was designed either by cellulose surface modification or by incorporation of functional components. The properties and performances of 3D printed cellulose constructs as well as their potential applications in the fields of medical, electronics, and smart textile are discussed. Finally, perspective and current important limitations of 3D printing with cellulose materials for advanced application are provided.

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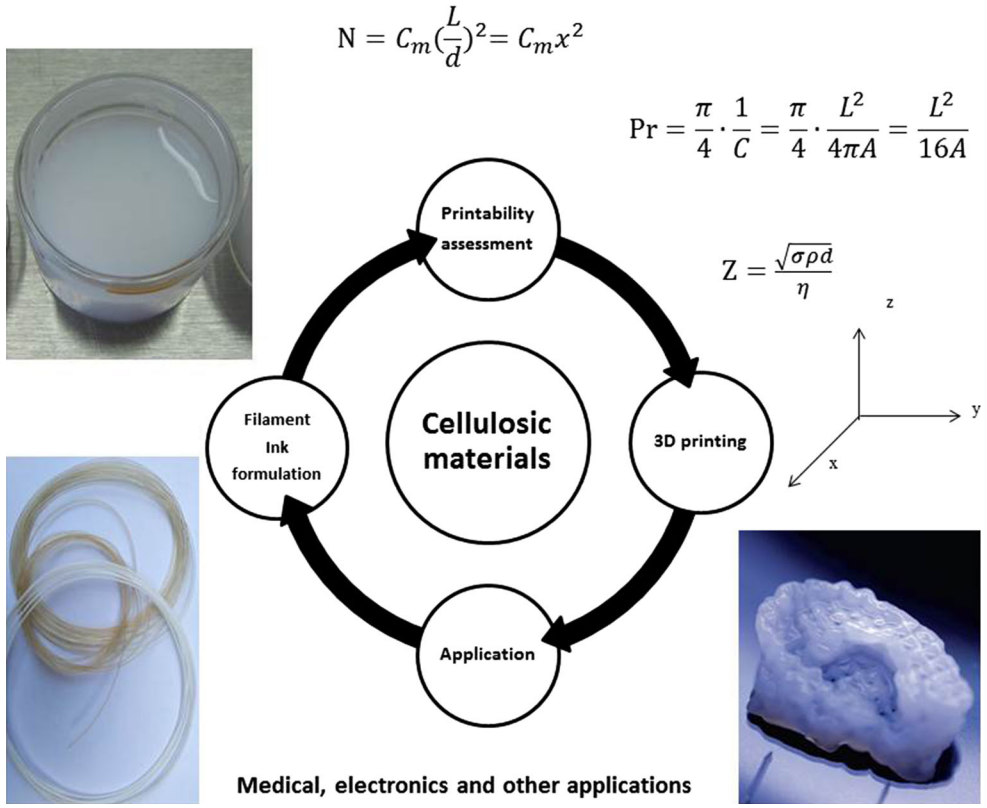
Graphical Abstract



Keywords Additive manufacturing · Cellulose materials · Rheology · Printability · Shape fidelity

Introduction

3D printing, also known as additive manufacturing is an emerging technology and has drawn great attention in recent years. 3D printing is a process of fabricating products with raw material directly from a 3D digital model in a layer by layer manner (Gibson et al. 2015). It was first commercialized by 3D-Systems in 1987 and is nowadays widely used not only for models and prototypes but also for end use products. 3D printing offers great benefits in fabrication of objects, including less material, customized geometry, and cost effective. A wide variety of applications for 3D printing with different materials were developed.

The most commonly used materials in 3D printing are polymers, composites, metals, ceramic, sand and wax (Jungst et al. 2016; Kalsoom et al. 2016; Kirchmajer et al. 2015; Ligon et al. 2017; Wang et al. 2017b). Up-to-date databases of 3D printing materials have been developed by Senvol and Imprimalia 3D, which is freely available online (for detail, see URL http://senvol.com/database/; http://www.3dprintingdatabase.org/en). General information about the 3D printing materials and applicable 3D printers are provided. It was reported that polymers such as polylactic acid (PLA), acrylonitrile butadiene styrene (ABS) and nylon, the most commonly used 3D printing material could induce potentially hazardous incidents. Volatile organic compounds and ultrafine aerosol that might be harmful to humans are detected in 3D printing processes. 3D printed objects with such polymers are measurably toxic to zebrafish embryos, a model organism widely used in biological research (Oskui et al. 2015). Designing and manufacturing low-emitting and less toxic 3D printing materials are imminent. In order to reduce the related safety risks and unpleasant smells with synthetic polymers,

manufacturers and end-use customers are inclined towards using natural polymers, which is renewable and biodegradable (Rejeski et al. 2018). A lot of attentions have been paid to develop printable biopolymer composites with improved performance. Natural polymer hydrogels such as collagen, alginate, chitosan and hyaluronic acid have been used to prepare scaffolds by 3D printing and showed great potential in the promising new fields of tissue engineering and regenerative medicine (Chimene et al. 2016; Jungst et al. 2016; Shen et al. 2016). 3D printing of cellulosic materials presents an opportunity to fabricate 3D objects from a cheap and sustainable source.

Cellulose, the main structural component of plant cell wall, is the most abundant renewable biopolymer. Highly ordered cellulose chains form cellulose nanocrystaline. Cellulose nanocrystaline together with disordered cellulose embedded in a multi-component matrix composed of hemicelluloses, lignin, and a small amount of pectin, forming a hierarchical structure. The structural organization and interfacial interaction of cell wall components on different level strongly affect the mechanical performance of cell walls. The hierarchical structure and complex composition of cell walls offer a favorable basis in design and fabrication with materials having superior properties. 3D printing technologies could offer new ways to design and manufacture fascinating materials by mimicking the structure and component properties of cell walls (Studart 2016). Cellulose materials in the form of lignocellulose, bleached pulp, dissolving pulp are adequately available in the market. With decades of research and exploration, micro-/nano-sized cellulose such as microcrystalline cellulose (MCC), cellulose nanofibrils (CNF), cellulose nanocrystalline (CNC) and bacterial cellulose (BC) with tailor made properties could be isolated (Habibi et al. 2010; Isogai and Bergström 2018; Moon et al. 2011). Green and sustainable liberations of CNF by TEMPO oxidation were extensively studied (Isogai and Bergström 2018; Isogai et al. 2011; Saito et al. 2007). Tailored productions of CNC with CNF by recyclable dicarboxylic acids were demonstrated (Jia et al. 2017b; Wang et al. 2017a). We also did some work in this area (Wang et al. 2012a, b, 2013, 2014a, b, 2016; Chen et al. 2015; Wang and Zhu 2015, 2016). Nowadays, pilot plant facilities made large-scale production of cellulose nanoparticles available.

Cellulose materials without chemical modification are generally considered infeasible for extrusion or sintering based 3D printing since cellulose materials thermally decompose before they can melt and become flowable when heated. On the other hand, nanocellulose hydrogels showing a shear-thinning behavior might be considered as extrudable precursors for 3D printing. The new era driven by 3D printing with cellulose materials to replace fossil based plastic materials might be come. Here in this paper, recent developments in 3D printing with cellulose materials are reviewed. First, a brief introduction to 3D printing technologies and cellulose materials was provided. Next, the improvement and diversification of properties of 3D printed cellulose composites via the different techniques are investigated. In particular, progresses done in last 5 years are emphasized. The applications of 3D printed cellulose composites in biomedical, electronics and textiles are then explored. Finally, limitations of current 3D printing technologies and future direction are provided.

3D printing technology

The printing technology of 3D printer is the key part of the whole 3D printing process, playing a vital role in connecting digital 3D models, 3D printing materials, and final applications. Efforts must be made to meet the technical challenges in material development and process control (Oropallo and Piegl 2015). According to the ways how the layers deposited to create parts and the materials that are used, 3D printer can be classified into different categories. In this article, 3D printing systems with cellulose materials are generally divided into three categories (although there may be many more, more close attention was paid to those three): (1) extrusion based 3D printing systems, including fused deposition modeling (FDM) process, direct ink writing (DIW), and microextrusion 3D bioprinting; (2) Inkjet 3D printing, and (3) 3D spinning. Some conceptual knowledge about laminated object manufacturing (LOM) and selective laser sintering is provided. Typical cellulosic material reinforced plastic filaments for FDM are listed in Table 1; while extrusion based 3D printing techniques of cellulose material based inks are summarized in Table 2.

Table 1 Typical cellulosic material reinforced plastic filaments for FDM

Materials (cellulose material content, %)	Filament processing method	Filament diameter (mm)	FDM printer	Nozzle size (mm)	Printing temperature	Potential application	References
Wood flour/PLA (5%)	Extrusion	1.75	Self-assembled FDM 3D printer	0.4	210	Functional, load-bearing applications	Tao et al. (2017)
Micro-nanocellulose/PLA (0–30%)	A twin-screw extruder	1.75	Z603S, Jgaurora Ltd	0.4	190	Structure materials	Wang et al. (2017c)
ColorFabb recycled wood flour/PLA (15%)	–	2.85	Prusa i3 rework 3D printerwas	0.3	210	4D printing actuation functionality	Le Duigou et al. (2016)
Cellulose fiber/PLA (0–20%)	2-step extrude	2.85	Lulzbot TAZ 5 3D printer	–	210	automotive industry	Kearns (2017)
Cellulose nanocrystals/polyvinyl alcohol (2–10%)	A single screw extruder	1.7	Sharebot Next Generation 3D printer	0.35	–	improve the performance of PVOH	Rigotti et al. (2017)
Hydroxypropyl cellulose/Domperidone (80–90%)	A twin-screw extruder	1.75	Replicator 2X	0.2	210	Drug delivery	Chai et al. (2017)
Cellulose nanocrystal/poly(ε-caprolactone) (0–10%)	A twin screw extruder	3	Thing-O-Matic 3D printer	0.3	185	Bone tissue engineering	Hong (2015)
Cocoa shell waste/poly(ε-caprolactone) (0–50%)	A single-screw extruder	1.75	Prusa i3 Hephestos 3D printer	0.3	120	Household and biomedical application	Tran et al. (2017)

Extrusion based 3D printing

Extrusion based 3D printing is one of the most widely used processes in which extrudable material is selectively dispensed through a nozzle and deposited in a layer-by-layer manner. Before the deposition of the second layer, the first layer needs to maintain its structural fidelity. Fused deposition modeling (FDM) process (Fig. 1a), direct ink writing (DIW), and microextrusion 3D bioprinting (Fig. 1b), belong to the material extrusion category. Because of the great availability of materials, extrusion based 3D printing is currently the most widely-used techniques (Chung et al. 2013; Kirchmajer et al. 2015). Cellulose materials including lignocellulosic material, cellulose derivative, and cellulose nanoparticles were reported being used as materials for extrusion-based 3D printing. Production of filaments with smaller diameter by extrusion based 3D printing is still challenging due to die swell that occurs when viscous liquefied materials are extruded a through a small diameter nozzle (Hochleitner et al. 2015). The extrudability or printability of cellulose based materials in 3D printing are vital for quality of 3D printed constructs.

Stereolithography printing

Stereolithography, a vat photopolymerization process that liquid photopolymer is selectively cured by light-activated polymerization, remains one of the most applicable and most powerful 3D printing technologies. Figure 2 shows a stereolithography printing apparatus. Due to the high resolution of light source, it has higher manufacturing accuracy, which gives smaller layer thickness, higher detail information, and better surface quality. An increasing number of liquid photopolymers are developed and employed to stereolithography for different applications. It was reported that cellulose nanocrystals were added to optically curable resins to reinforce the mechanical properties.

Table 2 3D printing of cellulose material based inks

3D printing technique	Cellulose material based ink formulation (component content or ratio)	Printer	Fabrication parameter	Gelation/solidification method	Potential application	References
Micro-extrusion printing	NFC/alginate/water (1–2%)/(0–1%)	3D discovery	Nozzle diameter 150-420 μm Pressure 6–60 kPa Speed 10–20 mm/s	$CaCl_2$ cross-linking	Tissue engineering	Ávila et al. (2016), Håkansson et al. (2016b), Henriksson et al. (2017), Müller et al. (2017), Markstedt et al. (2015), (2017), Nguyen et al. (2017)
	Methylcellulose/ alginate/H_2O (0–9%)/ (0–3%)	Biofactory bioprinter	Nozzle diameter 0.21–0.25 mm	Crosslinking	Tissue engineering	Li et al. (2017a)
	Methylcellulose/ alginate 9%/3%	Bioscaffolder 2.1	Nozzle diameter 250 μm	$CaCl_2$ cross-linking	Tissue engineering	Schutz et al. (2017)
	Nanocellulose 3.9%	3D bioplotter		$CaCl_2$ cross-linking freeze dry	Wound dressing	Rees et al. (2015)
	Nanocellulose/alginate/ glycerin (0.75–1.3%)/ (0–4.5%)/(0–50%)	Custom-built dispensing system	Nozzle diameter 150–410 μm, speed 2 mm/s	$CaCl_2$ cross-linking	Biomedical application sensors	Leppiniemi et al. (2017)
	Cellulose/ionic liquid < 10%	Customized makerbot 3D printer	Nozzle diameter 200–410 μm	Regenerated and freeze dry		Markstedt et al. (2014)
	CNF 1%	Custom built extruder	Nozzle diameter 2/4 mm, speed 0.5 cm/ s	Dry	Cell constructs	Torres-Rendon et al. (2016)
	CNC 0.5% CNF/CNT 1%/1%	F4200n robot	Nozzle diameter150–300 μm, presure 50 psi, speed 5–10 mm/s	Freeze dry/ethanol	Flexible electronic devices	Jia et al. (2017a), Li et al. (2017c)
	MFC/lignosulfonate\ (0.5–2%)/(20–50%)	Seraph robotics model 3	Nozzle diameter 960 μm, speed of 35 mm/s	Dry	Energy storage	Shao et al. (2015)
	CMC/silver nanowire 20%/1.9%	Delta FDM 3D printer	Nozzle diameter 840 μm speed 0.7 mm/s	Dry	Electronics	Park et al. (2017)
	CNC 0.5–40% CNC/2-hydroxyethyl methacrylate (CNC10% or 20%)	Abl 900010	Nozzle diameter 200–410 μm, pressure 2–4 bar, speed 10–20 mm/s	Cured with UV	Building blocks	Siqueira et al. (2017)

