Chapter 13 3D Printing using Cellulose Nanoparticles

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ABSTRACT

Cellulose is naturally available and most abundant biopolymer on earth. It is one of the main constituents of cellulosic materials, such as wood, plant fibres (flax, hemp, jute), among others. Due to their high surface properties and high aspect ratio, excellent mechanical properties, cellulose is extensively used in composite reinforcements. Cellulous nanoparticles (CNP) can be utilised in developing cellulose nanocomposites with enhanced mechanical and thermal properties for various applications: biomedical and other engineering applications. Three-dimensional (3D) printing also known as additive manufacturing (AM) is an emerging advanced manufacturing process widely used in key industry sectors including, but are not limited, to automotive, aerospace, electronics, construction and biomedical fields, owing to their several attractive attributes in comparison with conventional or subtracting manufacturing technology. In recent years, this technology has been explored in fibre reinforced polymeric composites, such as cellulose composites and nanocomposites. This chapter aims at investigating 3D printing as a viable fabrication method for cellulose nanoparticles incorporated nanocomposites and comparing their important mechanical properties with respect to key 3D printing factors and process parameters, including CNPs properties and morphologies.

Keywords: Cellulose nanoparticles (CNP), Additive manufacturing (AM), Fused deposition modelling (FDM), Cellulose nanocomposites.

13.1 Introduction

Cellulose is a linear biopolymer which consist of amorphous and crystalline domains in an alternative manner. Cellulose is the main structural element of cellulosic materials, such as wood, natural plant fibres: flax, kenaf, jute and hemp, to mention but a few. Cellulose is also the most important organic and renewable biopolymer produced by plants. Cellulose is also linked with other important constituents, such as hemicelluloses and lignin. Cellulose nano fibres (CNFs) and cellulose nanocrystals (CNCs) are considered part of Cellulose nanoparticles (CNPs) which can be taken out from wood and natural plant fibres. These CNPs are utilised in many applications as reinforcing materials in polymer nanocomposites. Due to their attractive properties, such as high surface areas, high aspect ratio (length divided by diameter) and high mechanical properties, especially strength and modulus, as well as their renewable attributes, these materials have been used as multifunctional reinforcements in composites and nanocomposites. Cellulose nanoparticles obtained from nanocellulose exploits cellulose as a novel career to make nanoparticles (NPs)[1].

The incorporation of nanofillers to improve the properties of polymers has been used as effective ways for last three decades. Polymer nanocomposites developed by Toyota have shown a significant properties enhancement (strength and stiffness) with the incorporation of small amount of nanoparticles incorporation into polymer matrices[2,3]. Because of the high surface areas and aspect ratios over host polymers, high interfacial regions and intercalation and exfoliation structures, nanocomposites from these materials show some unique and outstanding properties in comparison with their conventional microcomposites counterparts[4,5,6].

In recent years, three-dimensional (3D) printing also known as additive manufacturing (AM) technology has gained a significant interest in academic and industrial communities for developing high performance complex products in relatively low cost[7]. Due to the advancement in technologies, 3D manufacturing process has played significant roles in production of complex geometries. 3D printing of cellulose nanoparticles (CNPs) combined with different polymers has been suggested as a viable route for producing cellulose nanocomposites[8].

In conventional manufacturing process also known as subtracting manufacturing, required shapes and sizes are achieved by removing or subtracting parts. In such process, significant amount of materials is wasted and obtaining a complex shapes and geometries is not easy. The process of forming or shaping of materials into desired objects involving three key manufacturing processes[9], namely:

1. Subtractive manufacturing: The desired shape and size are obtained by the removal or subtracting part of material. Some examples include drilling, milling, turning and grinding.
2. Formative manufacturing: In this process, the desired shape is obtained by the application of pressure or forces, as applicable in forging, casting, injection

moulding, among others. This process is also known as near net shape manufacturing process, which only requires minimum amount of finishing process.

3. 3D printing/AM: The desired shape is obtained by successive addition of materials layer by layer during this process. Also, any complex shape of 3D object can be made from a digital model through 3D printing[10].

