THREE-DIMENSIONAL (3D) PRINTING BASED ON CELLULOSIC MATERIAL: A REVIEW

MOHAMED A. DIAB and MOHAMED EL-SAKHAWY

National Research Centre, Cellulose and Paper Department, Dokki 12622, Egypt
✉ *Corresponding author: M. El-Sakhawy, elsakhawy@yahoo.com*

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During the last few years, the resources for additive manufacturing (AM) advancements have changed rapidly to meet the market demands. Nonetheless, the need for natural composites with enhanced mechanical properties and thermal decomposition in additive manufacturing is not yet widely established. With the growing number of research carried out recently in this field, the production of natural composites for AM materials is becoming increasingly important, due to their thermal performance and biocompatibility. Cellulose is the major biopolymer that has several desirable properties, which have stirred attention to be integrated into AM products. 3D printing techniques have been discussed with special attention to the extrusion method. The advancements in three-dimensional (3D) cellulose-based material printing, and its applications are discussed in this review.

Keywords: 3D printing, additive manufacturing, cellulosic composites, extrusion

INTRODUCTION

Intensive research is carried out to meet growing manufacturing demands stemming from fast-rising population growth. It is known that using non-renewable resources causes substantial global carbon emissions. Moreover, today, just 10% of the plastics used are recycled, leading to further environmental problems.[1] The reduction in petroleum supplies, along with the increase in plastic consumption, is leading the search for new supplies and technologies to make the plastic industry more sustainable and benign for the environment. Viable plastic products should be manufactured without environmental damage from fossil fuels, readily reused, and biodegradable under some environmental conditions with low power production.

Cellulose is the major sustainable resource on the earth, with various favorable properties, such as wide availability, biodegradability and its surface is ready for chemical modification.[2] Smart properties of cellulose-based materials facilitate their use in various fields, such as the paper industry, packaging, textiles, absorbents, pharmaceutical industries, energy storage devices, biosensors, and biofuel production.[3] Different cellulose forms, such as cellulose nanofibrils (CNF), cellulose nanocrystals (CNC), and bacterial nanocellulose (BNC), could be produced. Using different substrates and extraction procedures yielded various nanocelluloses in terms of structure, crystallinity, and properties.[4,5]

Additive manufacturing (AM) is the layer-by-layer method to produce exact three-dimensional (3D) prototypes, with the help of a computer-aided design (CAD) program.[6] Due to the vast prediction of AM in biomedical applications, several biodegradable polymers are utilized as scaffold for 3D printing. AM with cellulose-based materials is a favorable option, owing to its low cost and low environmental impact.

3D PRINTING TECHNIQUES

In recent studies, biomass-derived components are presented as an additional part or enhancer for providing functionalities to 3D-printed objects. However, the incorporation of cellulosic materials influences the polymer mold in production performance, concerning the thermal stability and rheology properties.[7]

The 3D-printer printing tools are very important for the whole 3D printing technique, as they have a significant role in linking digital 3D-models and printing materials. Researches have to solve the practical tasks of material development and process management. The 3D printing

methods with cellulosic materials are usually separated into three groups: (1) Extrusion-based 3D printing systems, including fused deposition modeling (FDM), direct ink writing (DIW), and micro-extrusion 3D-bioprinting; (2) Inkjet 3D printing, and (3) 3D-spinning.[8] The features and limitations of these procedures are discussed below.

Fused deposition modeling

FDM, also known as fused filament fabrication, is a 3D printing tool of the extrusion technique, usually used to print fibre-reinforced polymer composites. The features of thermoplastic polymers, specifically, their low melting temperature and good flow abilities, encourage their utilization in the FDM process. A limited number of thermoplastics are used, such as polyamide acrylonitrile butadiene styrene, and polylactic acid (PLA). The pre-formed filament is filled mechanically via a pair of gears into the liquefier system. The rate of loading is controlled by the program for printing. To confirm proper friction between the filament and the gears, the filament diameter is adjusted, along with the default hole between the two gears. As the filament is regularly loaded into the liquefier, the subsequent cold end drives the previous melt end through the fixed-diameter nozzle onto the preheated plate or the previous layer with continuous lines (Fig. 1). The intended design is then fashioned and precipitated on the Z-axis.[9,10]