Table 2 continued

3D printing technique	Cellulose material based ink formulation (component content or ratio)	Printer	Fabrication parameter	Gelation/solidification method	Potential application	References
	Cellulose acetate 25–35%	Printrbot simple metal	Nozzle diameter 200 μm	Solvent evaporation	Antimicrobial materials	Pattinson and Hart (2017)
	NFC/clay/monomer 0.73%/9.7%/7.8%	ABG 10000, Aerotech	Nozzle diameter 150–1500 μm	UV cure	4D printing	Gladman et al. (2016)
	CNC/Kymene (10–20% CNC) CNC/kymene (2.8%/0.06)	Custom build diw printer	Nozzle diameter 200–500 μm	Freeze dry	Tissue scaffold drug delivery	Li et al. (2017b, 2018b)
	Cellulose acetate/acetic acid (30/70)	3DN-300	Nozzle diameter 0.84 mm, speed 5 mm/s, pressure 20–41 psi for	Solvent evaporation/antisolvent	Textiles	Tenhunen et al. (2018)
	Acetoxypropyl cellulose/acetone (80/20)					
	Cellulose cotton linters/[Emim]OAC (10/90)					
Inkjet 3D printing	Cellulose/ionic liquid 2–4.8%	Dimatix, Dmp-2831 printer	Temperature 55 °C droplet spacing 150 μm	Oven dry	Biomedical applications	Gunasekera et al. (2016)
	CNFs/glycerol 1%/0.1%	Custom-made Urtidium B200			Electronic textiles	Nechyporchuk et al. (2017)
Stereolithography printing	CNC/PEGDA 0–1.2%	Formlabs	Wavelength 405 nm, 250 mw, spot size 140 μm	UV cure	Medical industry	Palaganas et al. (2017)
	CNC/resins mixture 0.5–5%	3D systems VIPER si2 multimaterial machine	Wave leght 355 nm 100 mW	UV cure	Manufacture application	Kumar et al. (2012)
3D spinning	Cellulose acetate/(DMAC/DMSO) 20%(55/45)	Custom made set-ups		Freeze dry	Tissue engineering	Atila et al. (2015)

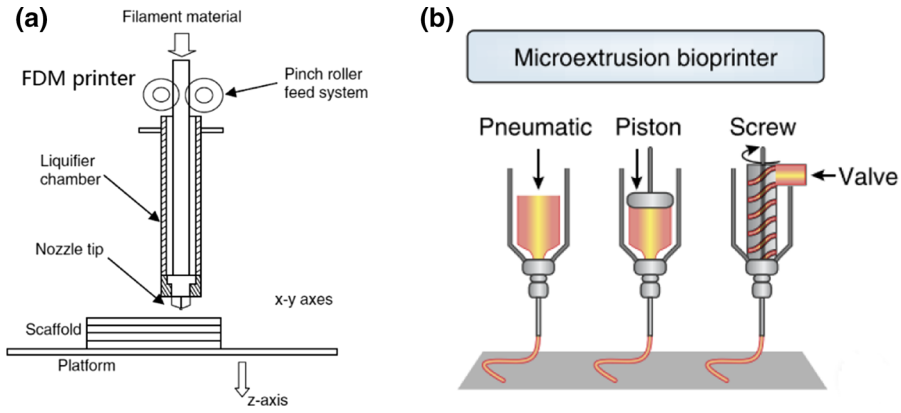


Fig. 1 Extrusion based 3D printer. Reprinted with permission from Gibson et al. (2015), Murphy and Atala (2014)

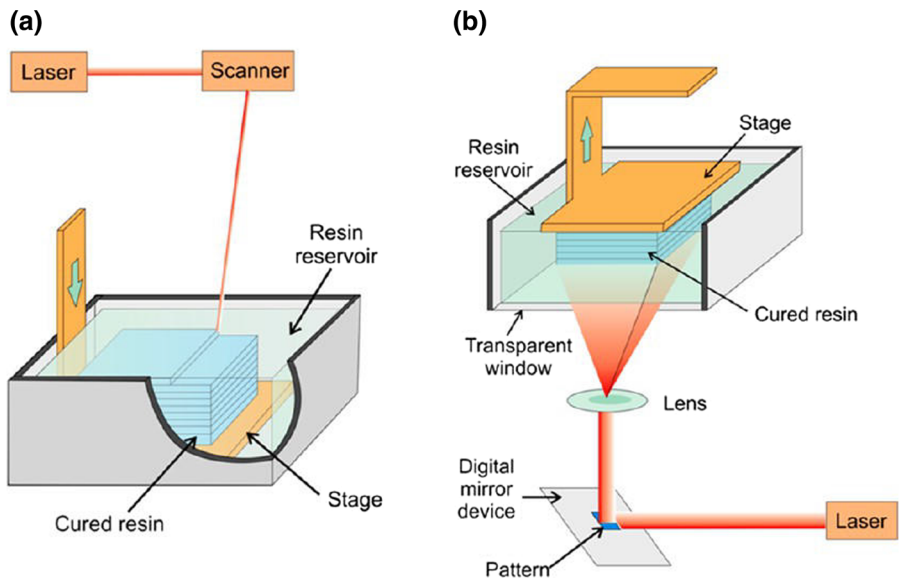


Fig. 2 Schematic of a SLA printing apparatus. Reprinted with permission from Gross et al. (2014)

The addition of CNC barely affects the processability of the resin (Feng et al. 2017; Kumar et al. 2012; Palaganas et al. 2017).

Inkjet 3D printing

Inkjet 3D printing is a process in which drops of liquid with diameters in the micrometer range ejected by either thermal or acoustic forces and deposited onto a user-defined position of a substrate (Fig. 3). Inkjet 3D printers are featured with high resolution, precision and speed, making it a promising platform for functional 3D structure developments. Recently, nanocellulose based inkjet inks have gained great attention (Gunasekera et al. 2016; Nechyporchuk et al. 2017).

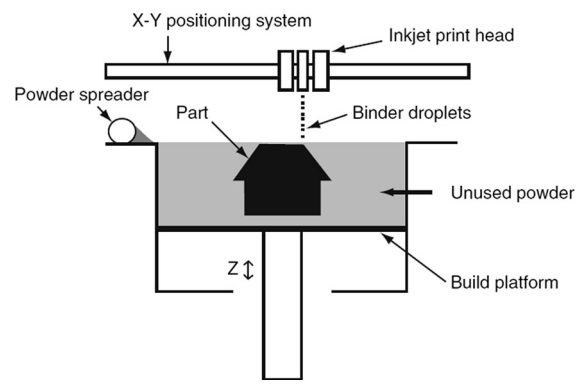


Fig. 3 Schematic of an inkjet 3D printer. Reprinted with permission from Gibson et al. (2015)

3D spinning

Electro-, dry-, and wet-spinning of cellulose materials have been used to manufacture renewable sub-micron fibers and ultrafine filaments with strong, tough oriented structure (Lundahl et al. 2017). Figure 4 shows the schematic of 3D electrospinning and experimental setup. Techniques for accurately defined deposition were adopted to overcome electrical instabilities. Successively stacking of sub-micron filaments in a controlled fashion forms 3D scaffold structure (Lee and Kim 2014). Porous scaffolds with high resolutions have been fabricated with cellulose solution/suspension or derivatives either by 3D electro-, dry-, or wet-spinning (Atila et al. 2015).

Laminated object manufacturing and selective laser sintering

Laminated object manufacturing, one of the earliest 3D printing technologies, was originally developed from laminated paper sheets coated with a thermoplastic adhesive, supplied from a continuous roll, which formed the layers of the final part (Fig. 5) (Wimpenny et al. 2003). The finals products of LOM with paper based materials is similar to plywood, which could be used as floors, walls and roofs in home constructions, or an engineering material for outdoor applications. Fabrication 3D scaffold by selective laser sintering with cellulose–starch and cellulose acetate thermoplastic materials was also reported in literature (Salmoria et al. 2009).

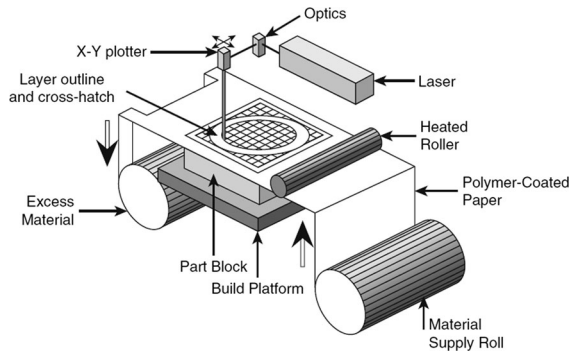


Fig. 5 Schematic representation of the LOM process. Reprinted with permission from Wimpenny et al. (2003)

3D printing with lignocellulosic materials

Many researches has been attempted for the FDM 3D printing with lignocellulose materials but facing multiple challenges. Thermally decomposition occurred before lignocellulose become extrudable. Lignocellulose materials were mainly used as enforcement component to improve the mechanical properties

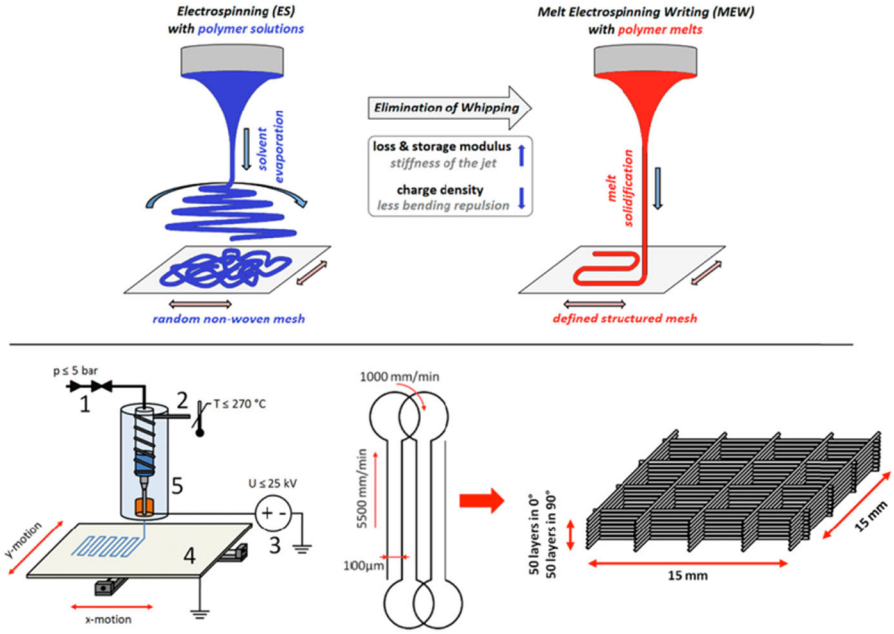


Fig. 4 Schematic of 3D electrospinning and experimental setup. Reprinted from Hochleitner et al. (2015) under the Creative Commons Attribution Licence

or help to reduce global carbon emissions in preliminary researches.

Lignocellulose fillers reinforce polymer composites in FDM and other 3D printing process

Lignocellulose powder can be used as a component in 3D printing with conventional plastic materials and adhesives. Henke and Treml used wooden chips and binding agents including methyl cellulose, gypsum, sodium silicate and cement as raw material, and aerosolized water as activator in 3D printing for construction applications (Henke and Treml 2013). Kariz et al. (2015) used a mixture of wood powder and adhesive for 3D printing (Fig. 6). Brites and coworkers' research indicated that the addition of wood powder (cork) can be processed with HDPE by extrusion based 3D printing. Similar work was done by Rosenthal et al. (2017) in a liquid deposition modeling process. These results showed the feasibility of using of lignocellulosic material in 3D printing processes. However, it was also indicated that 3D printed wood based bulk materials exhibits poor mechanical behavior, which could not be used for structural applications.

Various polymer filaments with lignocellulose were prepared with improved quality. PLA composite filament filled by wood flour (5 wt%) was developed by Tao (2017) (Fig. 7). Similar PLA or polypropylene (PP) filaments with higher wood flour, namely 10, 20, and 30%, were fabricated by twin screw extrusion and further used in FDM process (Montalvo Navarrete et al. 2017). Wood flour filaments are printable in FDM process. However, the objects obtained by 3D printing have much lower mechanical properties than those objects produced by traditional manufacturing processes. The existence of wood flour changed the microstructure of the matrix, leading to a decrease of the interface compatibility of the composites. Uniformly structured filaments based on micronized cocoa shell waste (up to 50% by weight), and biodegradable poly (ε-caprolactone), PCL, have been prepared and used in 3D printing. The problem, such as nozzle blockage occurred in the early phase of the research due to larger wood flour particles (Tran et al. 2017). Uniformly controlling the size of wood floor particle is a key strategy to overcome this issue. It was indicated that mechanical properties of the filaments was sufficient for FDM process. The mechanical properties of the final 3D printed objects were not provided in the study. Commercial FDM filaments made from polymers with algae, bamboo, coffee grounds, hemp, or other lignocellulose materials are available. Most filaments currently on the market have an undisclosed quantity of additives, giving filaments higher mechanical properties and increasing printability. The reuse of recycled biodegradable 3D printed wastes, 3D parts or filaments for sustainable 3D printing is an important issue to be addressed (Pakkanen et al. 2017).

Problems concerning 3D printing with lignocellulose materials are discussed. The possible reasons responsible for the poor quality of 3D printed lignocellulosic materials include variations of raw material quality, distribution of lignocellulose powder in polymer matrix, insufficient adhesion between hydrophilic lignocellulosic material and hydrophobic polymer matrix, and shape deviation of the components

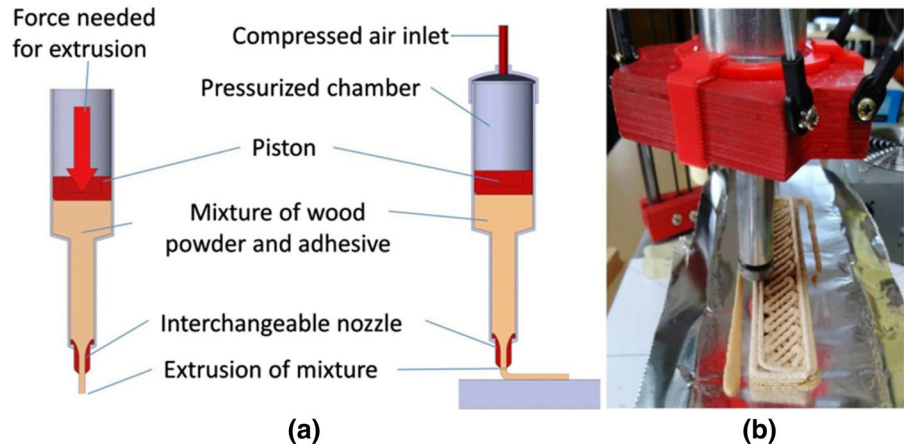


Fig. 6 Extrusion based 3D printer and 3D printing with a mixture of wood powder and adhesive. Reprinted with permission from Kariz et al. (2015)

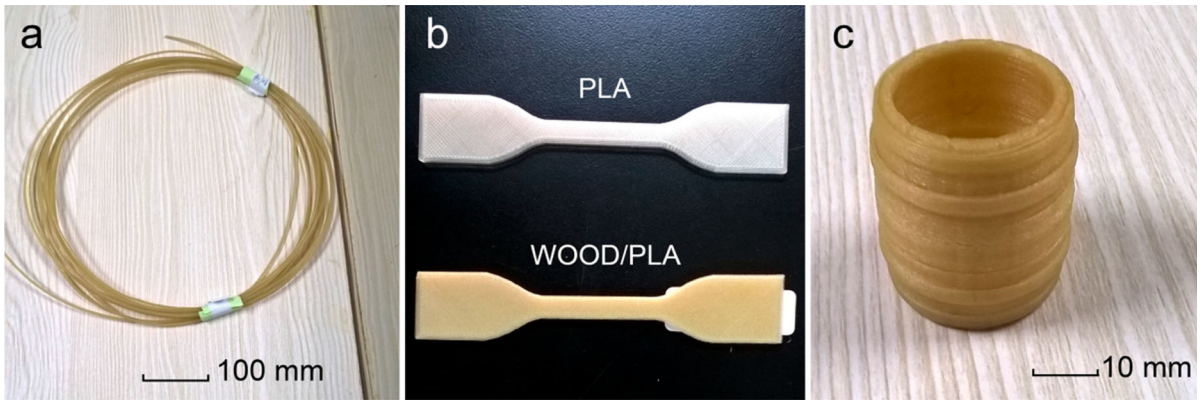


Fig. 7 Filament, test specimens and 3D product. Reprinted from Tao et al. (2017) under the Creative Commons Attribution License

caused by the irregular swelling or shrinkage of wood. Researchers are motivated to find ways that would address the challenges mentioned above. A variety of innovative techniques were adopted to overcome these challenges.