13.2 Overview of Additive Manufacturing

13.2.1. Background

In this chapter, the term AM and 3D printing is used interchangeably. AM, as defined accordance to ISO/ASTM 52900-15, is “process of joining materials to make parts from 3D model data, usually layer upon layer, as opposed to subtractive manufacturing and formative manufacturing methodologies”[9]. As briefly outlined in the above section, 3D printing broadly involves the deposition of particles or drops in the form of layer by layer to form a shape (3D geometries) from a digital model manly from computer-aided design (CAD). 3D printing is also synonymised with additive techniques, additive fabrication, layer manufacturing and freedom fabrication. In this process, complex shapes are produced, which is completely the opposite of subtracting manufacturing process under which this would not be possible. 3D printing therefore is a novel manufacturing process that facilitates fabrication of very complex structures (metallic/alloys, ceramic and polymers) with unique materials properties in comparison with traditional manufacturing processes (subtractive and formative).

13.2.2. Advantages and Limitations of Additive Manufacturing Processes

AM process offers several advantages when compared with traditional manufacturing process, as its key benefits are subsequently outlined[11]:

1. Complex shape with lightweight structures can be produced.
2. Decreased buy-to-fly ratios.
3. Improved and optimised design flexibility with variety (little time required to change the design in CAD).
4. Less materials waste as opposed to traditional manufacturing processes.
5. Responsive production (for low volume AM offers faster lead times than traditional manufacturing).
6. Shortened and simplified manufacturing supply chain.
7. By using less materials, less wastes, less energy, AM can emerge as energy efficient manufacturing process.
8. Improvement in quality when optimised for specific functions, such as hollow and lattice structures.

Despite several benefits, AM also has some limitations as outlined below:

1. Mechanical properties of AM printed parts are often lower than that of traditional manufacturing process
2. High production cost and considerable time required to set processing parameters
3. Difficult for AM technologies to compete with some traditional manufacturing, such as injection moulding in terms of reliability and reproducibility.
4. Lack of selection of materials portfolio (mainly suitable to thermoplastics).

13.3 Review of Additive Manufacturing Methods for Polymers

13.3.1. Additive Manufacturing of Different Polymers

In recent years, AM techniques have been extensively used for the fabrication of polymeric composite parts. It is worth reiterating that in all branches of 3D printing technology, the principal characteristics involve are that 3D objects are formed by deposition of layer by layer, using either filament or powder as feed materials. With 3D printing, both metal and alloy as well as polymeric composite materials can be made. Under the 3D printing family, key processes include the following[12]:

- Extrusion
- Direct energy deposition
- Ink solidification and
- Photopolymerisation.

In this section, 3D printing relating to polymeric materials are discussed. Figure 13.1 illustrates different types of 3D printing methods[13].

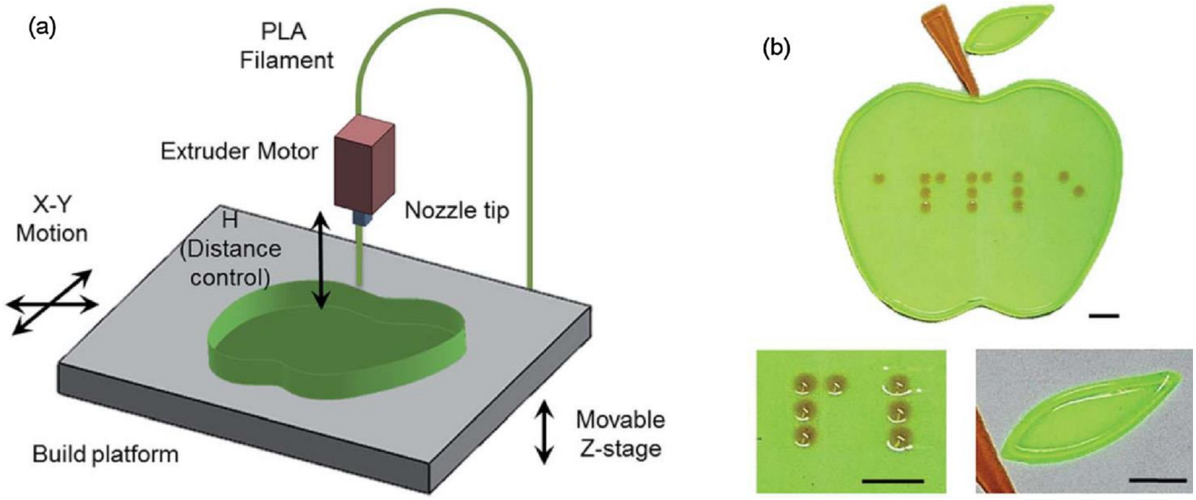

Figure 13.1 (a) A schematic diagram of 3D printing (b) A graphic type of tactilebraille pattern: A 3D-printed image of an apple[14].