Direct ink writing

Direct ink writing (DIW) is another extrusion-based 3D printing process. In this process, the ink is commonly spread by a pneumatic pressure system to a platform on the X–Y plane through a needle (Fig. 2). Similarly to the FDM procedure, the 3D structure is produced by way of a syringe movement. The ink poured into the syringe is composed of resin and its curing agent. Heat treatment or ultraviolet radiation is used for ink curing after extrusion. The filaments dissolve, unlike in the case of FDM, to the designed form, with proper flowability, and solidify after that by cooling. To prepare the inks, cellulose products, in the appropriate ratio, are combined with other compounds, in the required solvent, under stirring. DIW is very sensitive to the rheology of components, since it estimates the printability and finally, the features of the obtained parts. Fast and simple evaluation tools for hydrogel dispensing methods and efficiency are required for scientists to improve novel ink preparations. Understanding the dynamics of fibre alignment and rheological properties is required to design inks and printing techniques.[11] A current analysis of ink formulations with other studied materials has been reported and could be utilized for cellulosic bio-ink printability estimation. Ink printability is influenced by the gelation behaviour, rheological parameters and viscoelasticity of the ink, as well as by printing factors, such as extrusion power, feed rate, holding temperature, time, printing distance, and interlayer diffusion in various 3D printing tools with different procedures.[12] Varying the viscoelastic ink formulation and/or concentration shows a path to spreading the printability window.[13]

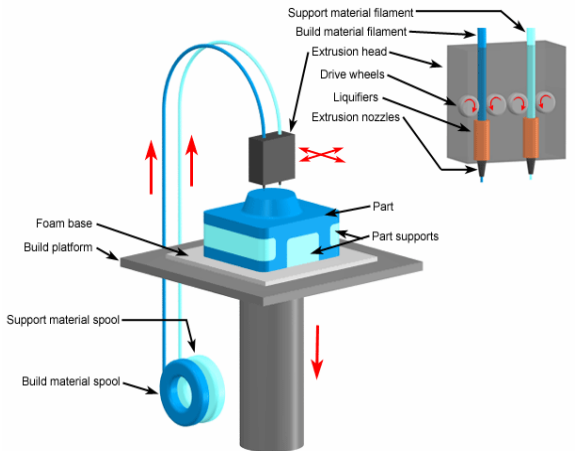

Figure 1: Fused deposition modeling (FDM)

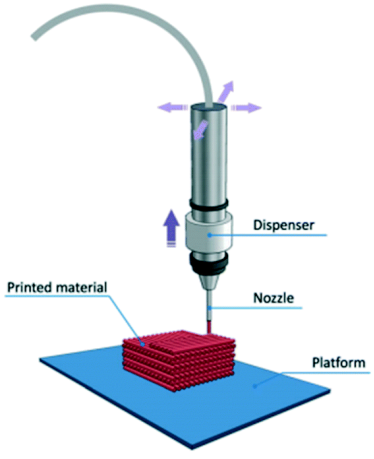

Figure 2: Direct ink writing (DIW)

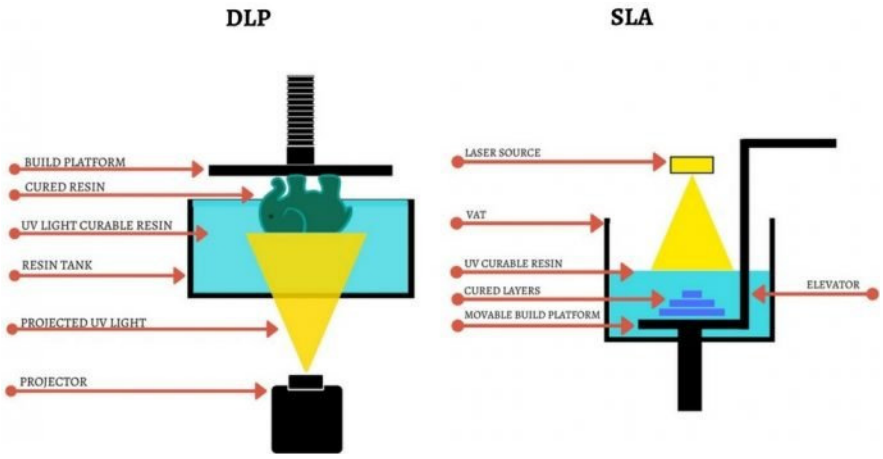

Figure 3: Stereolithography (SLA)/digital light processing (DLP)