A lot of efforts including physical and chemical modification of the interface between untreated lignocellulose powder and the polymer matrix have been made to avoid these defects. Substantial improvements in the quality of the 3D printed objects have been achieved. Wooden composite structures with superior mechanical properties were FDM printed (Fig. 8) (Pitt et al. 2017). The mechanical performances of these 3D printed objects are comparable to or even better than commercial particleboard and fiberboard. The enhanced mechanical properties of printed objects were mainly ascribed to an enhanced interlayer interaction by overlapping of filaments, a uniform dispersion of wood powder, a densification of feedstock paste and fiber in situ directional alignment. PLA filaments reinforced with laccase-assisted hydrophobic modified thermomechanical pulp fibers exhibited the lowest water wettability and excellent interaction and interfacial adhesion between matrix (Filgueira et al. 2017). State-of-the-art fiber-reinforced polymers (including cellulose nanofiber) in additive manufacturing technologies were reviewed by Parandoush and Lin (2017).

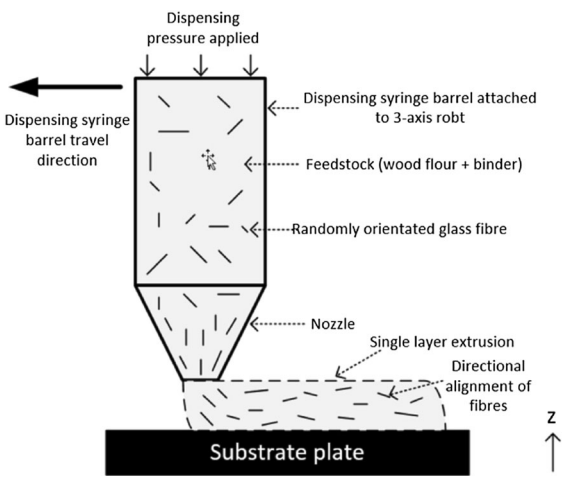


Fig. 8 Schematic of the extrusion based 3D printing and hypothesis of fiber alignment. Reprinted from Pitt et al. (2017) under the Creative Commons Attribution License

4D printing with lignocellulose materials for smart materials was also developed. By taking advantage of wood grain inherent anisotropic and hygroscopic structures, wood composites were 3D printed by Tibbits and his co-worker at the Self-Assembly Lab of MIT for self-bending devices with a wood based filament that actuate in a moisture gradient or other environmental stimuli (Correa et al. 2015). This 3D printing of smart material, known as 4D printing was achieved by differentiated printing or differentiated multi material printing with wood based filament and other polymer filaments. By mimicking the wood grain, curling or folding deformations of smart materials were fabricated by designing the pattern and orientation of the fibers, the height of each layer, and the interlayer interaction with wood based filament, or by taking the advantage of the differences in volumetric expansion/contraction, bending rigidity, and elasticity modulus between two layers with multi material filaments. Similar work was done by mimicking a pinecone with a bilayer microstructure, 4D

printed hygroscopic composites with a programmable moisture-actuated functionality were fabricated with lignocellulose filament by Le Duigou et al. (2016) (Fig. 9). The influence of processing parameters was studied in detail to promote the development of mechanical to actuation functionality of composites. These 3D printed materials could be able to change their shape or properties over time to respond to external stimuli such as temperature, pH, humidity, and illumination, and can be used for sensing and actuation (Shin et al. 2017). Although progresses of 3D printing with lignocellulose material have been made, much remains to be done before printed object works as functional end products. It is necessary to further optimize technological parameters for 3D printing of lignocellulose filler reinforced matrix composites.

Cellulose or cellulose derivatives micro-/nano-particle reinforced polymer matrix composites in FDM process

Similar to lignocellulose, pure cellulose particles could also be used as a component for 3D printing filaments to enhance the mechanical strength of 3D printed products. The hydrophilicity and less thermal stability of cellulose micro/nanoparticles restrict the range of choice of polymer matrix and the processing methods of the composites (Oksman et al. 2016). The dispersion, distribution, and the interfacial interaction of cellulose particle in thermoplastic composites are essential parts of research and development of the manufacturing process of cellulose enhanced 3D printing matrix.

In order to overcome the problem mentioned above, different techniques including size reduction, surface modification, and melt mixing processes were adopted to improve the performance of cellulose/polymer filaments prepared. Kearns used micro-sized recycled cotton cellulose powder, with PLA as base thermoplastic polymer and polyhydroxyalkanoate (PHA) as an additive for developing filaments. Micro-sized or nano-sized cellulose with higher aspect ratio could substantially increase the mechanical performance of filaments. Mechanical tests indicated that the filament prepared is aligning with plant-based filaments currently on the market (Kearns et al. 2016; Kearns 2017). Similarly, cellulose nanocrystals (CNC) nanocomposites-polyvinyl alcohol (PVOH) filaments containing various amounts of CNC (from 2 to 20 wt%) were produced and a progressive enhancement of physical strength and thermal properties of the PVOH composites was observed (Rigotti et al.). 10% CNC was used as a multi-functional additive to reinforce 3D printable poly(ε-caprolactone) nanocomposite performance for bone tissue engineering applications. The result indicated that mechanical properties of PCL composite were significantly enhanced while surface hydrophobicity of PCL composite was slightly reduced due to the addition of hydrophilic CNC (Hong 2015).

Surface modified MCC reinforced PLA filaments were successfully manufactured and subsequently printed using a FDM printer (Murphy and Collins 2016). The study indicated that surface modification could improve the compatibility between hydrophilic MCC and hydrophobic PLA, resulting in an increase in PLA crystallinity and therefore exhibited an increase in storage modulus. This research offered a novel route for robust, tailored, fully degradable 3D printing filament production with surface modified cellulose. 3D printing filaments with up to 30 wt%

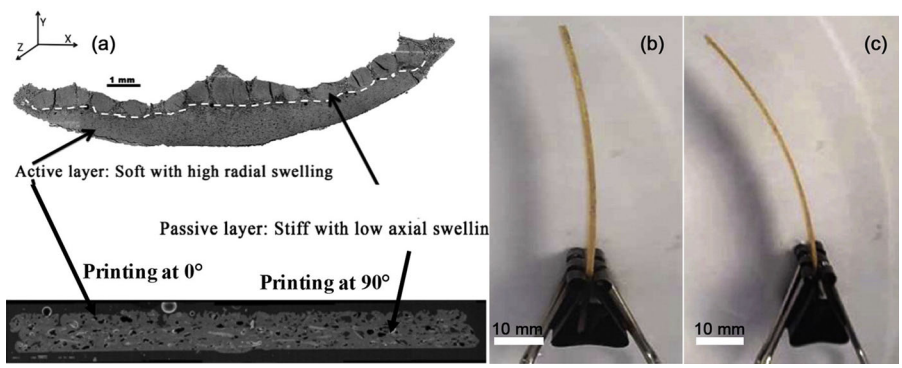


Fig. 9 3D printed smart materials with lignocellulose material: 4D printing: principle of 3D printed functional wood fiber composites and Hygroscopic programmed 3D printed wood material transformations. Reprinted with permission from Le Duigou et al. (2016)

surface modified micro/nanocellulose- PLA composite was developed by Wang et al. (2017c). Interfacial compatibility of micro/nanocellulose and PLA was improved substantially by using a silane-coupling agent (KH-550). The addition of PEG worked as a plasticizer and the printability of the filament was greatly enhanced. Under optimum condition, the mechanical property of 3D printed micro/nanocellulose- PLA composites remained at a comparable level to that of pure PLA. L-lactide-graft-cellulose nanofibers (PLA-g-CNFs) and PLA composite filaments were produced by melt extrusion for FDM process. Surface modification contributed to the growth of PLA crystalline regions, while the post extrusion annealing resulted in a significant increase of mechanical strength of the filaments due to the reorganization of amorphous regions and less-perfect crystalline regions into more perfect crystalline regions (Dong et al. 2017).

3D printed tablets were developed with cellulose or cellulose derivatives as viscosity increasing agents, suspending agents, providing different drug delivery profiles, such as immediate, controlled/sustained or delayed release. Hydroxypropyl cellulose (Chai et al. 2017), hydroxypropyl methylcellulose, microcrystalline cellulose (Goole and Amighi 2016) and ethyl cellulose (Kempin et al. 2017) were used as a base component for FDM filaments to prepare controlled release tablets. The types of the base polymers greatly influence drug release profile. Therefore, a desired control release profile could be obtained by selecting appropriate polymers and drug loading. Careful control of 3D printing parameters is needed to be optimized to minimize cellulose derivatives degradation and to improve cellulose materials dispensability within the matrix polymer.

Cellulose hydrogels in 3D printing processes

Tailoring cellulose hydrogel properties for advanced 3D printing ink development

As a potential candidate for bioink, cellulose solution or suspension with shear thinning behavior and a sufficient zero shear viscosity could meet the two minimum requirements for extrusion based 3D printing, namely, (1) good extrudability through micro sized nozzles; (2) good shape fidelity of the dispensed filaments. These properties make nanocellulose hydrogel a great potential for biomedical and other applications. Rheological property of hydrogel ink is considered to be one of the most important factors that affecting 3D printing process (Holzl et al. 2016). A number of critical reviews and researches on rheology of nanocellulose suspensions are available (Gao et al. 2016; Hubbe et al. 2017; Nechyporchuk et al. 2014, 2016; Puisto et al. 2012; Shao et al. 2015). Rheology of nanocellulose suspension was affected by a group of interlinked parameters. Here, the influences of viscosity, shear-thinning, fluid flow and gelation on 3D printing processes are discussed. CNC morphology and rheological behavior of aqueous CNC inks of varying solid loading are shown in Fig. 10.

A suitable viscosity of cellulose suspension is required for 3D printing processes. The viscosity of suspension is mainly determined by cellulose concentration and degree of polymerization. Other factors like temperature, ionic strength or pH also affect suspension viscosity. It was reported that surface charge significantly affects the rheology of cellulose nanocrystal suspensions, and of course viscosity behavior (Shafeiei-Sabet et al. 2013).

Nanocellulose suspensions exhibit a shear thinning behavior, which has been widely reported in literatures. In a static state, nanosized cellulose fiber entangled together, forming a loosen hydrogel network; when the shear force applied, the entangled fibers break up, resulting to the alignment of cellulose fiber and a decrease in viscosity. In a suspension of relatively high solids content, the entangled network-like structure transformed into individual entangled fragments, possibly with some individual fibrils (Hubbe et al. 2017; Xu et al. 2017). Once the shear is removed, nanocellulose fiber re-entangled together.

The viscosity of nanocellulose suspensions measured by cylindrical rheometer and pipe rheometer does not always agree, which is possibly caused by wall depletion of the rheometer cylinders. In a study conducted by Lauri, the rheological properties of nanocellulose suspensions in a real flow pipe were investigated by a pipe rheometer equipped with an optical coherence tomography (OTC) device (Fig. 11) (Lauri et al. 2017). Further studies of the complexed rheological behavior of nanocellulose suspension in a real flow tube, like in a 3D printer tube or nozzle, are urgently needed in order to theoretical understand the 3D printing process with cellulose hydrogels.

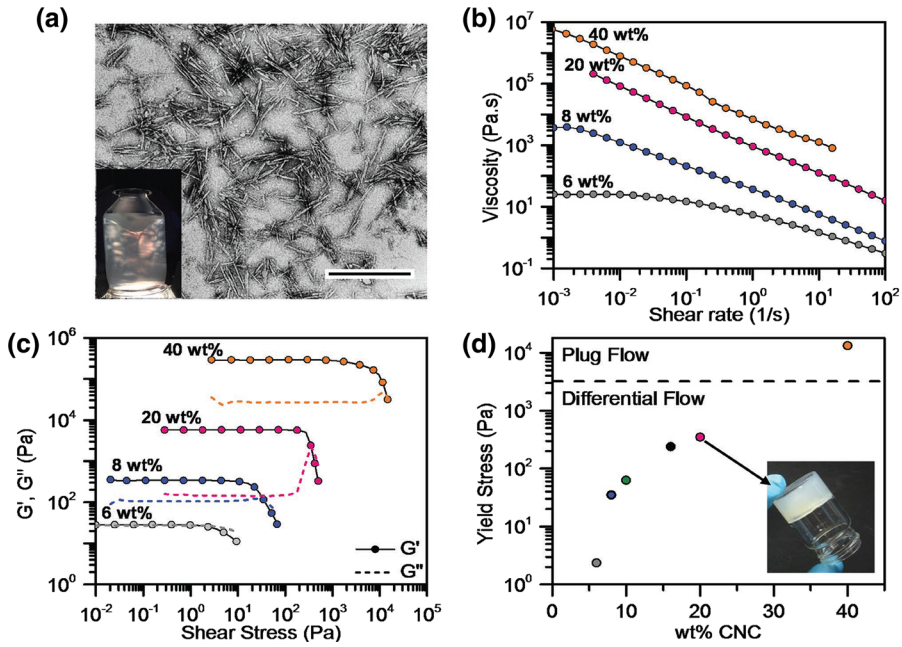


Fig. 10 Morphology of CNC and CNC ink rheological behavior. Reprinted with permission from Siqueira et al. (2017)

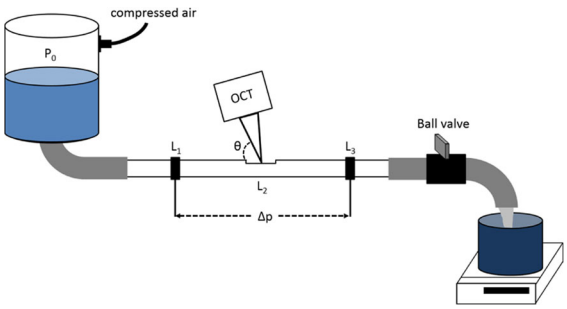


Fig. 11 Schematic diagram of the pipe rheometer. Reprinted with permission from Lauri et al. (2017)

The flow behavior of the cellulose hydrogel during the process of 3D printing was described by computational fluid dynamics (CFD) model. CFD modeling could be used to predict dependencies among cellulose hydrogels properties (i.e., viscosity, shear-thinning), extrusion parameters (i.e., nozzle geometry, extrusion pressure and printing speed), and other printing performances (i.e., shear stress distribution diagram within the nozzle, printing resolution and objects integrity) (Blaeser et al. 2016; Leppiniemi et al. 2017; Muller et al. 2017). Figure 12 shows the cylindrical metal nozzle and conical plastic nozzle geometries of the printer head.