Particle or Solid Powder Fusion based 3D Printing

Selective Laser Sintering*:* With the selective laser sintering (SLS*)* process, complex 3D parts and components are fabricated, using solid powder materials depositing layer by layer. Solidification is obtained by using thermal energy from focused laser radiation systems.

Liquid Resin driven 3D Printing

Stereolithography: Stereolithography (SLA) is a vat photopolymerisation in which liquid photopolymer or liquid resin is selectively cured by light activated polymerisation. The photopolymerisation process converts the liquid resin to solid via crosslinking. This technique offers higher accuracy and smooth surface finish when compared with fused deposition modelling (FDM) and SLS. However, its drawback is considered as low speed or slow printing process.

Extrusion based 3D Printing

During this 3D printing method, extrudable material is forced through a nozzle and deposited in layer by layer manner. This is one of the most popular categories of 3D printing processes. Within this category, the following methods are considered:

Direct Ink Writing: Hydrogel and slurries are utilised as ink in this technique, which is stored in a syringe-like reservoir connected to jetting nozzle.

Fused Deposition Modelling is also known as fused filament fabrication (FFF) or fused layer manufacturing (FLM). For polymeric composites, the popular 3D printing method used is FDM. In FDM process, the model is designed in CAD and then the file is transformed into stereolithigraphy that contains layer by layer information, where polymers of polymer composite filaments are deposited via controlled heated nozzle.

In addition, computer-aided manufacturing (CAM) drives the nozzle and stepper motor controls the extrusion head. This is one of the most commonly used 3D printing methods, because of its versatility and availability in relatively low cost. Moving forward, easily available and commonly used polymers include poly lactic acid (PLA) and acrylonitrile butadiene styrene (ABS). However, the components fabricated by using this process are inferior in mechanical properties when compared with the parts, for example, produced by injection moulding techniques[15]. Moreover, one of the limitations of this technique with CNPs is nozzle jam, caused by agglomeration of nanofillers[16].

Inkjet 3D Printing: During this process, micro-meter range diameter drops off liquid (droplets) jetted by either thermal or acoustic forces. The deposited materials are cured by cross-linking methods, such as ultraviolet light. This process offers good accuracy and high quality parts.

The mechanical properties of parts made by FDM are influenced by various parameters, including:

- Viscosity
- Heat capacity and cooling rate
- Geometry of the products and orientation
- Nozzle diameter
- Raster-to-raster air gap
- Layer thickness and related curing characteristics

Due to its simplicity, easy user interaction and cost effectiveness, FDM technique is extensively used in the fabrication of polymer composites.

Commonly used Polymers in FDM

The selection of polymers for 3D printing depends on what type of 3D processes are being used. For FDM, it is important that the materials to be printed must come in filament form. For SLA, the materials to be used must be in liquid resin form, whereas for SLS, materials must be available in powder form. Only thermoplastics are usable in FDM, which means they are normally heated, softened and cooled to solidify. Important thermoplastic polymers, such as PLA and ABS are commonly used polymers in FDM process. The processing parameters, such as temperature, viscosity and molecular weight, significantly influence the mechanical properties of the printed parts. Additionally, important factors such as filament size, speed of printing and the mechanical properties of filament play similar important roles in 3D-printed parts.

Poly lactic acid (PLA) is a linear aliphatic thermoplastic polyester. It has very attractive attributes, such as renewable and fully biodegradable. This polymer is produced from renewable and biodegradable materials. PLA has good thermal stability and excellent mechanical properties when compared with other common thermoplastics. Polyamides (PAs), PA11 and PA12 are other polymers, which are mainly used in SLS. when compared with SLA and FDM, SLS process does not require supporting materials.

Acrylonitrile butadiene styrene (ABS) is one of the most popular thermoplastic polymer used in FDM. The mechanical properties are significantly influenced by the processing parameters.

Polypropylene (PP) is also used as one of the polymers in 3D printing. However, it is important that PP has high melting temperature which requires high temperature to be printed.

High-density polyethylene (HDPE) is another polymer used in 3D printing. It produces good products, due to its higher strength and stiffness as well as excellent abrasion properties. HDPE also has good impact, fatigue and creep behaviours. Polycarbonate (PC) is another polymer used in 3D printing, which possesses toughness, clarity and high thermal resistance.

The most important required properties of these polymers are thus stated[15]:

- Chemically resistant
- Flame-retardant
- Corrosion resistance
- Lower moisture absorption
- Low viscosity.