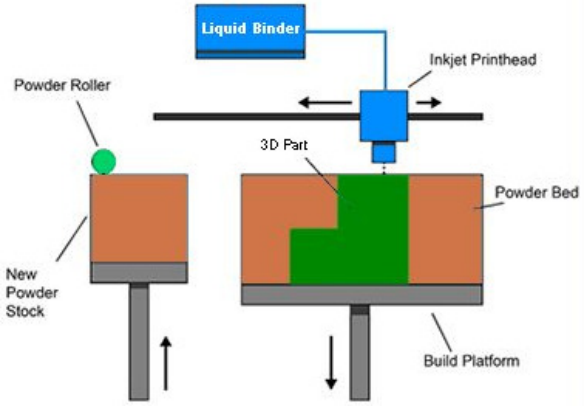

Figure 4: Binder jetting processing

Cellulose is inherently hydrophilic; it forms a stable aqueous suspension in different forms. So, cellulosic hydrogels are considered a remarkable ink candidate for direct DIW 3D printing. Rheological properties and apparent viscosity produced sufficient stress for elastic repair to avoid failure.[14]

Stereolithography (SLA)/digital light processing (DLP)

SLA is one of the early 3D printing processes. A two-dimensional (2D) SLA form is produced by UV or light photo-reactive resin. During SLA printing, the plate is immersed in a resin container, where the area between the pre-cured layer (or surface) and the container base is designed as the desired thickness of the layer. The photo-polymerization of the resin starts with point-by-point UV light scans to the 2D template in the selected positions. The DLP technique is similar to that of SLA, but the desired photo-polymerization is initiated by dropping the related UV design to the X-Y objective plane in the situation of point scanning (Fig. 3). So, the DLP method prints faster than the SLA. Recent researches suggested the use of cellulosic inks in SLA/DLP for 3D printing processes.[15,16] 3D printing with a CNC nanocomposite hydrogel by the stereolithography process was used to form a material with enhanced properties, appropriate for tissue engineering.[17]

Binder jetting

Unlike the other tools discussed above, binder jetting precipitates the liquid binder on powdered raw resources to create each layer. The powder is periodically spread on the platform or the previous layer by printing, and the bonding adhesive is then precipitated into the powder to achieve the intended pattern. After the first layer has formed, the platform leaves a layer height, accompanied by the dispersion of another powder

layer by a leveling roller for the next cycle of precipitation of the binder (Fig. 4). This method has been adapted for manufacturing drug delivery tablets with cellulose-based materials.[18]

Inkjet printing

Inkjet printing exhibits superior printing resolution than FDM or DIW. The ink droplets solidify and precipitate over the selected substrate surface through thermal, chemical, or electrical processes during the printing (Fig. 5). UV radiation and laser sintering are used at present to precipitate the material and add benefits to the resulting solid structure. Droplet speed and melting, substrate surface energy, printing speed, nozzle diameter, and ink viscosity are the parameters that affect the quality of inkjet printing.[19] Ionic liquids were used as solvents for cellulose, with co-solvents as rheological modifiers, in inkjet printing processes.[20] Using cellulose nanofibre-based conductive composites, by means of inkjet printing, sustainable electronic textiles have been invented.[21]

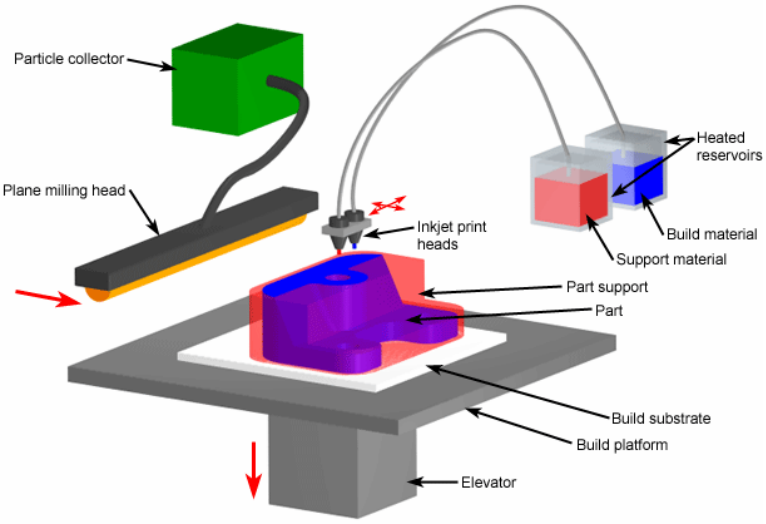

Figure 5: Inkjet 3D printing processing

3D-spinning printing

In 3D printing, 3-dimensional target objects are fashioned by adding several consecutive thin layers of material. In this perspective, electrospinning can be used to produce a variety of 3D forms with nano- or micro-fibrous hierarchical structures. Cellulose acetate/pullulan solution scaffolds were fabricated by electrospinning to 3D filaments with variable thickness, of nano- to micro-scale size.[22]