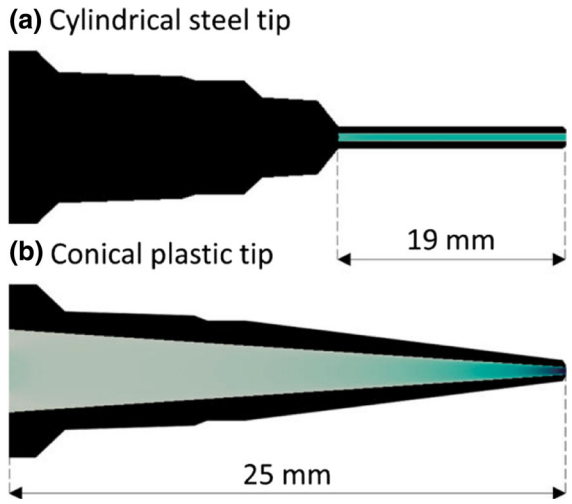


Fig. 12 Extrusion 3D printer nozzle geometries. Reprinted from Leppiniemi et al. (2017) under the ACS AuthorChoice License

The degree of entanglement of nanocellulose suspension could be estimated by crowding factor as demonstrated in Eq. 1 (Wang et al. 2013).

$$N = C_m \left(\frac{L}{d}\right)^2 = C_m x^2 \quad (1)$$

where C_m is the solid content of nanocellulose suspension (wt%), L is the average length and d is the diameter of the nanocellulose, and x stands for the average aspect ratio (L/d) of fibrils.

A ''gel crowding factor'' was established by Martinez et al. (2003) and Celzard et al. (2009) at which fiber interact significantly. According to Martines and Celzard findings, fiber suspension becomes a gel when N_{gel} is in the range of 16–60. Below this value ($N < 16$), nanocellulose suspensions are essentially diluted, whereas above this value ($N \geq 60$) they completely immobilized, forming a rigid network. Therefore, the critical mass concentration for nanocellulose gelation could be determined by Eq. 2. (Wang et al. 2013). The effect of degree of entanglement or crowding factor on 3D printability of nanocellulose suspension is still unclear and further studies are needed.

$$C_m = 16\left(\frac{L}{d}\right)^2 = \frac{16}{x^2} \quad (2)$$

Gelation could be physical cross-linking, chemical cross-linking or a combination of both processes. Physical interaction usually forms a weak gel, which is not strong enough for applications intended for tissue engineering. The application required high mechanical performance must be strengthened by ionic or chemical cross-linking (Kirchmajer et al. 2015; Malda et al. 2013). 3D cellulose nanocrystal aerogel structures are successfully printed by direct ink writing with a wet-strength polyamide-epichlorohydrin cross linker (Li et al. 2017b, 2018b). Adsorption of nonionic polysaccharides, cations or other cross-linkers onto nanocellulose could greatly increase the effective volume fraction of dilute nanocellulose dispersions and lower the requirement for the mass solid consistency, thus tuning nanocellulose gelation (Chau et al. 2015; Fall et al. 2013; Hu et al. 2014; Mendoza et al. 2018; Zander et al. 2014). Addition of other hydrogel materials, such as hyaluronic acid, gelatin, agarose, and alginate, gives architecture with inter-penetrated networks (IPN) architecture which enhances the mechanical performance of the 3D construct. Several studies have been reported to take advantage of this for tailoring rheological properties and gelation behavior of nanocellulose based 3D printing bioink. A nanocellulose-alginate bioink was formulated by taking advantages of the shear thinning properties of cellulose nanofibrils and the fast cross-linking ability of alginate (Markstedt et al. 2015). All-wood-based ink and 3D printed constructs were fabricated by Gatenholm's group. Nanocellulose and modified xylan ink showed excellent printing properties and remained intact after 3D printing (Markstedt et al. 2017). Recently, a photoactive bis(acyl)phosphane oxides (BAPOs) modified CNC Hydrogels were developed and used for 3D printing. The printed shape-persistent and free-standing 3D constructs exhibit improved mechanical performances and superior swelling ability (Fig. 13) (Wang et al. 2018).

Mechanical properties of the 3D printed hydrogels are important to maintain structure integrity. Increase the proportion of non-volatile hydrogel components can prevent volume shrinkage, maintaining the integrity of the 3D structures after curing or solification (Håkansson et al. 2016b; Leppiniemi et al. 2017). However, high concentrations of polymer in hydrogels may be detrimental to cell proliferation, migration, and adhesion (Gatenholm et al. 2016; Malda et al. 2013). Hence, the need for coordinating of hydrogel concentration becomes an important factor controlling the performance of 3D printed products.

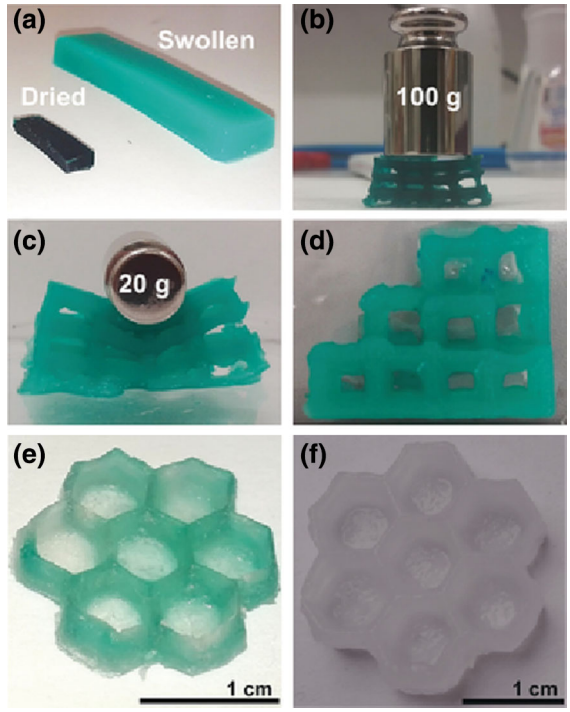


Fig. 13 3D printed CNC-BAPO objects. Reprinted with permission from Wang et al. (2018)

Improving the deposition process on the quality of inter-layer bonding and understanding the material diffusion process of cellulose hydrogel in multi-layers could greatly enhance the performance of cellulose hydrogels in 3D Printing. The inter-layer bonding between the 3D printed methylcellulose/alginate hydrogel was significantly improved by the incorporation of a trisodium citrate solution (TCS), acting as a calcium ions chelating agent (Li et al. 2017a). It was found that TSC concentration and volume in the chelating process, and the Ca^{2+} concentration during cross-linking are important to improve the interfacial bonding. Up to 150 layers 3D constructs with high shape fidelity were printed.

Assessment of printability and shape fidelity of 3D printed constructs

Due to the complexity of rheology behavior and fluid dynamics models, a rapid and facile assessment method for hydrogel dispensing process and performance is urgently needed for researchers to develop new ink formulations (Paxton et al. 2017). Standardized methods to evaluate printability of hydrogel do not yet established. Existing printability analysis of inks formulations with other research materials was conducted and could be used for cellulose based bioink printability assessment. The printability of the ink was not only affected by the ink rheological parameters, viscoelasticity and gelation behaviors, but also affected by printing parameters such as extrusion force, feedrate, printing distance, holding temperature and time, and interlayer diffusion in different 3D printing instruments with different techniques.

Prevalently, the printability of hydrogels was qualitatively judged by visual inspection, manual measurements and automatically measurement with digitalized photos of quality/fidelity after printing (He et al. 2016; Malda et al. 2013; Murphy et al. 2013). Ribeiro et al. (2017) proposed a method to quantitatively evaluate the printability of inks based on shape fidelity. Gatenholm et al. (2016), reported an S test for printability by weighing the printed 'S' parts. More recently, a semi-quantification method for printability (Pr) based on the analysis of optical images of printed constructs was proposed by Ouyang et al. (2016), Kyle et al. (2017). For an ideal printability status, the interconnected channels of the constructs grids would demonstrate square shape. Otherwise, poor printability was reflected by the deterioration of shape fidelity. The printability (Pr) based on square shape was defined by the following function:

$$\mathrm{Pr} = \frac{\pi}{4} \cdot \frac{1}{C} = \frac{\pi}{4} \cdot \frac{L^2}{4\pi A} = \frac{L^2}{16A} \tag{3}$$

where L is perimeter and A is area, and $C = \frac{4\pi A}{L^2}$ means circularity.

However, these methods only reflect the outer surface, lacking intrinsic information with the printing material. Rapid, comparable and reproducible characterizations of the printability of inks are urgently needed. Derby defined Z, a combination of fluid properties and printer parameter, as printability parameter for inkjet printing with printable fluids (Fig. 14) (Derby 2010, 2015; Gunasekera et al. 2016):

$$\mathrm{Z} = \frac{\sqrt{\sigma \rho d}}{\eta} \tag{4}$$

where ρ means density, η means viscosity, σ means surface tension and d means nozzle length.

The acceptable range for printability parameter, Z, is between 1 and 10, in which stable drop could be formed for inkjet printer. With other parameters constant, the printability parameter Z could be used to estimate the printability of specified ink.

These proposed quantitative accessments of printability make potential ways for fast, reliable, reproducible comparisons between samples.

A simple and easy two step screening process for the development and formulation of bioinks with good printability was proposed by Paxton et al. (2017)

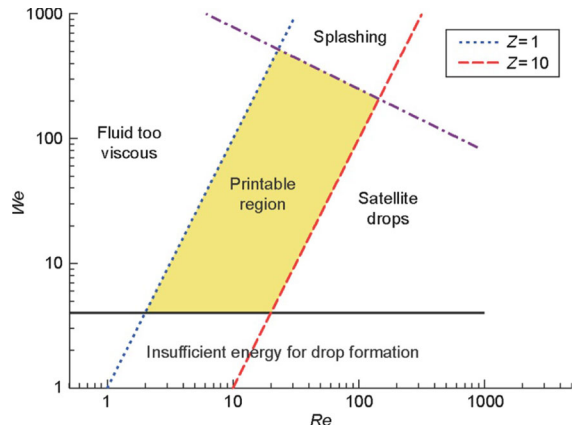


Fig. 14 Printable fluid region defined by Reynolds number (*Re*) and Weber number (*We*). Reprinted from Derby (2015) under the Creative Commons Attribution License

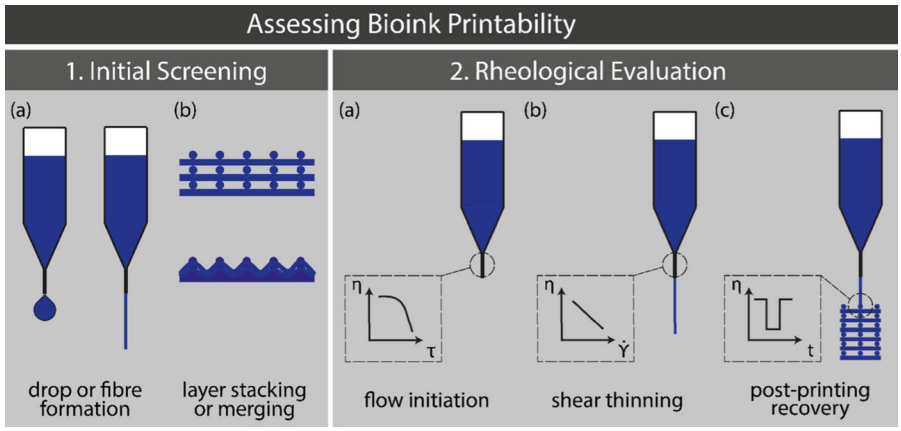


Fig. 15 A two-step assessment for bioink printability. Reprinted from Paxton et al. (2017) under Creative Commons Attribution Licence

(Fig. 15). The fomulation of the bioink should be optimized based on 3D printing experiments and bioink properties characterization. Molecular design criteria and strategies for 3D printable supramolecular or macromolecular hydrogels are proposed based on rheological considerations and cross-linking approaches by Jungst et al. (2016). Gatenholm developed generic design rules for 3D printing bioink formulations containing nanocellulose, which lead to the commercialized a nanocellulose/alginate based bioink as CELLINK (Fig. 16).

The printability and shape fidelity of cellulose hydrogel were not only affected by its inherent properties as discussed above, but also affected by printer/printing parameters, such as nozzle size, feed rate, pressure, printing angle, and distance between nozzle and substrate (He et al. 2016; Kyle et al. 2017; Zhao et al. 2015). The printing parameters choose for each cellulose sample had to be optimized to improve both printability and shape fidelity. The optimum parameters for an extrusion based 3D printer are the conditions at which continuous filaments with a uniform diameter could be deposited (Leppiniemi et al. 2017).

Cellulose solution for 3D printing

It was interesting to see cellulose solvent solutions (i.e., ionic liquid, NMMO) were used as inks for 3D printing. Markstedt et al. (2014) exhibited the first demonstration of microextrusion bioprinting with the solution of cellulose in ionic liquid to fabricate three-dimensional objects. Recently, similar research performed by Gunasekera et al. (2016) demonstrated that the existence of a co-solvent together with an ionic liquid is able to manipulate cellulose solution printability to a favorable 3D ink-jet printing range. Similar work was reported by Li et al. (2018a) with cellulose/NMMO solution. Cellulose concentration is relatively low (i.e. $< 5\%$) in these study and the solvents must be removed by adding anti-solvent, resulting in limited dimensional stability and a low density structure. Pattinson and Hart create a new cellulose 3D printing process with a high cellulose loading (25–35 wt%) in acetone solutions. The pressure-flow behavior of cellulose acetate in acetone solution was systemically investigated to make a balance between printability, and fidelity of the extruded line. 3D printed cellulose acetate constructs have been achieved via extrusion followed by acetone evaporate. Post NaOH treatment could convert cellulose acetate into cellulose by deacetylation. The modulus and strength of 3D printed cellulose acetate objects were comparable to that of PLA or ABS counterparts. Deacetylation by NaOH treatment further increased the mechanical properties attributed to the newly formed hydrogen bonding, significantly exceeding the mechanical properties of PLA, ABS, and Nylon (Fig. 17) (Pattinson and Hart 2017). One limitation of 3D printing with cellulose in solvent solution is that ionic liquid or organic solvents could possibly dissolve polymers used in most printheads and tubes. The customized 3D printer should be designed to avoid the possible destruction of the solvent (Chia and Wu 2015).