13.3.2. Applications of 3D Printing Processes

3D printing processes have widely been used in many key industrial sectors, such as automotive, aerospace, construction, biomedical and tooling, jigs and fixtures[15]. Depending on the properties requirements, different types of AM techniques are suitable for specific applications. As far as using AM techniques for composites and nanocomposites fabrication and understanding their properties are concerned, the processing parameters and other various factors still not fully investigated and understood. Moreover, 3D printing of CNPs using bio-resins is one of the key areas, which is not fully explored yet.

13.3.2. Mechanical Properties of 3D-Printed CNP Reinforced Polymers

A composite material as defined accordance to ASTM D3878-18, is “a substance consisting of two or more materials, insoluble in one another, which are combined to form a useful engineering material possessing certain properties not possessed by the constituents”. Polymer nanocomposites (PNCs) are composite materials, where nanoparticles or nanofillers are mixed in polymer matrices. With the incorporation of small amount (1-5 wt.%) of nanoparticles or nanofillers can improve the mechanical, thermal and barrier properties of neat polymers by 3 to 5 times[4]. When nanocomposites are fabricated using AM techniques, they ae used as normal polymers. It is generally observed that when nanoparticles are incorporated into polymers, with right mixture (intercalation or exfoliation), a significant enhancement in strength and stiffness are obtained. However, the toughness of nanocomposites is generally decreased[17].

Cellulose nanoparticles are obtained from renewable sources and are sustainable as they have attractive attributes such as biodegradability, good biocompatibility. Therefore, nanocellulose/nanoparticles reinforced nanocomposites exhibit high performance and sustainable features, when compared with conventional glass or carbon fibre composites. Moreover, nanocellulose or nanoparticles reinforced nanocomposites provide synergic properties of nanoparticles and cellulose. Fabricating these environmentally friendly composites using 3D printing has attracted attention from industries and research community.

A comprehensive study was carried out on nanocomposites, using solution casting of cellulose microfibrils obtained from modified stems[18]. Their findings showed that there was a significant improvement in the mechanical properties as a result of cellulose microfibrils reinforcement into the matrix. The tensile modulus was reported to improve from 0.6 to 34.5 MPa with the incorporation of 10 wt.% of filler. Their report further highlights that the elongation at break was decreased significantly; from 362 to 115%. It is further highlighted that the reinforcing effects depends on the dispersion of fillers into the matrix and their morphologies.

Cellulose nanofibers (CNFs) reinforced PLA based nanocomposites have been fabricated by extrusion based 3D printing[19]. They reported that the incorporation of PLA-g-CNFs improved the storage modulus. Similarly, post extrusion annealing treatment contributed to the improvement of tensile strength and moduli by 28 and 63% of the filaments, respectively. The improvements in properties were attributed to chemical modification and uniform distribution of CNFs into PLA matrix.

Another study has been conducted on lignin coated cellulose nanocrystal (L-CNC) reinforced acrylonitrile butadiene styrene (ABS) by combining extrusion and 3D printing[20]. They reported that thermal stability of 3D-printed nanocomposites parts increased significantly. Similarly, tensile properties were also enhanced with the incorporation of L-CNC into ABS matrix. The key factors for the properties improvements were caused by the proper dispersion of L-CNC into ABS and determining the threshold content of L-CNC. At higher concentrations of L-CNC, it was difficult to attain good mixture and it led to poor interfacial interactions between L-CNC and ABS matrix. Their work suggested that 4 wt.% of L-CNC was threshold value in which an adequate dispersion, a higher surface areas and good interfacial properties were achieved and it led to both tensile strength and modulus improvements. A strong interfacial adhesion was crucial for the improved properties. However, it was also reported that at higher L-CNC concentration, elongation was reduced. Figure 13.2 depicts the morphology of tensile fractured surfaces of 3D-printed L-CNC/ABS nanocomposites with varying contents of L-CNC.