Significant factors that affect printability during 3D printing

Since the shapes in most 3D printing processes are fabricated from thin filament layers, the filament manufacturing process, filament material composition and the filament thermo-plasticity play a vital role in this process. The working and printing parameters of each process should also be considered. These parameters include bed temperature, nozzle temperature and diameter, raster angle and width, and shape orientation.[23]

Extrusion temperature is a critical factor for filament preparation, which is chiefly managed by the glass transition temperature (Tg) and the degradation temperature (Td) of the polymer. In 3D printing, the ink material is an essential issue in selecting the printing method and the processing conditions, such as the printer settings and extrusion temperature. Cellulose ethers, with moderate and high molecular weights, exhibit gelation under the influence of thermal energy, which is a desired feature for 3D printing. Also, the natural thermoplastic features, modest Tg, and large thermal processing choice, as well as rheological characteristics (viscosity, viscoelasticity, yield stress, rigidity) recommend cellulose and its derivatives as suitable polymers with broad applications in 3D printing.[24]

Hydrogels are generally printed with the extrusion-based printing technique. Appropriate materials for 3D printing should have suitable rheological properties to readily flow through the nozzle, while the gel forms. Viscoelastic materials can extrude smoothly through the nozzle. So, understanding the rheological behavior of the materials is necessary to print composites with optimal properties and fidelity. Cellulosic hydrogels for 3D printing should exhibit shear-thinning performance to allow continuous flow through nozzles, and rapidly recover a solid-like response, with a sufficiently high storage modulus and yield stress to maintain its filamentary shape after printing.[25]

3D PRINTING WITH CELLULOSE AND ITS DERIVATIVES

Cellulose and its derivatives are already being used as valuable and efficient bio-feed stocks for 3D printing.[26,27]

Cellulose materials, without chemical modification, are in general considered impracticable for 3D printing, because they thermally decompose before they can melt and become flowable when heated. Cellulose dissolved in *N*-methyl morpholine *N*-oxide (NMMO) can be utilized as a 3D-printing ink at 70 °C via DIW printing technique. After cooling, the solidified cellulose/NMMO matter, regenerated into cellulose scaffolds in water, showing remarkable compressive Young's and tensile moduli.[28] A cellulose gel, made out of cellulose dissolved in aqueous sodium hydroxide and urea, was used as a bio-ink material for 3D printing using the extrusion technique. The printing results confirmed the capability of the applied method to 3D print complex parts by the newly developed bio-ink.[29] Cellulose dissolved in an ionic liquid (1-ethyl-3-methylimidazolium acetate) could be used as a 3D bio-ink to produce spatially tailored design objects from regenerated cellulose. The printed solutions were regenerated by coagulating the gel (by a non-solvent), within a few seconds.[30]

The regenerated cellulose film (RCF) has a smooth surface, high transmittance, and flexibility. RCF can completely link with conductive materials to fabricate high-efficiency CRCF. The developed CRCF offers significant predictions in the field of flexible electrical appliances, such as flexible substrates, portable sensors, fuel cells, *etc*. The exceptional properties displayed by RCF are assisting in increasing the high efficiency of green RCF-based optoelectrical devices. Cellulose is an inherently protected substance; conductive materials must therefore be provided to formulate the CRCFF in the cellulosic network.[31,32] Raghunathan *et al.* designed an *in-situ* polymerization process for the preparation of conductive polypyrrole in the cellulose substrate, where the amount of monomer pyrrole has a major impact on the effectiveness of CRCF. Composites exhibited higher constant dielectric and low dielectric loss, which are important in the application of capacitors.[33,34] Lui *et al.* explained a spin-coating process to produce CRCF based on polypyrrole (PPy). The produced CRCF with a three-layer PPy had a transmittance of 30% and a conductivity of 0.042 S/cm.[35]

By chemical modification, a cellulose hydrogel could acquire various functional groups. For instance, nanocellulose/alginate hydrogels were modified by interaction with avidin to get a 3D-printing ink.[36] Useful 3D printing inks could include a blend of various functional chemicals, such as conductive particles, antimicrobial agents, PPy, CNTs, graphene, or magnetic nanoparticles.[26] Abouzeid *et al.* and Erkoc *et al.* have improved a hydrogel ink for 3D printing by the extrusion technique, which consisted completely of natural polymers, namely cellulose, gelatin, and alginate or PVA. The natural hydrogel as a 3D-ink presented a promising 3D-ambiance for proliferation and cell growth, with the advantages of low-cost environmentally friendly materials, with a fast and easy post-crosslinking approach to mimic natural tissues.[37,38]