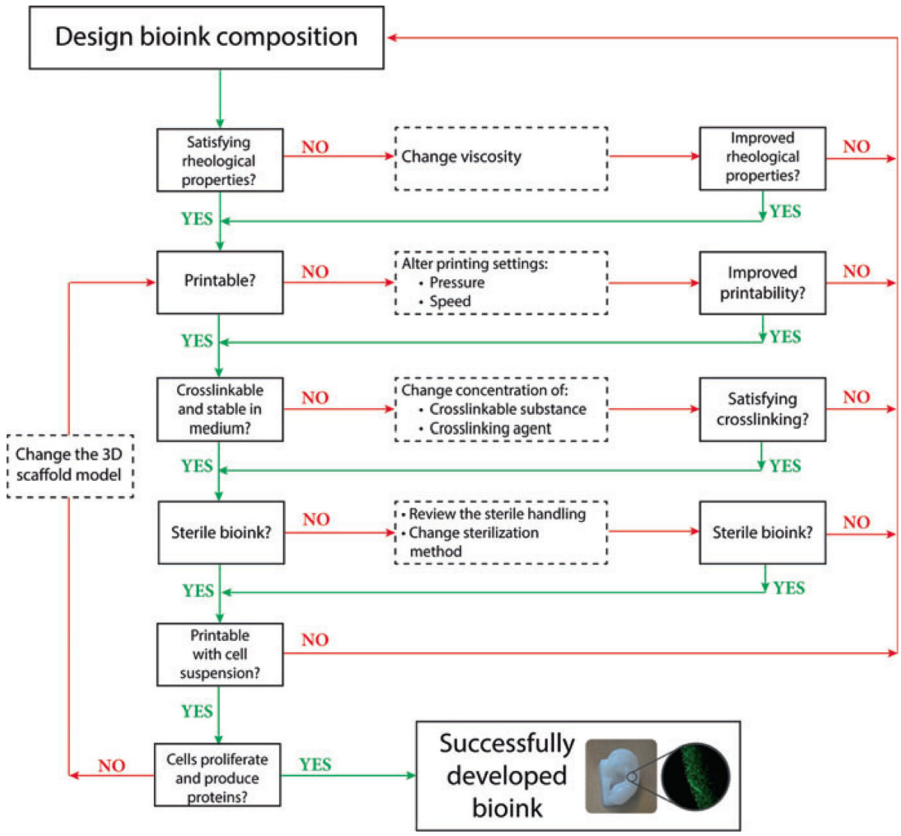


Fig. 16 Flow chart of the development and characterization of bioink. Reprinted with permission from Gatenholm et al. (2016)

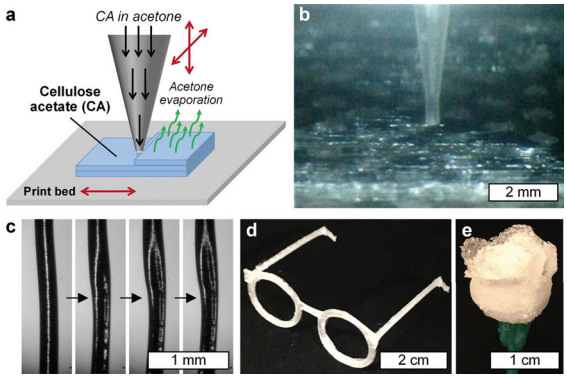


Fig. 17 3D printing with cellulose acetate in acetone solution and 3D printed objects. Reprinted with permission from Pattinson and Hart (2017)

Shear induce alignment of nanocellulose in 3D printing process

The shear-induced alignment of anisotropic CNC suspension enables the 3D printed objects with enhanced mechanical properties in the longitudinal direction. Textured cellular CNC architectures were printed via the direct ink writing approach at a relatively high CNC loading (0.5–40 wt%) by Studart et al. To further study shear induced alignment and improve the mechanical performance of 3D printed structures, the alignment of CNC along the flow direction and at the interface between two adjacent filaments were determined and optimized (Siqueira et al. 2017).

The alignment process of cellulose nanofiber in a flow focusing channel has been systematically studied and modeled by Håkansson (2015), Hakansson et al. (2014, 2016a) (Fig. 18). Shear induced alignment of nanocellulose during 3D printing was also reported by Lewis and her team (Fig. 19) (Gladman et al. 2016). Taking advantage of anisotropic swelling behavior, bioinspired programmable structures that alter shape by water-soaking were fabricated, forming complex 3D geometries.

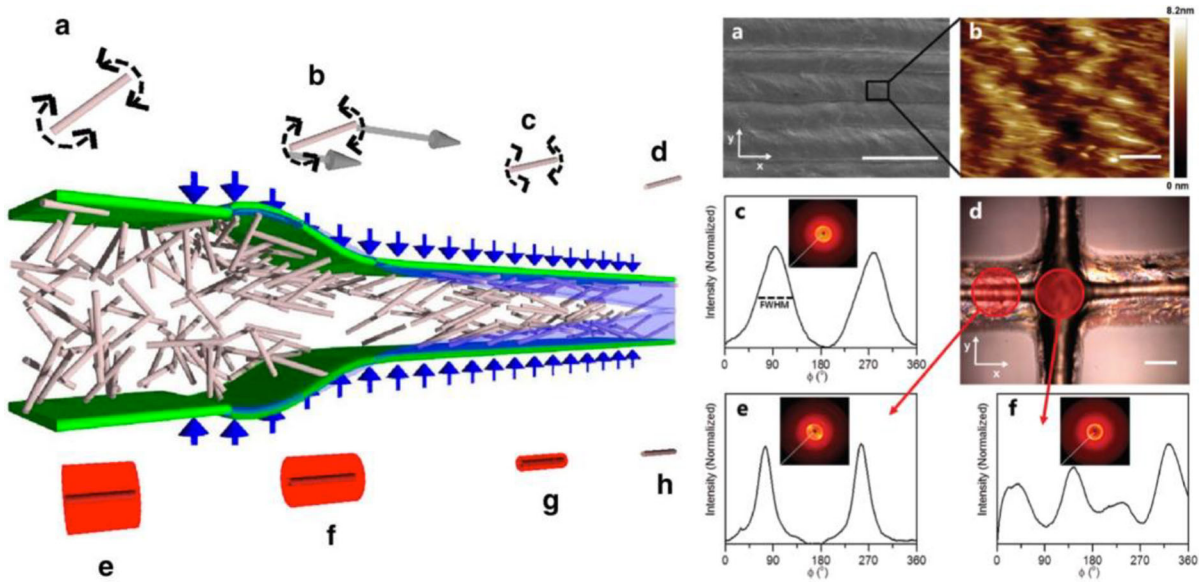


Fig. 18 Shear induced alignment of nanocellulose in 3D printing process. Reprinted from Hakansson et al. (2014) under the Creative Commons License and with permission from Siqueira et al. (2017)

3D printing with functionalized cellulose hydrogels

With the broad chemical modifying capacity, cellulose hydrogel could be chemical functionalized with different types of functional molecules. In a more recent study (Leppiniemi et al. 2017), nanocellulose-alginate hydrogels was bioactivated by the covalent attachment of avidin to cellulose. The 3D printed avidin-functionalized nanocellulose – alginate constructs could immobilize the bioactive components via biotin – avidin interaction, indicating the potential wound dressing applications. The incorporation of functional chemicals in the printing ink such as antimicrobial agents (i.e., toluidine blue and rose bengal), conductive particles (i.e., silver nanoparticle, carbon nanotubes, graphene, polypyrrole) (Fu et al. 2017; Li et al. 2017c; Nechyporchuk et al. 2017; Park et al. 2017; Rymansaib 2016), or magnetic nanoparticles could also be used as strategy for fabricating functional 3D printed constructs.

3D printing with cell-laden cellulose hydrogels

Cell-laden cellulose hydrogel scaffolds were fabricated by 3D printing and the effects of nozzle size and shape, and other printing parameters on cell viability was investigated. Fibroblast and hepatoma cells-laden cellulose nanocrystal/alginate hybrid scaffolds were printed with cell viabilities of 71.00% and 67.06% on day 0, 58.91% and 49.51% on day 3, respectively (Wu et al. 2018). The possible reason for this low cell viability may be due to the lack of cell-binding sites in the hydrogel. Human chondrocytes-laden nanofibrillated cellulose—alginate based bioink showed a cell viability of 73% after 1 day and 86% after 7 days, respectively (Markstedt et al. 2015). It was found that the 3D printing process had no significant influence on cell vitality with the optimal bioink formulation and printing parameter (Ávila et al. 2016). A recent study conducted by Nguyen and coworker found that human-derived induced pluripotent stem cells (iPSCs) and irradiated chondrocytes-laden nanocellulose/alginate bioink is suitable for bioprinting of cartilage. A noticeable increase in cell number and good survival rate after printing was detected (Nguyen et al. 2017). 3D scaffolds with uniform adipocytes cell distribution were fabricated with nanocellulose and hyaluronic acid bioink. The cell viability was 95% after 1 week culture. It was noticed that more lipids are accumulated in the cell and more adipogenic marker genes PPARγ and FABP4 are expressed in 3D printed scaffolds than standard 2D cells culture (Henriksson et al. 2017). It was fond that a proper extrusion pressure and shear stress is a key factor to maintaining high cell integrity and cell viability (Blaeser et al. 2016; Muller et al. 2017).

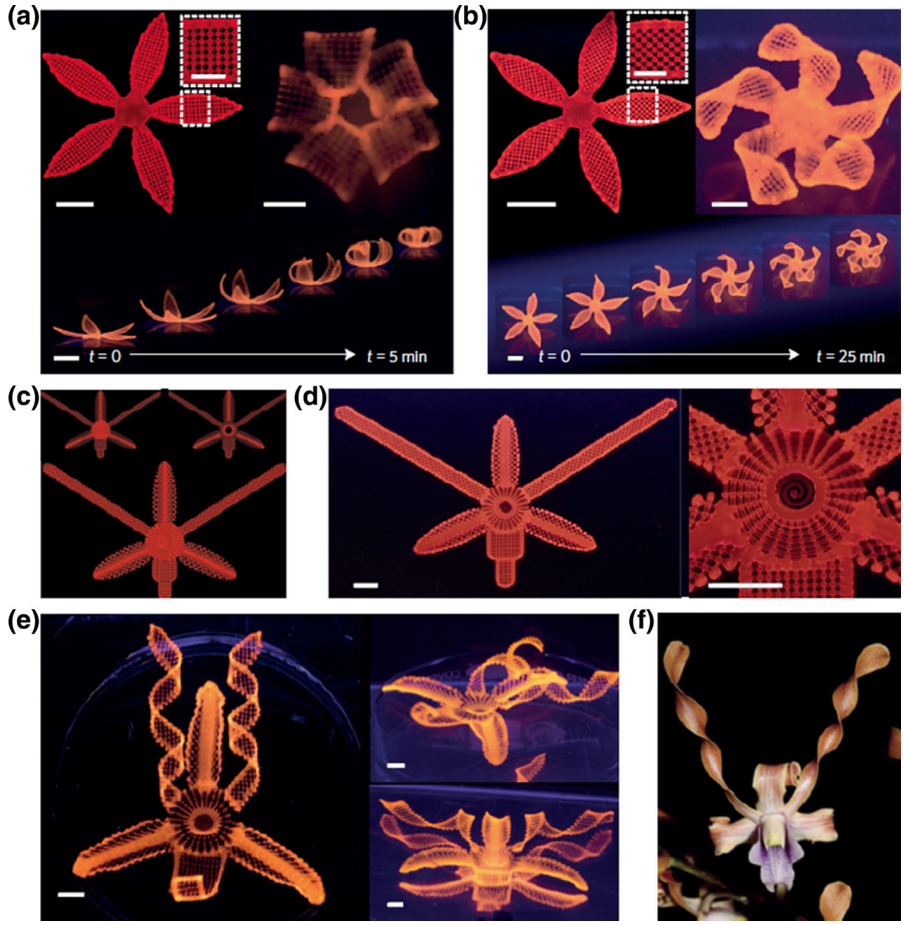


Fig. 19 Flower morphologies fabricated by biomimetic 4D printing. Reprinted with permission from Gladman et al. (2016)

Inkjet based 3D printing of cellulose hydrogels

Regular inkjet printers generally require relatively low viscosities (< 20 mPa.s). Viscosity-solids data listed by Hubbe et al. (2017) under the conditions of a shear rate of 1 s^{-1} from 40 studies indicated that viscosities of cellulose hydrogel are in the range of 10^{-3} to 10^{4} Pa.s. Co-solvents were added to cellulose/ionic liquids solution to increase cellulose concentration and lower the overall viscosity to meet the requirement for 3D ink-jet printing (Gunasekera et al. 2016). Cellulose nanofibril-based inks were 3D inkjet printed onto cellulose fabrics for a potential application in e-textile. This all cellulose approach increased the compatibility between the inks and the substrate (Nechyporchuk et al. 2017). More studies related to the affinity of the cellulose based ink to cellulose fabric; durability and function loss during wear are needed to perform.

3D Spinning of cellulose hydrogels

Combination of electrospinning and 3D printing could be used to fabricate 3D constructs with various nano-/microfibrous hierarchical structures, accomplished by changing electrospinning apparatus and processing parameters (Yang et al. 2018). Freestanding 3D electrospinning cellulose acetate/pullulan scaffolds with adjustable thickness were successfully developed for the first time by Tezcaner's group (Atila et al. 2015). Through optimization of the parameters for cellulose acetate/pullulan solution, scaffolds with ultrafine filaments in nano/micro scale size, the smallest being lower than 10 μm, could be fabricated. It was also reported that cellulose derivatives and Ioncell-F fibers were 3D spun on textiles (Lundahl et al. 2017).

Application of 3D printed cellulose materials and future direction

Natural lignocellulose based materials, such as wood, cotton, etc. have been used as engineering materials in forest products, pulp and paper, and textiles industries for centuries. With the developing of 3D printing technology, 3D printing with lignocellulose materials for engineering materials applications is recently developed. As mentioned above, lignocellulose materials exhibit many interesting properties, including sustainability, hydrophilicity, biocompatibility, biodegradability, non-toxicity and broad chemical modifying capacity. Cellulose materials have been widely used for decoration elements, medical application, biological devices, electronics, energy storage, as well as textiles applications. Critical review articles on cellulose chemistry and application from different perspectives are available (Giese et al. 2015; Habibi 2014; Habibi et al. 2010; Klemm et al. 2005, 2011; Moon et al. 2011; Shatkin et al. 2014; Wu et al. 2013; Zhu et al. 2016; Shen et al. 2016). Nowadays, 3D printing is widely used not only for prototypes but also for functional end use products. 3D printed cellulose materials in combination with other polymers are being studied extensively for versatile applications (Gatenholm et al. 2016; Li et al. 2016b; Ligon et al. 2017; Piras et al. 2017; Sultan et al. 2017).