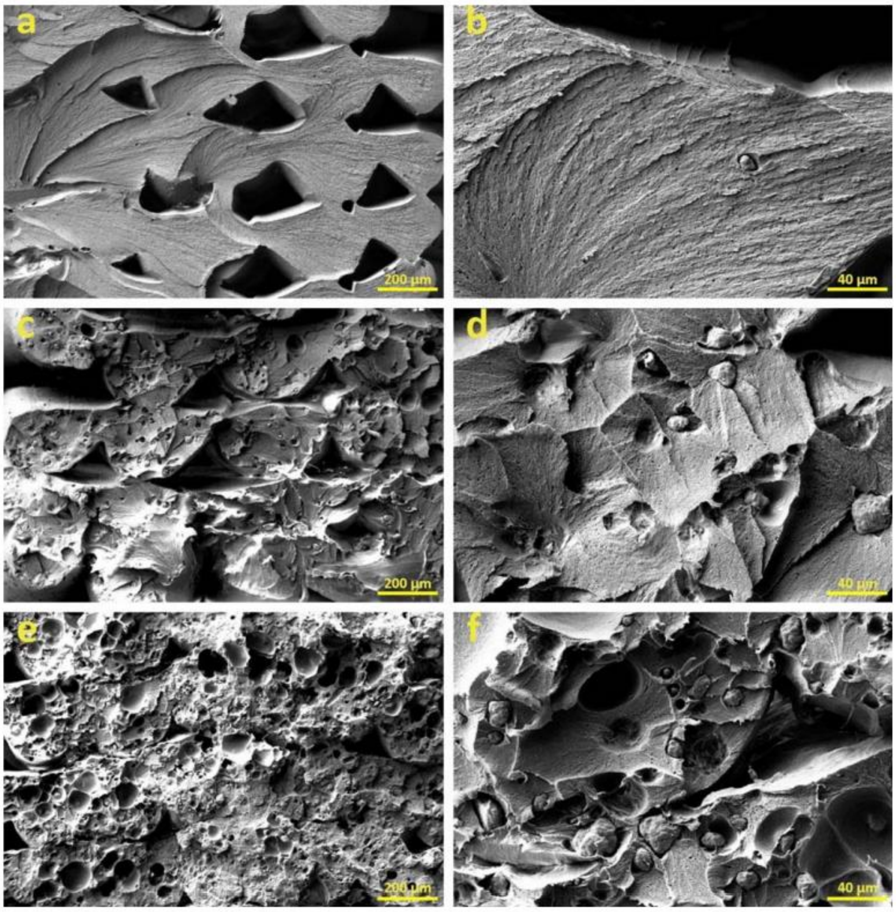

Figure 13.2 Morphology of tensile fractured surfaces of 3D-printed L-CNC/ABS nanocomposites with varying contents of L-CNC (a, ab neat ABS; c, d 4 wt.% L-CNC; e, f 10wt.% L-CNC)[20].

More also, cellulose nanofbrill-reinforced PP composites have been investigated[21]. They reported that 3D-printed by material extrusion process of CNF-PP filament composites exhibited a significant improvement in the mechanical properties. According to their findings, the flexural strength and modulus of neat PP were enhanced by 5.9 and 26.8% with the addition of 10 wt.% of CNF. The improvement in flexural properties was attributed to the rigidity of CNF. They emphasised in their discussion that improper mixing is detrimental to the mechanical properties of CNF-PP nanocomposites. Agglomeration of CNF in PP can cause porosity and stress concentration points and parts can fail prematurely. It is also important to find out threshold concentration level of CNF into PP. For example, they could not realise the benefits of CFN with 3 wt.% into neat PP. The improvement of mechanical properties of nanoparticles reinforced polymeric nanocomposites depends on strong interfacial interaction between the nanoparticles and host polymers, among others.

The composite samples used in the work carried out on PLA and polypropylene (PP) filaments with higher wood flour contents of 10, 20 and 30% were fabricated by twin-screw extrusion and compared with FDM process[22]. Their results suggested that the mechanical properties of 3D-printed parts were inferior to twin-screw extruder. This behaviour was attributed to decreased compatibility between the wood four and the matrix as well as the nozzle blockage. The filament quality also plays important role in the final properties of 3D-printed parts. Therefore, there are several techniques proposed to improve the interface between reinforcements and matrices.

Palaganas and co-workers investigated the properties of 3D-printed CNC-filled biomaterial[23]. Their report suggested that the properties of cellulose nanocrystal composites fabricated by using SLA was significantly improved. Their report highlighted that the 3D-printed PEGDA hydrogel exhibited tensile strength of 0.6 MPa. With the incorporation of 0.3 wt.% of CNC, the tensile strength was recorded at 1.2 MPa, improvement by 100%. However, further increase in CNC incorporation did not contribute any improvement in the tensile strength of the nanocomposites. Similarly, elongation at break behaviour of PEGDA was also enhanced by 110% with the loading of CNC at 0.3 and 1.2 wt.%. The significant enhancement in the properties were attributed to uniform distribution of CNC particles into PGDA. Figure 13.3 illustrates the enhancement of tensile properties for various CNC wt.% loadings. Additionally, the strong interaction at the interface with high aspect ratio of CNC and resulting larger surface area were the key factors for the property enhancement. Furthermore, it is worth noting that the 3D-printed parts were fully cured, unlike 2D printed parts of similar materials. Their report further reiterates that the 3D-printed parts are cured layer by layer, which guarantees the solidification in the innermost section of the model and helps to contribute to the enhanced mechanical characteristics of complex 3D-printed structures.