Cellulose composites with other natural polymers, for instance, alginates and gelatins, have been widely considered for the development of aerogels and hydrogels for 3D printing. 3D printing widens the uses of cellulose in biomedical applications (such as wound dressing devices, prostheses, and tissue engineering), wearables, electronics, and load-bearing applications. Cellulose-based compounds have been extensively searched for 3D printing formulations as a binder, matrix, rheology modifier, excipient, and reinforcement. In these processes, composites are used to create a gel or ink with particular rheological properties appropriate for 3D print configuration, which could be regenerated by heat or UV curing, chemical crosslinking, or just by drying under atmospheric conditions, by freeze-drying or heating.[11]

3D printing with cellulose ethers

Cellulose ethers can be particularly easily prepared industrially by replacing the cellulose hydroxyl groups with other functional groups, as methyl, hydroxyethyl, *etc*.[35] Cellulose ethers include methylcellulose (MC), ethylcellulose (EC), hydroxyethylcellulose (HEC), hydroxypropyl cellulose (HPC), hydroxypropyl methylcellulose (HPMC), and carboxymethylcellulose (CMC). Depending on the type and degree of substitution, cellulose ethers are soluble in water, aqueous alkaline solutions or different types of organic solvents. 3D prints with these cellulose ethers have established applications in controlled drug release and tailored drug dosage formulations.[36]

Cellulose ethers can be widely used in 3D printing, for specific components, as their flexible features include high chemical stability, physiological protection, good solubility, and good biodegradability. The modified bio-feedstocks for 3D printers could be formulated with a mixture of cellulose derivatives and nanocellulose, to get accurate and smooth extrusion, and attain attractive artwork with controllable shape. The improvement of a hydrogel composite stock, involving cellulose fibres and CMC hydrocolloid, for 3D printing was studied by Mulakkal *et al.* to be applied in architectures with different microstructures for induced morphing.[39] CMC and its derivatives have been fabricated as smart bioinks for 3D bioprinting. The abnormal features of CMC in 3D bioprinting applications, as in tissue engineering, have been elaborated in detail.[40] CMC chemically modified using methacrylic anhydride has been investigated as a bio-based photocurable ink for digital light processing (DLP) 3D printing.[41]

HEC solutions have a pH-dependent gelation time and present shear-thinning properties, which allows the rheology adjustment for 3D printing using various additives. HEC (10 wt%) with MCC, lignin, and/or citric acid was used as ink to print 2D surfaces with functional properties.[11]

Hydroxypropyl methylcellulose (HPMC) has certain advantages over conventional materials, such as low printable temperature, low cost and high biodegradability. Shear-dependent viscosity makes the HPMC hydrogel an appropriate ink throughout the 3D printing process for a stable printed structure without deformation. The printed support material was compatible with acrylonitrile butadiene styrene (ABS), which is the material to formulate the main structure for 3D printing.[42]

Cellulose esters as matrixes

The use of cellulose esters, such as cellulose acetate (CA), acetoxypropyl cellulose (APC), and cellulose acetate butyrate (CAB), has also been investigated as expectant materials for 3D printing. The DIW technique was used for 3D printing with rigid CA and flexible APC onto cellulosic fabrics to produce textiles with convenient functionalized properties.[43]

Pattinson and Hart (2017) dissolved cellulose acetate (CA) in acetone and then 3D printed the viscous, yet a flowable solution. Solid CA configurations, with high toughness and isotropic strength, were constructed by acetone evaporation. 3D printing of CA-based items, with adapted biochemical functionality (as antimicrobial properties), can be achieved directly by the inclusion of antimicrobial agents. The results showed that a concentration of 25-35 wt% was appropriate for 3D printing, since it allowed to reach a compromise between shape retention and flowability. Minute eyeglass frames and a small rose were printed.[44] CA has good tissue engineering properties, with high mechanical properties, and the material is able to imitate the cell-matrix for cell proliferation studies.[45]

3D printing with microcrystalline cellulose (MCC)

MCC is a crystalline white powder obtained from the depolymerization of cellulose by common physical or chemical treatments. MCC is a brilliant applicant for the production of 3D-bio-feed stocks, particularly, for the manufacture of drug tablets through the 3D printing technology.[46] MCC was employed as a squeeze and pushing agent in conjunction with HPMC polymer to fabricate a 3D-printed multiple-dosage system, which included three different drugs with distinct release profiles, combined into a single tablet, using a pneumatic extrusion 3D printer. MCC, as a disintegrating agent, was used in 3D printing to prepare oral dosage forms with pulsatile drugs release profiles.[47] MCC was applied as a supporting constituent for PLA, at 1-5 wt%, in a solvent casting method and was effectively subjected to hot-melt extrusion (HME) for filament preparation and FDM 3D printing. MCC was modified with a coupling agent (titanate) to develop its compatibility with hydrophobic PLA.[28]