3D printing with cellulose materials for medical applications

3D printing technology is believed to revolutionize medicine. As for tissue engineering and drug delivery, regenerative medicine and wound healing this is where the application of 3D printing of cellulose hydrogels becomes particularly interesting to scientists in developing novel formulations with exciting properties to meet the requirement for clinic applications (Dumanli 2017; Ligon et al. 2017; Studart 2016). Nanocellulose-alginate double network 3D constructs with remarkable performance have been developed and evaluated by Gatenholm group and commercialized for research community (Markstedt et al. 2015; Ávila et al. 2016; Gatenholm et al. 2016; Håkansson et al. 2016b; Henriksson et al. 2017; Müller et al. 2017; Nguyen et al. 2017). 3D printed cell-laden nanocellulose-alginate bioink show an $85.7 \pm 1.9\%$ cell viability after 7 days of cultivation. Cell viability, proliferation, migration in cellulose based hydrogels could be affected by a group of 3D printing parameters, which has not been fully explored yet (Holzl et al. 2016). 3D printed cell-laden alginate/methylcellulose constructs also showed high viability after 3 weeks of cultivation (Schutz et al. 2017). The potential medical applications of 3D printed cellulose constructs are exciting. However, there are still numerous obstacles to be overcome. Cellulose nanomaterials haven't been officially approved for tissue engineering application. There is a long way ahead to go for 3D printed cellulose materials before getting into the clinic.

3D printing has been also extensively investigated for wound dressing and drug delivery (Rees et al. 2015; Ursan et al. 2013; Yu et al. 2009). 3D-printed functionalization nanocellulose-alginate wound dressing products are tailored to meet the needs in controlled release of therapeutic molecules and cell-based applications. The customized wound dressing products enable gradual release with active ingredients (Leppiniemi et al. 2017). Human adipose mesenchymal stem cell decorated and glutaraldehyde cross-linked nanocellulose threads was fabricated to relieve inflammation and improve wound healing (Mertaniemi et al. 2016). The first 3D printed drug product approved by US Food and Drug Administration (FDA), Spritam® is available in the US market. Different type of cellulose and its derivatives, such as microcrystalline cellulose, hydroxypropyl methylcellulose, and ethylcellulose, working as thickening agents, rheology modifiers or acting as a drug carrier were used in 3D printing (Goole and Amighi 2016). Properties of drug matrices play a vital role in drug release profiles. Personalized drug release profiles were manipulated by tailoring the drug formulation and geometry in 3D printing process. Independently controlled and well-defined release profiles of different drugs in one pill were achieved by Khaled et al. (2015).

3D printing with cellulose materials for electronics applications

Works have been done in the development 3D structured cellulose materials for flexible electronics, such as battery, supercapacitor, wearable electronics and sensors, which are expected a more widespread usage (Du et al. 2017; Hoeng et al. 2016; Jia et al.

2017a; Li et al. 2016b; Penttilä et al. 2013) 3D printing can well control the geometry of the printed electronics. The performance of electronics devices fabricated by 3D printing typically outweighs their traditionally manufactured counterparts (Zhang et al. 2017). 3D printing of designed battery electrode pastes with conductive cellulose composites is demonstrated. A three-layered lithium battery consists of 3D printed anode, electrolyte, and cathode pastes was developed, which shows a great potential for low-cost energy storage and flexible electronics (Park et al. 2017). Highly conductive (649 ± 60 S cm^{-1}) microfibers were fabricated by extruding the NFC and GO gel, or NFC and carbon nanotube gel (Li et al. 2014, 2017c). Similar work was done by Shao et al. (2015), microfibrillated cellulose/lignosulfonate construct were 3D printed and carbonized as an anode in Li-ion batteries, showing highly conductivity (550–500 S m^{-1}). A novel low temperature 3D printing technology with nanocellulose hydrogel as raw material resulted in production of porous, conductive anode material for microbial fuel cells, showing excellent performance over carbon fiber cloth electrodes (Rymansaib 2016). Those cellulose-based conductive materials could also be used for flexible sensors fabrication. 3D printed sensors could be possibly integrated into packaging for in situ food quality monitoring, and wearable textiles that would be capable of monitoring heart rate, blood pressure, and the state of movement. An novel nanocellulose/CdS quantum dot photoelectric ink was fabricated, which exhibits excellent printability, it could therefore be used in 3D printing for electronic devices (Tang et al. 2016).

Other application

3D printing with cellulose material for smart packaging and textile applications is developing rapidly and looks more promising. With good mechanical performance and excellent flexibility, printed cellulose structures are suitable for textile applications (Hu and Cui 2012). Electronic textiles are fabricated with inkjet-printed cellulose nanofibril-base conductive composite, which could be used for flexible, wearable sensors and displays (Nechyporchuk et al. 2017). An all-cellulose approach for surface tailoring and functionalizing fabrics was manufactured by 3D printing with cellulose acetate on cellulose fabrics. The products exhibits excellent mechanical durability and flexible structures (Tenhunen et al. 2018). It was reported that paper microfluidics for sensing platforms was fabricated by matrix-assisted 3D printing of cellulose nanofiber (Shin and Hyun 2017). The application of 3D food printing with cellulose nanofiber as dietary fiber for development of healthy, customized snack products has been also reported (Lille et al. 2018). 3D printing technologies introduce flexibility for food industry and allow designing food with alternative ingredients and complex shapes. Although a number of cellulose-based materials with excellent performances have been fabricated by 3D printing, the potential has not been fully explored yet.

Summary and perspective

This paper presents the development and assessment of 3D printing with cellulose materials. The formulation development and assessment parameters involved, especially for extrusion based 3D printing, including cellulose hydrogel rheology, fiber entanglement, fiber alignment, gelation, printability and shape fidelity, and processing parameters are examined and reviewed with the literature to illustrate the developing process. The functionality of 3D printing cellulose materials via cellulose surface modification or via the incorporation of functional materials was achieved. A deeper understanding of cellulose properties and 3D printing process help us speed up the development of new cellulose material for advanced applications.

Although significant developments were achieved via 3D printing with cellulose materials aimed for a variety of applications, the potential has not been fully explored yet. The 3D printed cellulose material properties, such as strength are generally inferior compared to their counterparts obtained by conventional manufacture processes due to the insufficient interlayer bonding. With the development of cellulose chemistry and process technology, cellulose materials should be tailored made and their properties should be tuned according to the 3D printing technology employed or the specific requirements for different applications. By biomimetic of the fascinating capabilities of natural materials, cellulose may be used as the main building block for 3D printed constructs. Further investigations are needed to evaluate the cellulose performance in 3D printing. High-

throughput techniques to screen the formulation of cellulose based materials for 3D printing are missing. General criteria and design strategies to evaluate performance cellulose materials in 3D printing are required. Standard assessment methods for printability of cellulose based inks are needed. 3D printing with cellulose materials is only just beginning and major breakthroughs are expected to come true in the near future.

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References

Atila D, Keskin D, Tezcaner A (2015) Cellulose acetate based 3-dimensional electrospun scaffolds for skin tissue engineering applications. Carbohydr Polym 133:251–261. https://doi.org/10.1016/j.carbpol.2015.06.109

Ávila HM, Schwarz S, Rotter N, Gatenholm P (2016) 3d bioprinting of human chondrocyte-laden nanocellulose hydrogels for patient-specific auricular cartilage regeneration. Bioprinting 1:22–35. https://doi.org/10.1016/j.bprint.2016.08.003

Blaeser A, Duarte Campos DF, Puster U, Richtering W, Stevens MM, Fischer H (2016) Controlling shear stress in 3d bioprinting is a key factor to balance printing resolution and stem cell integrity. Adv Healthc Mater 5(3):326–333. https://doi.org/10.1002/adhm.201500677

Celzard A, Fierro V, Kerekes R (2009) Flocculation of cellulose fibres: new comparison of crowding factor with percolation and effective-medium theories. Cellulose 16(6):983–987. https://doi.org/10.1007/s10570-009-9314-0

Chai X, Chai H, Wang X, Yang J, Li J, Zhao Y, Cai W, Tao T, Xiang X (2017) Fused deposition modeling (fdm) 3d printed tablets for intragastric floating delivery of domperidone. Sci Rep 7:2829. https://doi.org/10.1038/s41598-017-03097-x

Chau M, Sriskandha SE, Pichugin D, Therien-Aubin H, Nykypanchuk D, Chauve G, Methot M, Bouchard J, Gang O, Kumacheva E (2015) Ion-mediated gelation of aqueous suspensions of cellulose nanocrystals. Biomacromol 16(8):2455–2462. https://doi.org/10.1021/acs.biomac.5b00701

Chen L, Wang Q, Hirth K, Baez C, Agarwal UP, Zhu JY (2015) Tailoring the yield and characteristics of wood cellulose nanocrystals (cnc) using concentrated acid hydrolysis. Cellulose 22(3):1753–1762. https://doi.org/10.1007/s10570-015-0615-1

Chia HN, Wu BM (2015) Recent advances in 3d printing of biomaterials. J Biol Eng 9(1):4. https://doi.org/10.1186/s13036-015-0001-4

Chimene D, Lennox KK, Kaunas RR, Gaharwar AK (2016) Advanced bioinks for 3d printing: a materials science perspective. Ann Biomed Eng 44(6):2090–2102. https://doi.org/10.1007/s10439-016-1638-y

Chung JHY, Naficy S, Yue ZL, Kapsa R, Quigley A, Moulton SE, Wallace GG (2013) Bio-ink properties and printability for extrusion printing living cells. Biomater Sci 1(7):763–773. https://doi.org/10.1039/c3bm00012e

Correa D, Papadopoulou A, Guberan C, Jhaveri N, Reichert S, Menges A, Tibbits S (2015) 3d-printed wood: programming hygroscopic material transformations. 3D Print Addit Manuf 2(3):106–116. https://doi.org/10.1089/3dp.2015.0022

Derby B (2010) Inkjet printing of functional and structural materials: fluid property requirements, feature stability, and resolution. Annu Rev Mater Res 40(1):395–414. https://doi.org/10.1146/annurev-matsci-070909-104502

Derby B (2015) Additive manufacture of ceramics components by inkjet printing. Engineering 1(1):113–123. https://doi.org/10.15302/J-ENG-2015014

Dong J, Li M, Zhou L, Lee S, Mei C, Xu X, Wu Q (2017) The influence of grafted cellulose nanofibers and postextrusion annealing treatment on selected properties of poly(lactic acid) filaments for 3d printing. J Polym Sci Part B Polym Phys 55(11):847–855. https://doi.org/10.1002/polb.24333

Du X, Zhang Z, Liu W, Deng Y (2017) Nanocellulose-based conductive materials and their emerging applications in energy devices—a review. Nano Energy 35:299–320. https://doi.org/10.1016/j.nanoen.2017.04.001

Dumanli AG (2017) Nanocellulose and its composites for biomedical applications. Curr Med Chem 24(5):512–528. https://doi.org/10.2174/0929867323666161014124008

Fall AB, Lindström SB, Sprakel J, Wågberg L (2013) A physical cross-linking process of cellulose nanofibril gels with shear-controlled fibril orientation. Soft Matter 9(6):1852–1863. https://doi.org/10.1039/c2sm27223g

Feng X, Yang Z, Chmely S, Wang Q, Wang S, Xie Y (2017) Lignin-coated cellulose nanocrystal filled methacrylate composites prepared via 3d stereolithography printing: mechanical reinforcement and thermal stabilization. Carbohydr Polym 169:272–281. https://doi.org/10.1016/j.carbpol.2017.04.001

Filgueira D, Holmen S, Melbø JK, Moldes D, Echtermeyer AT, Chinga-Carrasco G (2017) Enzymatic-assisted modification of thermomechanical pulp fibers to improve the interfacial adhesion with poly(lactic acid) for 3d printing. ACS Sustain Chem Eng 5(10):9338–9346. https://doi.org/10.1021/acssuschemeng.7b02351

Fu K, Yao Y, Dai J, Hu L (2017) Progress in 3d printing of carbon materials for energy-related applications. Adv Mater 29(9):1603486. https://doi.org/10.1002/adma.201603486

Gao X, Shi Z, Kuśmierczyk P, Liu C, Yang G, Sevostianov I, Silberschmidt VV (2016) Time-dependent rheological

behaviour of bacterial cellulose hydrogel. Mater Sci Eng C 58:153–159. https://doi.org/10.1016/j.msec.2015.08.019

Gatenholm P, Martinez H, Karabulut E, Amoroso M, Kölby L, Markstedt K, Gatenholm E, Henriksson I (2016) Development of nanocellulose-based bioinks for 3d bioprinting of soft tissue. In: Ovsianikov A, Yoo J, Mironov V (eds) 3d printing and biofabrication. Springer, Cham, pp 1–23. https://doi.org/10.1007/978-3-319-40498-1_14-1

Gibson I, Rosen DW, Stucker B (2015) Additive manufacturing technologies. Springer, New York. https://doi.org/10.1007/978-1-4939-2113-3

Giese M, Blusch LK, Khan MK, MacLachlan MJ (2015) Functional materials from cellulose-derived liquid-crystal templates. Angew Chem Int Ed 54(10):2888–2910. https://doi.org/10.1002/anie.201407141

Gladman AS, Matsumoto EA, Nuzzo RG, Mahadevan L, Lewis JA (2016) Biomimetic 4d printing. Nat Mater 15(4):413–418. https://doi.org/10.1038/nmat4544

Goole J, Amighi K (2016) 3d printing in pharmaceutics: a new tool for designing customized drug delivery systems. Int J Pharm 499(1–2):376–394. https://doi.org/10.1016/j.ijpharm.2015.12.071

Gross BC, Erkal JL, Lockwood SY, Chen CP, Spence DM (2014) Evaluation of 3d printing and its potential impact on biotechnology and the chemical sciences. Anal Chem 86(7):3240–3253. https://doi.org/10.1021/ac403397r

Gunasekera DH, Kuek S, Hasanaj D, He Y, Tuck C, Croft AK, Wildman RD (2016) Three dimensional ink-jet printing of biomaterials using ionic liquids and co-solvents. Faraday Discuss 190:509–523. https://doi.org/10.1039/c5fd00219b

Habibi Y (2014) Key advances in the chemical modification of nanocelluloses. Chem Soc Rev 43(5):1519–1542. https://doi.org/10.1039/c3cs60204d

Habibi Y, Lucia LA, Rojas OJ (2010) Cellulose nanocrystals: chemistry, self-assembly, and applications. Chem Rev 110(6):3479–3500. https://doi.org/10.1021/cr900339w

Håkansson KMO (2015) Online determination of anisotropy during cellulose nanofibril assembly in a flow focusing device. RSC Adv 5(24):18601–18608. https://doi.org/10.1039/c4ra12285b

Hakansson KM, Fall AB, Lundell F, Yu S, Krywka C, Roth SV, Santoro G, Kvick M, Prahl Wittberg L, Wagberg L, Soderberg LD (2014) Hydrodynamic alignment and assembly of nanofibrils resulting in strong cellulose filaments. Nat Commun 5:4018. https://doi.org/10.1038/ncomms5018

Håkansson KM, Lundell F, Prahl-Wittberg L, Soderberg LD (2016a) Nanofibril alignment in flow focusing: measurements and calculations. J Phys Chem B 120(27):6674–6686. https://doi.org/10.1021/acs.jpcb.6b02972

Håkansson KM, Henriksson IC, de la Peña Vázquez C, Kuzmenko V, Markstedt K, Enoksson P, Gatenholm P (2016b) Solidification of 3d printed nanofibril hydrogels into functional 3d cellulose structures. Adv Mater Technol 1(7):1600096. https://doi.org/10.1002/admt.201600096