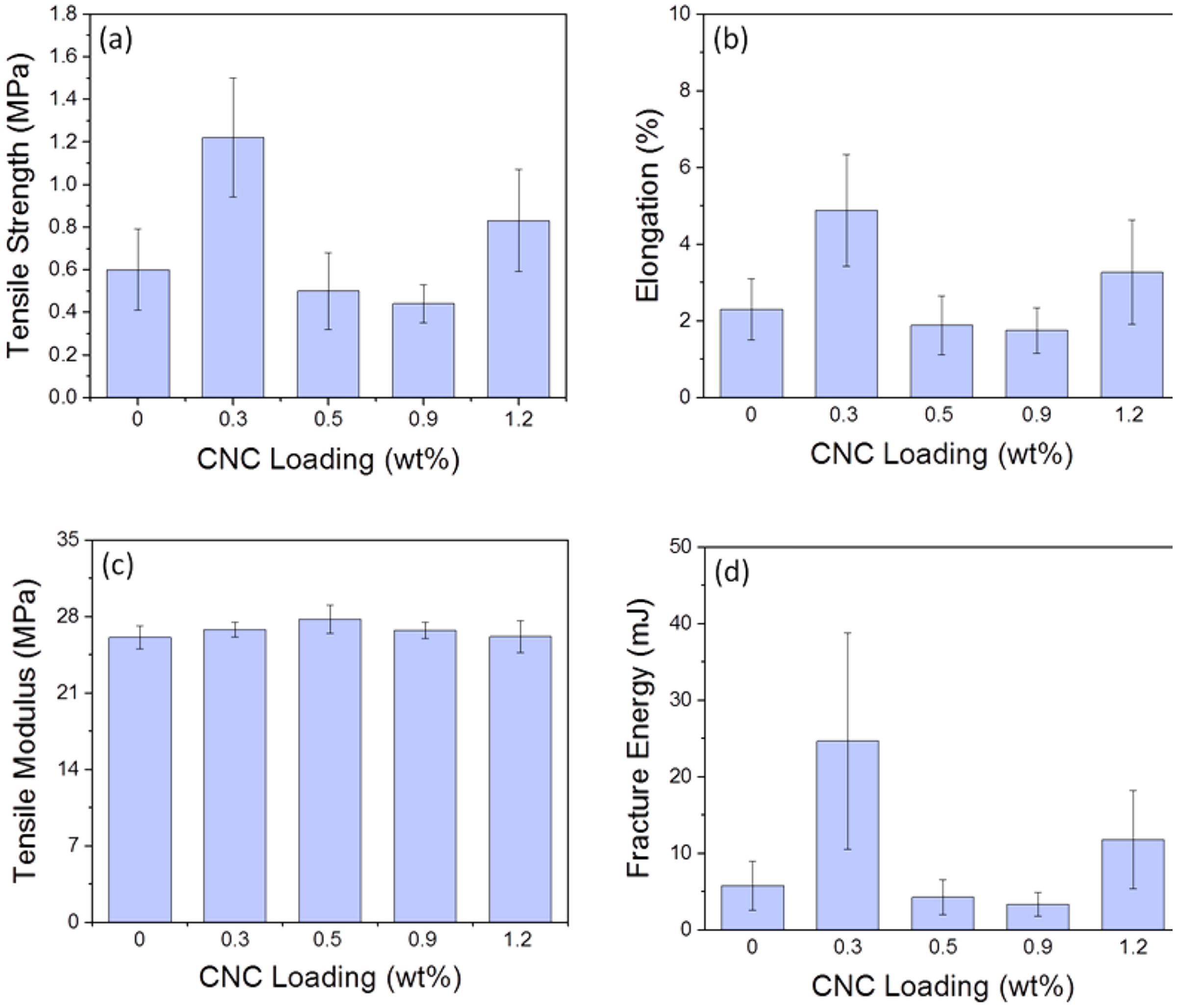

Figure 13.3 Influence of CNC concentrations on tensile properties (a) tensile strength, (b) strain/elongation, (c) tensile modulus and (d) fracture energy for 3D-printed PEGDA hydrogels[23].