MCC in cement-based composites can satisfy the necessities for 3D printing. The ample enhancement in rheological properties and

buildability, in addition to the environmental advantages, encourage the utilization of MCC in 3D-printing to reinforce the cement-based materials.[48]

3D printing with nanocelluloses

Nanocelluloses, CNF and CNC, are well-known classes of cellulose derivatives. In addition to amorphous regions, CNF is known to include crystalline regions, with a fibril diameter of 5-100 nm and lengths of around several micrometres, whereas CNC can be prepared from crystalline regions of cellulose by acid hydrolysis or oxidation methods (ammonia persulfate or TEMPO oxidants). CNC has a high crystallinity of 54-88%, a dimensional volume of 50-500 nm, and a diameter of 3-10 nm. Nanocellulose is biodegradable, non-toxic and biocompatible, with benign effects on the environment and safe for health. Due to its superior mechanical and optical properties, high aspect ratio, enhanced tensile strength, low thermal expansion coefficient, nanocellulose finds numerous applications in hydrogels, coating additives, paper making, flexible screens, food packaging *etc*. It also finds bio-medical applications, as in drug delivery and in fabricating temporary implants.[49] A simple method of producing a complex nanocellulose as a 3D composite design for biomedical and energy applications was developed by combining the technical abilities of 3D printing tools with a wet densification method.[11]

The application of CNCs in various 3D printing methods as building blocks or reinforcing agents has been reviewed.[50] The development, challenges and applications of the CNC-based bioinks in 3D printing have been considered.[51]

CNCs are highly dispersible in water as nanoparticles, which allow them to be entirely washed out by water; this offers an efficient and green way to remove the CNC support matter in post-processing. Since the CNC gel is completely water-based and is derived from natural sources, the process of 3D printing was considered sustainable, environmentally friendly, and potentially recyclable.[52] The 3D printing technology was used to formulate viscoelastic hydrogels composed of anisotropic CNC using the extrusion technique. The results proved that optimal fidelity and print resolution was attained at 20 wt% CNC hydrogels, which exhibited a high degree of CNC orientation (72%-73%) along the printing direction.[53]

Bio-based inks suitable for 3D printing applications were produced by cross-linking of cellulose CNFs with various metal cations. It was found that merely the gels integrated with divalent cations, as Ca^{2+} and Mg^{2+}, were appropriate for 3D printing.[54] A highly conductive and strong carbon nanotube/nano-fibrillated cellulose composite (CNT–NFC) has been developed by a fast and scalable 3D-printing technique by extruding the spinning solution. Merging the high mechanical strength and electrical conductivity of the CNT–NFC composite during 3D-printing recommends this composite as a promising candidate for wearable electronic devices.[55]

3D printing with cellulose polymer composites

The core concepts of green chemistry revolve around the reduction of wastes to be created by new generations. In this modern digital technology, this effect can be initiated by the introduction of renewable natural materials in 3D printing applications. In addition to their mechanical properties, the bio-filler and hydrogel matrix abilities of cellulose-based polymers make their use in sustainable additive manufacturing a future goal. There are different techniques for the processing of CNF-reinforced nanocomposites. However, layer-by-layer (LbL) assembly, electro-spinning and wet-spinning, vacuum-assisted filtration, cast-drying and freeze-drying, and various micro-patterning techniques are the most cited in recent literature.[56]

A bio-composite filament using CNF as a filler and polylactic acid (PLA) as a matrix was developed for fused deposition modeling (FDM) 3D printing. CNF increased the tensile strength, elongation at break, and thermal stability of the PLA/PEG600/CNF composite, signifying enhanced compatibility for desktop FDM 3DP.[49] Polybutylene succinate (PBS) with PLA/CNF nanocomposite was also extruded into filaments for prototype 3D printing. The results demonstrate a successful conversion of waste into valuable bio-nanocomposites with unique properties for compostable packaging applications.[57] CNF and graphene improved the polyurethane filament properties and printability. The achieved flexible and printable nanocomposites showed potential for biomedical applications.[58] A CNC based hydrogel ink with sodium alginate and gelatin matrix was developed and 3D printed into uniform scaffolds with gradient pore structure.[59] Antimicrobial alginate/cellulose hydrogels ink with *in-situ* synthesized copper nanoparticles

were developed. The ink has enhanced printability and improved performance toward antimicrobial 3D-printed matter.[60]

APPLICATIONS OF 3D PRINTED CELLULOSE MATERIALS

Multipurpose applications of 3D printing with biomass-derived cellulose have been reported for the development of a variety of advanced materials in medicine, electronics, smart packaging, textiles *etc*.