He Y, Yang F, Zhao H, Gao Q, Xia B, Fu J (2016) Research on the printability of hydrogels in 3d bioprinting. Sci Rep 6:29977. https://doi.org/10.1038/srep29977

Henke K, Treml S (2013) Wood based bulk material in 3d printing processes for applications in construction. Eur J Wood Wood Prod 71(1):139–141. https://doi.org/10.1007/s00107-012-0658-z

Henriksson I, Gatenholm P, Hägg DA (2017) Increased lipid accumulation and adipogenic gene expression of adipocytes in 3d bioprinted nanocellulose scaffolds. Biofabrication 9(1):015022. https://doi.org/10.1088/1758-5090/aa5c1c

Hochleitner G, Jüngst T, Brown TD, Hahn K, Moseke C, Jakob F, Dalton PD, Groll J (2015) Additive manufacturing of scaffolds with sub-micron filaments via melt electrospinning writing. Biofabrication 7(3):035002. https://doi.org/10.1088/1758-5090/7/3/035002

Hoeng F, Denneulin A, Bras J (2016) Use of nanocellulose in printed electronics: a review. Nanoscale 8(27):13131–13154. https://doi.org/10.1039/c6nr03054h

Holzl K, Lin S, Tytgat L, Van Vlierberghe S, Gu L, Ovsianikov A (2016) Bioink properties before, during and after 3d bioprinting. Biofabrication 8(3):032002. https://doi.org/10.1088/1758-5090/8/3/032002

Hong JK (2015) Bioactive cellulose nanocrystal reinforced 3d printable poly (epsilon-caprolactone) nanocomposite for bone tissue engineering. Doctoral thesis, Virginia Polytechnic Institute and State University

Hu L, Cui Y (2012) Energy and environmental nanotechnology in conductive paper and textiles. Energy Environ Sci 5(4):6423–6435. https://doi.org/10.1039/C2EE02414D

Hu Z, Cranston ED, Ng R, Pelton R (2014) Tuning cellulose nanocrystal gelation with polysaccharides and surfactants. Langmuir 30(10):2684–2692. https://doi.org/10.1021/la404977t

Hubbe MA, Tayeb P, Joyce M, Tyagi P, Kehoe M, Dimic-Misic K, Pal L (2017) Rheology of nanocellulose-rich aqueous suspensions: a review. BioResources 12(4):9556–9661. https://doi.org/10.15376/biores.12.4.9556-9661

Isogai A, Bergström L (2018) Preparation of cellulose nanofibers using green and sustainable chemistry. Curr Opin Green Sustain Chem 12:15–21. https://doi.org/10.1016/j.cogsc.2018.04.008

Isogai A, Saito T, Fukuzumi H (2011) Tempo-oxidized cellulose nanofibers. Nanoscale 3(1):71–85. https://doi.org/10.1039/c0nr00583e

Jia C, Bian H, Gao T, Jiang F, Kierzewski IM, Wang Y, Yao Y, Chen L, Shao Z, Zhu JY, Hu L (2017a) Thermally stable cellulose nanocrystals toward high-performance 2d and 3d nanostructures. ACS Appl Mater Interfaces 9(34):28922–28929. https://doi.org/10.1021/acsami.7b08760

Jia C, Chen L, Shao Z, Agarwal UP, Hu L, Zhu JY (2017b) Using a fully recyclable dicarboxylic acid for producing dispersible and thermally stable cellulose nanomaterials from different cellulosic sources. Cellulose 24(6):2483–2498. https://doi.org/10.1007/s10570-017-1277-y

Jungst T, Smolan W, Schacht K, Scheibel T, Groll J (2016) Strategies and molecular design criteria for 3d printable hydrogels. Chem Rev 116(3):1496–1539. https://doi.org/10.1021/acs.chemrev.5b00303

Kalsoom U, Nesterenko PN, Paull B (2016) Recent developments in 3d printable composite materials. RSC Adv 6(65):60355–60371. https://doi.org/10.1039/c6ra11334f

Kariz M, Sernek M, Kuzman MK (2015) Use of wood powder and adhesive as a mixture for 3d printing. Eur J Wood Wood Prod 74(1):123–126. https://doi.org/10.1007/s00107-015-0987-9

Kearns AJ (2017) Cotton cellulose fibers in 3d print material. Master Thesis, North Carolina State University

Kearns A, Farahbakhsh N, Venditti R, Jur J (2016) Cotton fibers in 3d printing. In: Solid Freeform Fabrication 2016: Proceedings of the 26th annual international solid freeform fabrication symposium—an additive manufacturing conference, pp 899–905

Kempin W, Franz C, Koster L-C, Schneider F, Bogdahn M, Weitschies W, Seidlitz A (2017) Assessment of different polymers and drug loads for fused deposition modeling of drug loaded implants. Eur J Pharm Biopharm 115(Supplement C):84–93. https://doi.org/10.1016/j.ejpb.2017.02.014

Khaled SA, Burley JC, Alexander MR, Yang J, Roberts CJ (2015) 3d printing of five-in-one dose combination polypill with defined immediate and sustained release profiles. J Control Release 217(Supplement C):308–314. https://doi.org/10.1016/j.jconrel.2015.09.028

Kirchmajer DM, Gorkin R III, In het Panhuis M (2015) An overview of the suitability of hydrogel-forming polymers for extrusion-based 3d-printing. J Mater Chem B 3(20):4105–4117. https://doi.org/10.1039/c5tb00393h

Klemm D, Heublein B, Fink HP, Bohn A (2005) Cellulose: fascinating biopolymer and sustainable raw material. Angew Chem Int Ed Engl 44(22):3358–3393. https://doi.org/10.1002/anie.200460587

Klemm D, Kramer F, Moritz S, Lindström T, Ankerfors M, Gray D, Dorris A (2011) Nanocelluloses: a new family of nature-based materials. Angew Chem Int Ed 50(24):5438–5466. https://doi.org/10.1002/anie.201001273

Kumar S, Hofmann M, Steinmann B, Foster EJ, Weder C (2012) Reinforcement of stereolithographic resins for rapid prototyping with cellulose nanocrystals. ACS Appl Mater Interfaces 4(10):5399–5407. https://doi.org/10.1021/am301321v

Kyle S, Jessop ZM, Al-Sabah A, Whitaker IS (2017) 'Printability' of candidate biomaterials for extrusion based 3d printing: state-of-the-art. Adv Healthc Mater 6(16):1700264. https://doi.org/10.1002/adhm.201700264

Lauri J, Koponen A, Haavisto S, Czajkowski J, Fabritius T (2017) Analysis of rheology and wall depletion of microfibrillated cellulose suspension using optical coherence tomography. Cellulose 24(11):4715–4728. https://doi.org/10.1007/s10570-017-1493-5

Le Duigou A, Castro M, Bevan R, Martin N (2016) 3d printing of wood fibre biocomposites: from mechanical to actuation functionality. Mater Des 96:106–114. https://doi.org/10.1016/j.matdes.2016.02.018

Lee M, Kim H-Y (2014) Toward nanoscale three-dimensional printing: nanowalls built of electrospun nanofibers. Langmuir 30(5):1210–1214. https://doi.org/10.1021/la404704z

Leppiniemi J, Lahtinen P, Paajanen A, Mahlberg R, Metsä-Kortelainen S, Pinomaa T, Pajari H, Vikholm-Lundin I, Pursula P, Hytönen VP (2017) 3d-printable bioactivated nanocellulose–alginate hydrogels. ACS Appl Mater Interfaces 9(26):21959–21970. https://doi.org/10.1021/acsami.7b02756

Li Y, Zhu H, Shen F, Wan J, Han X, Dai J, Dai H, Hu L (2014) Highly conductive microfiber of graphene oxide templated carbonization of nanofibrillated cellulose. Adv Funct Mater 24(46):7366–7372. https://doi.org/10.1002/adfm.201402129

Li T, Aspler J, Grenon J, Manfred T, Cormier LM, Zou X (2016a) Printed electronics and 3d printing as new manufacturing technologies-new opportunities for bio-based materials. In: NIP & digital fabrication conference. Society for imaging science and technology, pp 435–441

Li T, Aspler J, Kingsland A, Cormier LM, Zou X (2016b) 3d printing–a review of technologies, markets, and opportunities for the forest industry. J Sci Technol For Prod Process 5(2):30–37

Li H, Tan YJ, Leong KF, Li L (2017a) 3d bioprinting of highly thixotropic alginate/methylcellulose hydrogel with strong interface bonding. ACS Appl Mater Interfaces 9(23):20086–20097. https://doi.org/10.1021/acsami.7b04216

Li VC-F, Dunn CK, Zhang Z, Deng Y, Qi HJ (2017b) Direct ink write (diw) 3d printed cellulose nanocrystal aerogel structures. Sci Rep 7:8018. https://doi.org/10.1038/s41598-017-07771-y

Li Y, Zhu H, Wang Y, Ray U, Zhu S, Dai J, Chen C, Fu K, Jang SH, Henderson D (2017c) Cellulose-nanofiber-enabled 3d printing of a carbon-nanotube microfiber network. Small Methods 1(10):1700222. https://doi.org/10.1002/smtd.201700222

Li L, Zhu Y, Yang J (2018a) 3d bioprinting of cellulose with controlled porous structures from nmmo. Mater Lett 210:136–138. https://doi.org/10.1016/j.matlet.2017.09.015

Li VCF, Mulyadi A, Dunn CK, Deng Y, Qi HJ (2018b) Direct ink write 3d printed cellulose nanofiber aerogel structures with highly deformable, shape recoverable, and functionalizable properties. ACS Sustain Chem Eng. https://doi.org/10.1021/acssuschemeng.7b03439

Ligon SC, Liska R, Stampfl J, Gurr M, Mulhaupt R (2017) Polymers for 3d printing and customized additive manufacturing. Chem Rev 117(15):10212–10290. https://doi.org/10.1021/acs.chemrev.7b00074

Lille M, Nurmela A, Nordlund E, Metsä-Kortelainen S, Sozer N (2018) Applicability of protein and fiber-rich food materials in extrusion-based 3d printing. J Food Eng 220:20–27. https://doi.org/10.1016/j.jfoodeng.2017.04.034

Lundahl MJ, Klar V, Wang L, Ago M, Rojas OJ (2017) Spinning of cellulose nanofibrils into filaments: a review. Ind Eng Chem Res 56(1):8–19. https://doi.org/10.1021/acs.iecr.6b04010

Malda J, Visser J, Melchels FP, Jungst T, Hennink WE, Dhert WJ, Groll J, Hutmacher DW (2013) 25th anniversary article: engineering hydrogels for biofabrication. Adv Mater 25(36):5011–5028. https://doi.org/10.1002/adma.201302042

Markstedt K, Sundberg J, Gatenholm P (2014) 3d bioprinting of cellulose structures from an ionic liquid. 3D Print Addit Manuf 1(3):115–121. https://doi.org/10.1089/3dp.2014.0004

Markstedt K, Mantas A, Tournier I, Avila HM, Hagg D, Gatenholm P (2015) 3d bioprinting human chondrocytes with nanocellulose-alginate bioink for cartilage tissue

engineering applications. Biomacromol 16(5):1489–1496. https://doi.org/10.1021/acs.biomac.5b00188
Markstedt K, Escalante A, Toriz G, Gatenholm P (2017) Biomimetic inks based on cellulose nanofibrils and cross-linkable xylans for 3d printing. ACS Appl Mater Interfaces 9(46):40878–40886. https://doi.org/10.1021/acsami.7b13400
Martinez D, Kiiskinen H, Ahlman A-K, Kerekes R (2003) On the mobility of flowing papermaking suspensions and its relationship to formation. J Pulp Pap Sci 29(10):341–347
Mendoza L, Batchelor W, Tabor RF, Garnier G (2018) Gelation mechanism of cellulose nanofibre gels: a colloids and interfacial perspective. J Colloid Interface Sci 509(Supplement C):39–46. https://doi.org/10.1016/j.jcis.2017.08.101
Mertaniemi H, Escobedo-Lucea C, Sanz-Garcia A, Gandía C, Mäkitie A, Partanen J, Ikkala O, Yliperttula M (2016) Human stem cell decorated nanocellulose threads for biomedical applications. Biomaterials 82:208–220. https://doi.org/10.1016/j.biomaterials.2015.12.020
Montalvo Navarrete JI, Hidalgo-Salazar MA, Escobarnunez E, Rojas Arciniegas AJ (2017) Thermal and mechanical behavior of biocomposites using additive manufacturing. Int J Interact Des Manuf (IJIDeM). https://doi.org/10.1007/s12008-017-0411-2
Moon RJ, Martini A, Nairn J, Simonsen J, Youngblood J (2011) Cellulose nanomaterials review: structure, properties and nanocomposites. Chem Soc Rev 40(7):3941–3994. https://doi.org/10.1039/c0cs00108b
Müller M, Öztürk E, Arlov Ø, Gatenholm P, Zenobi-Wong M (2017) Alginate sulfate–nanocellulose bioinks for cartilage bioprinting applications. Ann Biomed Eng 45(1):210–223. https://doi.org/10.1007/s10439-016-1704-5
Murphy SV, Atala A (2014) 3d bioprinting of tissues and organs. Nat Biotechnol 32(8):773–785. https://doi.org/10.1038/nbt.2958
Murphy CA, Collins MN (2016) Microcrystalline cellulose reinforced polylactic acid biocomposite filaments for 3d printing. Polym Compos. https://doi.org/10.1002/pc.24069
Murphy SV, Skardal A, Atala A (2013) Evaluation of hydrogels for bio-printing applications. J Biomed Mater Res A 101(1):272–284. https://doi.org/10.1002/jbm.a.34326
Nechyporchuk O, Belgacem MN, Pignon F (2014) Rheological properties of micro-/nanofibrillated cellulose suspensions: wall-slip and shear banding phenomena. Carbohydr Polym 112:432–439. https://doi.org/10.1016/j.carbpol.2014.05.092
Nechyporchuk O, Belgacem MN, Pignon F (2016) Current progress in rheology of cellulose nanofibril suspensions. Biomacromol 17(7):2311–2320. https://doi.org/10.1021/acs.biomac.6b00668
Nechyporchuk O, Yu J, Nierstrasz VA, Bordes R (2017) Cellulose nanofibril-based coatings of woven cotton fabrics for improved inkjet printing with a potential in e-textile manufacturing. ACS Sustain Chem Eng 5(6):4793–4801. https://doi.org/10.1021/acssuschemeng.7b00200
Nguyen D, Hägg DA, Forsman A, Ekholm J, Nimkingratana P, Brantsing C, Kalogeropoulos T, Zaunz S, Concaro S, Brittberg M (2017) Cartilage tissue engineering by the 3d bioprinting of ips cells in a nanocellulose/alginate bioink. Sci Rep 7:658
Oksman K, Aitomäki Y, Mathew AP, Siqueira G, Zhou Q, Butylina S, Tanpichai S, Zhou X, Hooshmand S (2016) Review of the recent developments in cellulose nanocomposite processing. Compos A Appl Sci Manuf 83:2–18. https://doi.org/10.1016/j.compositesa.2015.10.041
Oropallo W, Piegl LA (2015) Ten challenges in 3d printing. Eng Comput-Ger 32(1):135–148. https://doi.org/10.1007/s00366-015-0407-0
Oskui SM, Diamante G, Liao C, Shi W, Gan J, Schlenk D, Grover WH (2015) Assessing and reducing the toxicity of 3d-printed parts. Environ Sci Technol Lett 3(1):1–6. https://doi.org/10.1021/acs.estlett.5b00249
Ouyang L, Yao R, Zhao Y, Sun W (2016) Effect of bioink properties on printability and cell viability for 3d bioplotting of embryonic stem cells. Biofabrication 8(3):035020. https://doi.org/10.1088/1758-5090/8/3/035020
Pakkanen J, Manfredi D, Minetola P, Iuliano L (2017) About the use of recycled or biodegradable filaments for sustainability of 3d printing. In: International conference on sustainable design and manufacturing. Springer, pp 776–785
Palaganas NB, Mangadlao JD, de Leon ACC, Palaganas JO, Pangilinan KD, Lee YJ, Advincula RC (2017) 3d printing of photocurable cellulose nanocrystal composite for fabrication of complex architectures via stereolithography. ACS Appl Mater Interfaces 9(39):34314–34324. https://doi.org/10.1021/acsami.7b09223
Parandoush P, Lin D (2017) A review on additive manufacturing of polymer-fiber composites. Compos Struct 182(Supplement C):36–53. https://doi.org/10.1016/j.compstruct.2017.08.088
Park JS, Kim T, Kim WS (2017) Conductive cellulose composites with low percolation threshold for 3d printed electronics. Sci Rep 7:3246. https://doi.org/10.1038/s41598-017-03365-w
Pattinson SW, Hart AJ (2017) Additive manufacturing of cellulosic materials with robust mechanics and antimicrobial functionality. Adv Mater Technol 2(4):1600084. https://doi.org/10.1002/admt.201600084
Paxton N, Smolan W, Bock T, Melchels F, Groll J, Jungst T (2017) Proposal to assess printability of bioinks for extrusion-based bioprinting and evaluation of rheological properties governing bioprintability. Biofabrication 9(4):044107. https://doi.org/10.1088/1758-5090/aa8dd8
Penttilä A, Sievänen J, Torvinen K, Ojanperä K, Ketoja J (2013) Filler-nanocellulose substrate for printed electronics: experiments and model approach to structure and conductivity. Cellulose 20(3):1413–1424. https://doi.org/10.1007/s10570-013-9883-9
Piras CC, Fernandez-Prieto S, De Borggraeve WM (2017) Nanocellulosic materials as bioinks for 3d bioprinting. Biomater Sci 5(10):1988–1992. https://doi.org/10.1039/c7bm00510e
Pitt K, Lopez-Botello O, Lafferty AD, Todd I, Mumtaz K (2017) Investigation into the material properties of wooden composite structures with in situ fibre reinforcement using additive manufacturing. Compos Sci Technol 138(Supplement C):32–39. https://doi.org/10.1016/j.compscitech.2016.11.008
Puisto A, Illa X, Mohtaschemi M, Alava M (2012) Modeling the rheology of nanocellulose suspensions. Nord Pulp Pap Res