13.3.2.1. Factors for properties enhancement of 3D-printed CNP reinforced Polymers

Considering the mechanical properties of 3D printed CNP reinforced polymers, the key factors for the mechanical properties enhancement are discussed in the following sections.

3D printing process and parameters: Mechanical properties of 3D printed parts depend on several factors. Among them, the 3D printing process used and key parameters and factors selected. For example, the form of filaments (solid or in paste form) influences the processability as well as the properties of the final parts. The reinforcement sizes significantly influences the overall mechanical properties. Discontinuous fibres used in nanoscale include graphene, cellulose nanoparticles, single walled carbon nanotube (SWCNT) and multi-walled carbon nanotubes (MWCNT). When these filers are used in 3D printing process, the mixing, wettability of reinforcements and compatibility between reinforcements and matrices are important. It is agreed fact that long fibres provide significantly improved mechanical properties than the short fibres reinforcement[24]. For example, it is reported that[24] the tensile strength of 13 wt% millimetre sized carbon composites provided a significant improvement in strength and modulus by 250% and 400% respectively in comparison with 10 wt% nanoscale SWCNT incorporation where the improvement was recorded 39% and 61%, respectively. Fibre wettability is related to viscosity of matrices. In order to achieve optimal mechanical properties, reaching the threshold fibre volume fraction and efficient load transfer from matrix to fibre is key. With 3D printing, the matrices used are mainly thermoplastics, which causes high viscosity at higher fibre volume fraction, it can lead to poor fibre matrix interfacial bonding. This issue causes clogging of nozzle.[25] Similarly, solidification defects and shrinkage related with different 3D printing process relating to reinforcements and matrices are another factor contributing to their mechanical properties.

When cellulose nanoparticles are used as fillers into thermoplastic matrices, the fabrication process plays very important role. A comprehensive work carried out by Ambone at al.,[26] with an aim to enhance the mechanical performance of 3D printed parts based in cellulose nanofibers (CNF) into PLA matrix fabricated by fused filament fabrication (FFF) 3D printing technique. Their work also compared 3D printed parts with traditional compression moulding process. Their results revealed that with the incorporation of 1 wt% of CNF into PLA contributed significant improvement in tensile strength and Young's modulus (increased by 84% and 63%, respectively). The morphological characterisation performed using X-ray microtomography showed that PLA/CNF biocomposites had less void contents compared to neat PLA. Additionally, varying concentration of CNF into PLA fabricated using compression moulding technique was also compared with 3D FFF method. They highlighted that addition of CNF into PLA improved the tensile strength and modulus. However, at the higher level of CNF concentration, the dispersion degree was reduced which affected the tensile strength.

PLA being hydrophilic matrix is prone to moisture related degradation. In their investigation[26], it was resulted that the moisture uptake percentages of 3D printed PLA was significantly reduced with CNF incorporation (Figure 13.4). The compression moulded PLA specimen absorbed very small amount of moisture (<0.3%) whereas 3D printed PLA specimen absorbed 1.5% of moisture. Noteworthy to highlight that at 3D printed PLA with 1wt% of CNF absorbed significantly less amount of moisture (0.4%) compared to compared to 3D printed PLA without CNF.