Medical applications

The exclusive benefits of cellulosic derivatives, including biocompatibility, low toxicity, and biodegradation, allow their extensive use in biomedical applications.[61] Cellulose (particularly, its nano-sized forms: CNC, CNF, and bacterial nanocellulose), cellulose-based hydrogels, and cellulose derivatives are considered as perfect materials with tremendous potential for applications in 3D-printed pharmaceuticals and the fabrication of multifunctional drug-delivery devices,[47] as new inks suitable for biomedical applications,[41] as 3D scaffolds,[62] in wound healing, controlled drug delivery, tissue engineering, and cell growth,[38] in cartilage and bone tissue engineering.[63]

Nanocellulosic materials have played a crucial role in 3D printing, owing to their biocompatibility, biodegradability, renewability and printability properties, as well as their live-cell support ability, and their shear thinning behaviour. The developments and challenges in 3D printing using nanocellulose-based hydrogels for mammalian cell viability and fast printing of customizable scaffolds, tissues, and organs have been discussed.[64] CNC and CNF, in 3D printing bio-inks, have attracted remarkable interest in biomedical applications. In multifunctional drug delivery systems, especially oral solid dosage forms, they offer perfect flexibility and control in dosing, design, and drug release with cost-effectiveness.[47] There have been successful applications for organ transplants, skin grafting, and cancer screening and treatment.[65] The effective surface area of CNF allows its broad applications in sustainable antibiotic delivery, antimicrobial films, and bio-sensing for wound healing, the improvement of drug delivery systems, and the preparation of scaffolds for tissue cultures.[66] 3D printed cartilage, using CNF and alginate/hyaluronic acid, was used for stem cell culture to incorporate an *in-situ* physiological environment.[49] CMC-based hydrogels were applied as 3D printer inks for tissue engineering applications, with the advantages of precise control of scaffolding and cells, and offering the possibility to design and simulate different tissues and organs with digital control.[67]

Electronics applications

Cellulose-based 3D printed objects, with the incorporation of particular metals to attain the desired functions, with stronger mechanical properties, are essential in the progress of electrical engineering applications. A cellulose acetate and aluminum composite sensor was 3D printed to detect the humidity of sweat in a contactless way. A CNF/alginate hydrogel modified with poly(3,4-ethylene dioxythiophene) could store electrical charge and exhibited high electrical conductivity. The electrical conductivity varies with the humidity; therefore, modified cellulose could be used as a humidity sensor.

Cellulose-based/silver nanowire composites have been investigated for the printing of electrically conductive materials. For example, the 3D printing of CMC/silver nanowire was conducted to fabricate a lithium battery, which verifies that cellulose-based electronics will be next-generation materials. The 3D-printed lithium-based anode and cathode with CNF showed elevated specific capacity, with the benefit of various designs through 3D printing.[45]

A group of robust, fluorescent shape-memory thermosets from cellulose and rosin-based photosensitive 3D-printing ink has been developed. These 3D-printed thermosets were degraded in the NaOH aqueous solution to produce flexible conductive hydrogels, which have significant application in smart photoelectric materials and flexible electronic materials.[68]

Textile applications

3D printing using cellulose-based products was studied to tailor stronger desired products. Cellulose acetate and acetoxypropyl cellulose were used in 3D printing on woven cotton-based textile to discover the feasibility of cellulose-based materials for advanced textile applications. CNF coating on fabrics was developed to fabricate electronic textiles for medical and other purposes that do not require washing.[45] 3D printing with nanocellulose can be also used for developing protective textiles.[49]

3D printing with cellulose-based materials on cellulosic fabrics was performed by direct

printing of cellulose derivatives on woven viscose, woven cotton, and knitted cotton and fabrics. The applicability of 3D printing for textiles with cellulose-based inks was assessed for surface tailoring of textiles. It was found that it reduces labour-intensive processing or the use of external glues, and may enable new and simple adaptation processes with minimized material usage.[43]

Food printing and packaging

A variety of natural dietary fibres, such as cellulose, hemicelluloses, starch, pectin and chitosan, have been gaining increasing interest in 3D food printing, owing to their nontoxicity, edibility, bioactivity, high abundancy, and long history of safe utilization in traditional food production.[69] 3D printing has been used in food applications to fabricate food with the desired dimension and shape. CNF in food printing assists in maintaining the printed food structure.[38]

In recent years, 3D printing has enjoyed enhanced utilization in the production of molds and prototypes for the industry. CNC and CNF have been used to produce new, high-value products for 3D manufacturing technology. 3D printing may have a perspective in the fabrication of advanced packaging products.[70] The application of CNC inks for packaging offers the desired packaging shape. Cellulosic nanomaterials have demonstrated excellent oxygen barrier properties for food and pharmaceutical applications.[45]

Table 1 demonstrates the applications of some cellulose polymer composites in 3D printing.