J 27(2):277–281. https://doi.org/10.3183/NPPRJ-2012-27-02-p277-281
Rees A, Powell LC, Chinga-Carrasco G, Gethin DT, Syverud K, Hill KE, Thomas DW (2015) 3d bioprinting of carboxymethylated-periodate oxidized nanocellulose constructs for wound dressing applications. Biomed Res Int 2015:925757. https://doi.org/10.1155/2015/925757
Rejeski D, Zhao F, Huang Y (2018) Research needs and recommendations on environmental implications of additive manufacturing. Addit Manuf 19:21–28. https://doi.org/10.1016/j.addma.2017.10.019
Ribeiro A, Blokzijl MM, Levato R, Visser CW, Castilho M, Hennink WE, Vermonden T, Malda J (2017) Assessing bioink shape fidelity to aid material development in 3d bioprinting. Biofabrication 10(1):014102. https://doi.org/10.1088/1758-5090/aa90e2
Rigotti D, Nguyen VDH, Cataldi A, Pegoretti A (2017) Polyvinyl alcohol reinforced crystalline nanocellulose in 3d printing application. In: The 21st International conference on composites materials. Xi'an, China, pp 1–8
Rosenthal M, Henneberger C, Gutkes A, Bues C-T (2017) Liquid deposition modeling: a promising approach for 3d printing of wood. Eur J Wood Wood Prod 76(2):797–799. https://doi.org/10.1007/s00107-017-1274-8
Rymansaib Z (2016) Printing materials and processes for electrochemical applications. University of Bath
Saito T, Kimura S, Nishiyama Y, Isogai A (2007) Cellulose nanofibers prepared by tempo-mediated oxidation of native cellulose. Biomacromol 8(8):2485–2491. https://doi.org/10.1021/bm0703970
Salmoria GV, Klauss P, Paggi RA, Kanis LA, Lago A (2009) Structure and mechanical properties of cellulose based scaffolds fabricated by selective laser sintering. Polym Test 28(6):648–652. https://doi.org/10.1016/j.polymertesting.2009.05.008
Schutz K, Placht AM, Paul B, Bruggemeier S, Gelinsky M, Lode A (2017) Three-dimensional plotting of a cell-laden alginate/methylcellulose blend: towards biofabrication of tissue engineering constructs with clinically relevant dimensions. J Tissue Eng Regen Med 11(5):1574–1587. https://doi.org/10.1002/term.2058
Shafeiei-Sabet S, Hamad WY, Hatzikiriakos SG (2013) Influence of degree of sulfation on the rheology of cellulose nanocrystal suspensions. Rheol Acta 52:741–751. https://doi.org/10.1007/s00397-013-0722-6
Shao Y, Chaussy D, Grosseau P, Beneventi D (2015) Use of microfibrillated cellulose/lignosulfonate blends as carbon precursors: impact of hydrogel rheology on 3d printing. Ind Eng Chem Res 54(43):10575–10582. https://doi.org/10.1021/acs.iecr.5b02763
Shatkin JA, Wegner TH, Bilek ET, Cowie J (2014) Market projections of cellulose nanomaterial-enabled products-part 1: applications. Tappi J 13(5):9–16
Shen X, Shamshina JL, Berton P, Gurau G, Rogers RD (2016) Hydrogels based on cellulose and chitin: fabrication, properties, and applications. Green Chem 18(1):53–75. https://doi.org/10.1039/c5gc02396c
Shin S, Hyun J (2017) Matrix-assisted three-dimensional printing of cellulose nanofibers for paper microfluidics. ACS Appl Mater Interfaces 9(31):26438–26446. https://doi.org/10.1021/acsami.7b07609
Shin D-G, Kim T-H, Kim D-E (2017) Review of 4d printing materials and their properties. Int J Precis Eng Manuf-Green Technol 4(3):349–357. https://doi.org/10.1007/s40684-017-0040-z
Siqueira G, Kokkinis D, Libanori R, Hausmann MK, Gladman AS, Neels A, Tingaut P, Zimmermann T, Lewis JA, Studart AR (2017) Cellulose nanocrystal inks for 3d printing of textured cellular architectures. Adv Funct Mater 27(12):1604619. https://doi.org/10.1002/adfm.201604619
Studart AR (2016) Additive manufacturing of biologically-inspired materials. Chem Soc Rev 45(2):359–376. https://doi.org/10.1039/c5cs00836k
Sultan S, Siqueira G, Zimmermann T, Mathew AP (2017) 3d printing of nano-cellulosic biomaterials for medical applications. Curr Opin Biomed Eng 2(Supplement C):29–34. https://doi.org/10.1016/j.cobme.2017.06.002
Tang A, Liu Y, Wang Q, Chen R, Liu W, Fang Z, Wang L (2016) A new photoelectric ink based on nanocellulose/cds quantum dots for screen-printing. Carbohydr Polym 148:29–35. https://doi.org/10.1016/j.carbpol.2016.04.034
Tao Y, Wang H, Li Z, Li P, Shi SQ (2017) Development and application of wood flour-filled polylactic acid composite filament for 3d printing. Materials 10(4):339. https://doi.org/10.3390/ma10040339
Tenhunen T-M, Moslemian O, Kammiovirta K, Harlin A, Kääriäinen P, Österberg M, Tammelin T, Orelma H (2018) Surface tailoring and design-driven prototyping of fabrics with 3d-printing: an all-cellulose approach. Mater Des 140:409–419. https://doi.org/10.1016/j.matdes.2017.12.012
Torres-Rendon JG, Köpf M, Gehlen D, Blaeser A, Fischer H, Laporte LD, Walther A (2016) Cellulose nanofibril hydrogel tubes as sacrificial templates for freestanding tubular cell constructs. Biomacromol 17(3):905–913. https://doi.org/10.1021/acs.biomac.5b01593
Tran TN, Bayer IS, Heredia-Guerrero JA, Frugone M, Lagomarsino M, Maggio F, Athanassiou A (2017) Cocoa shell waste biofilaments for 3d printing applications. Macromol Mater Eng 302(11):1700219. https://doi.org/10.1002/mame.201700219
Ursan ID, Chiu L, Pierce A (2013) Three-dimensional drug printing: a structured review. J Am Pharm Assoc 53(2):136–144. https://doi.org/10.1331/JAPhA.2013.12217
Wang Q, Zhu J (2015) Facile preparation of nanofiller-paper using mixed office paper without deinking. Tappi J 14(3):167–174
Wang Q, Zhu J (2016) Effects of mechanical fibrillation time by disk grinding on the properties of cellulose nanofibrils. Tappi J 15(6):419–423
Wang QQ, Zhu JY, Gleisner R, Kuster TA, Baxa U, McNeil SE (2012a) Morphological development of cellulose fibrils of a bleached eucalyptus pulp by mechanical fibrillation. Cellulose 19(5):1631–1643. https://doi.org/10.1007/s10570-012-9745-x
Wang QQ, Zhu JY, Reiner RS, Verrill SP, Baxa U, McNeil SE (2012b) Approaching zero cellulose loss in cellulose nanocrystal (cnc) production: recovery and characterization of cellulosic solid residues (csr) and cnc. Cellulose 19(6):2033–2047. https://doi.org/10.1007/s10570-012-9765-6

Wang QQ, Zhu JY, Considine JM (2013) Strong and optically transparent films prepared using cellulosic solid residue recovered from cellulose nanocrystals production waste stream. ACS Appl Mater Interfaces 5(7):2527–2534. https://doi.org/10.1021/am302967m

Wang Q, Zhao X, Zhu JY (2014a) Kinetics of strong acid hydrolysis of a bleached kraft pulp for producing cellulose nanocrystals (cncs). Ind Eng Chem Res 53(27):11007–11014. https://doi.org/10.1021/ie501672m

Wang Q, Zhu Q, Xu J, Sun J (2014b) Combined mechanical destruction and alkaline pretreatment of wheat straw for enhanced enzymatic saccharification. BioResources 9(4):6841–6850. https://doi.org/10.15376/biores.9.4.6841-6850

Wang Q, Wei W, Chang F, Sun J, Xie S, Zhu Q (2016) Controlling the size and film strength of individualized cellulose nanofibrils prepared by combined enzymatic pretreatment and high pressure microfluidization. BioResources 11(1):2536–2547. https://doi.org/10.15376/biores.11.1.2536-2547

Wang R, Chen L, Zhu J, Yang R (2017a) Tailored and integrated production of carboxylated cellulose nanocrystals (cnc) with nanofibrils (cnf) through maleic acid hydrolysis. ChemNanoMat 3(5):328–335. https://doi.org/10.1002/cnma.201700015

Wang X, Jiang M, Zhou Z, Gou J, Hui D (2017b) 3d printing of polymer matrix composites: a review and prospective. Compos B Eng 110:442–458. https://doi.org/10.1016/j.compositesb.2016.11.034

Wang Z, Xu J, Lu Y, Hu L, Fan Y, Ma J, Zhou X (2017c) Preparation of 3d printable micro/nanocellulose-polylactic acid (MNC/PLA) composite wire rods with high mnc constitution. Ind Crop Prod 109(Supplement C):889–896. https://doi.org/10.1016/j.indcrop.2017.09.061

Wang J, Chiappone A, Roppolo I, Shao F, Fantino E, Lorusso M, Rentsch D, Dietliker K, Pirri CF, Grutzmacher H (2018) All-in-one cellulose nanocrystals for 3d printing of nanocomposite hydrogels. Angew Chem Int Ed Engl. https://doi.org/10.1002/anie.201710951

Wimpenny DI, Bryden B, Pashby IR (2003) Rapid laminated tooling. J Mater Process Technol 138(1–3):214–218. https://doi.org/10.1016/s0924-0136(03)00074-8

Wu ZY, Li C, Liang HW, Chen JF, Yu SH (2013) Ultralight, flexible, and fire-resistant carbon nanofiber aerogels from bacterial cellulose. Angew Chem 125(10):2997–3001. https://doi.org/10.1002/anie.201209676

Wu Y, Lin ZY, Wenger AC, Tam KC, Tang X (2018) 3d bioprinting of liver-mimetic construct with alginate/cellulose nanocrystal hybrid bioink. Bioprinting 9:1–6. https://doi.org/10.1016/j.bprint.2017.12.001

Xu H-N, Tang Y-Y, Ouyang X-K (2017) Shear-induced breakup of cellulose nanocrystal aggregates. Langmuir 33(1):235–242. https://doi.org/10.1021/acs.langmuir.6b03807

Yang G, Li X, He Y, Ma J, Ni G, Zhou S (2018) From nano to micro to macro: electrospun hierarchically structured polymeric fibers for biomedical applications. Prog Polym Sci 81:80–113. https://doi.org/10.1016/j.progpolymsci.2017.12.003

Yu DG, Branford-White C, Ma ZH, Zhu LM, Li XY, Yang XL (2009) Novel drug delivery devices for providing linear release profiles fabricated by 3dp. Int J Pharm 370(1–2):160–166. https://doi.org/10.1016/j.ijpharm.2008.12.008

Zander NE, Dong H, Steele J, Grant JT (2014) Metal cation cross-linked nanocellulose hydrogels as tissue engineering substrates. ACS Appl Mater Interfaces 6(21):18502–18510. https://doi.org/10.1021/am506007z

Zhang F, Wei M, Viswanathan VV, Swart B, Shao Y, Wu G, Zhou C (2017) 3d printing technologies for electrochemical energy storage. Nano Energy 40:418–431. https://doi.org/10.1016/j.nanoen.2017.08.037

Zhao Y, Li Y, Mao S, Sun W, Yao R (2015) The influence of printing parameters on cell survival rate and printability in microextrusion-based 3d cell printing technology. Biofabrication 7(4):045002. https://doi.org/10.1088/1758-5090/7/4/045002

Zhu H, Luo W, Ciesielski PN, Fang Z, Zhu JY, Henriksson G, Himmel ME, Hu L (2016) Wood-derived materials for green electronics, biological devices, and energy applications. Chem Rev 116(16):9305–9374. https://doi.org/10.1021/acs.chemrev.6b00225