Table 1
Cellulose polymer composites in 3D printing applications

Cellulose source/type	Cellulosic composite	3D printing technique	Application	Ref.
Plum seed shells/CNC	PLA/PHB/CNC	FDM extrusion	Engineering applications	[71]
Heda Co. Ltd., China/hydroxypropyl methylcellulose (HPMC)	HPMC/PLA	FDM extrusion	Biomedical applications	[72]
Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China)/ Microcrystalline cellulose (MCC)	Acrylonitrile-butadiene-styrene (ABS)/cellulose nanocrystals/silica nanohybrids	FDM extrusion	Hybrid materials	[73]
Sigma Aldrich/ Microcrystalline cellulose (MCC)	Polycaprolactone (PCL)/ Microcrystalline cellulose (MCC)	FDM extrusion	Bone tissue engineering	[74]
Oil palm empty fruit bunch/cellulose nanofibrils (CNF)	Polyurethane (PU)/CNF/reduced-graphene oxide (rGO)	SLS	Bio-based resin	[75]
Guangzhou Chemical Reagent Factory (Guangzhou, China)/MCC	Polymethyl methacrylate (PMMA)/CNC/Ag-NP	Digital light projection	Dental clinical trials	[76]
University of Maine (ME, USA)/CNC	CNC/methacrylate (MA)	SLS	Electronics, energy, and tissue engineering	[77]
Aladdin Industrial Inc./Ethylcellulose	Rosin monomer (DAGMA)/ ethylcellulose macro-monomer (ECM)	SLS	Flexible electronics and smart photoelectric devices	[78]
Wood pulp/CNC	Poly(ethylene glycol) diacrylate (PEGDA)/ 1,3-diglycerolate diacrylate (DiGlyDA)/CNC	DLP	Biomedical applications	[15]
Bleached *Humulus japonicus* stem/CNC	CNC/gelatin	FDM extrusion	Tissue engineering	[79]
Norwegian spruce, Sarpsborg, Norway/CNF, Madison, USA/CNC	CNF/alginate CNC/alginate	DIW extrusion	Wound dressings and face masks	[80]

Hai Nan Yeguo Foods Co., Ltd., China/BC	Silk/gelatin/BC	FDM extrusion	Tissue regeneration and organ reconstruction	81
Stora Enso (Karlstad, Sweden)/CNF	CNF/xylan–tyramine (XT)	FDM extrusion	Packaging, health care products, clothes and furniture	14
Plant-based cellulose (fibers, medium)	Gelatin/cellulose/alginate	FDM extrusion	Medical prosthesis, tissue engineering, food additives, soft micro-robots, and pharmaceuticals	38
Bleached bagasse pulp/CNF	PVA/cellulose/alginate	FDM extrusion	Bone and tissue engineering	37
Eucalyptus pulp/CNC or CNF	2-Hydroxyethyl methacrylate/CNC or CNF	DIW	Biomedical applications and energy devices	13

CONCLUSION

3D printing procedures using cellulose-based materials have been reviewed; the properties of the formed 3D cellulose-based composites and factors affecting 3D printing with cellulosic materials have been discussed.

Owing to its amazing properties, cellulose, with all its known forms and derivatives, generously affords the basis for formulating and designing targeted 3D printed products. The full potential of cellulosic materials to integrate into AM is still to be investigated. Additional research should be done to increase the mechanical properties of the fabricated products. Interfacial adhesion could be enhanced by surface grafting of cellulose to increase its hydrophobicity. The filament's biodegradability could be enhanced by increasing the cellulose proportion in the 3D printing filaments. The extrusion method is favoured for integrating cellulose and cellulosic derivatives, owing to their rheological properties. Due to its enhanced mechanical properties, a high cellulose fraction could be employed and the formation of printed elements could be retained after printing. Considering specific application requirements, cellulosic materials can be synthesized so as to impart them with the intended properties, to make them suitable for incorporation into this AM emerging technology for developing a wide array of advanced materials for a variety of applications.

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