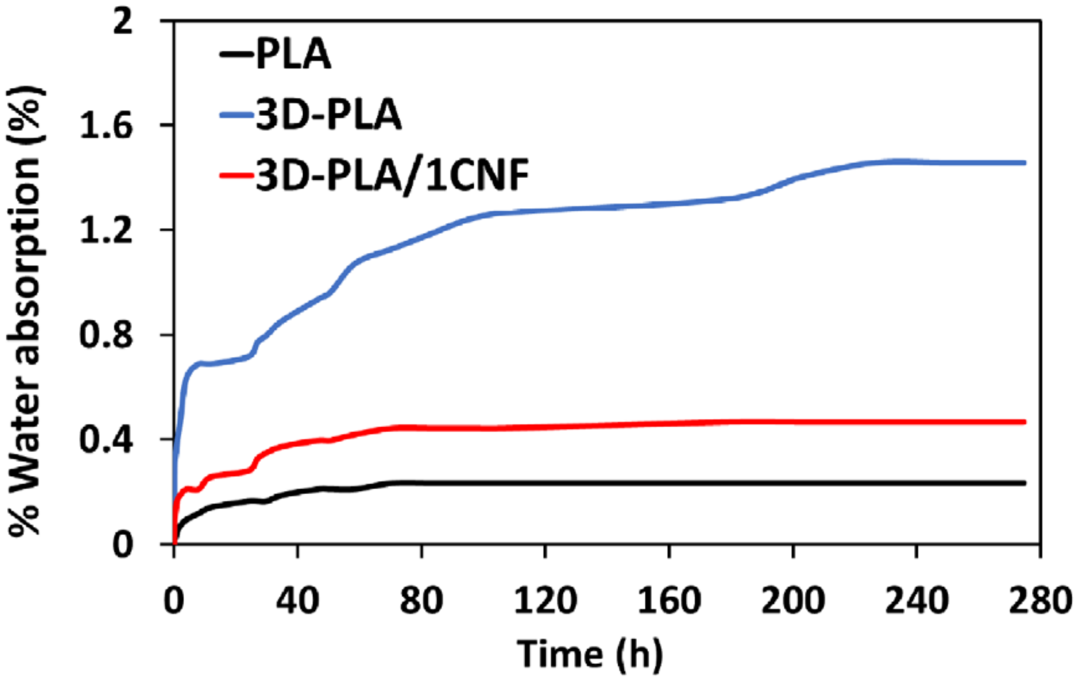

Figure 13.4 Moisture absorption behaviours of compression moulded PLA, 3D printed PLA and 3D printed PLA with 1 wt% CNF[26].

Moisture absorption degrades the fibre matrix inerface and reduces overall mechanical properties (strength and modulus) significantly. With the incorporation of 1 wt% of CNF into PLA certainly shows a signifcant achievement.

Structure-morphological characteristics- rheology behaviour and property relationships of CNPs

The structure property-rheology relationships are important to obtain optimum properties of CNPs reinforced polymer nanocomposites. The mechanical, thermal and other functional properties of CNP reinforced components are highly dependent on the morphological and structural characteristics such as size and geometry, aspect ratio (l/d), surface properties and their ability to disperse in the host polymers[27]. The property-structure of CNPs and their rheology have been studied by the various researchers. Cellulose nanofibers (CNFs) prepared by twin screw extrusion (TSE) and their properties by considering important parameters including nano-sized fraction, morphology and rheological aspects[28]. The tensile strength of film from neat and pre-treated fibres using carboxyl content 800 was record at 3.6 and 14.5 MPa, respectively. The tensile properties of films of fibres oxidised under the basic condition showed a significant improvement. The tensile strength at carboxyl concentration of 750, 1000 and 1350 were achieved 42, 48 and 52 MPa. Similarly, the tensile modulus was recorded at 2.8, 5.6 and 6.8 GPa, respectively. The constant improvement in the tensile properties was attributed due to increase of nanosized fraction of cellulose fibrils as reinforcement. It was further explained that CNFs are bonded by hydrogen bonds with closely interconnected networks which results in dense structure with a low porosity. This type of structure and morphology leads to be able to transfer stress from fibril-to-fibril[28]. It was also noted in their work that fabrication process significantly influences the overall mechanical properties. In comparison to high-pressure homogenisation (HPH), TSE would give lower mechanical properties. The reason for this difference was attributed to the lower fibrillation efficiency generally obtained via TSE in comparison to HPH. The report concluded that with FE-SEM, it was possible to observe random-in-plane web like network structure was achieved with layered morphology on the CNF. The carboxyl content prompted to an increase in nanoscale reinforcements, which further led to a significant improvement in the tensile properties[28].

Using hybrid approach

In order to improve the mechanical performance of composites and biobased composites, several improvement techniques are employed. Among them is using hybrid approach. In this approach, synergic influence of two or more materials are utilised. Nanoparticles such as CNFs, cellulose nanocrystals (CNCs), nano clays, and organically modified layered silicate are commonly used nano particles. The effects of CNFs and nano clays at lower concentration

(<1 wt.%) on the mechanical performance of kenaf/epoxy was investigated by Khant et al.[29]. It was reported that the tensile and flexural properties of kenaf/epoxy was significantly improved by incorporation stiff CNFs as fillers. For example, flexural properties of neat kenaf/epoxy composites was was significantly increased with the incorporation of nano clays and CNFs. The addition of organically modified nano clays, CNFs and nano clay hybridised kenaf/epoxy enhanced the flexural strengths by 35.2, 23.2 and 5.8%, respectively. The improvement in flexural modulus was 72, 60 and 51%, respectively. They also suggest that distribution and the wetting of fillers was critical in order to get enhanced performance[29]. Interfacial interaction of nano clay were higher than that of CNFs. Additionally, intercalated and exfoliated structure, (Figure 13.5) creating high interlayer spacing was also key factors for achieving high mechanical properties.

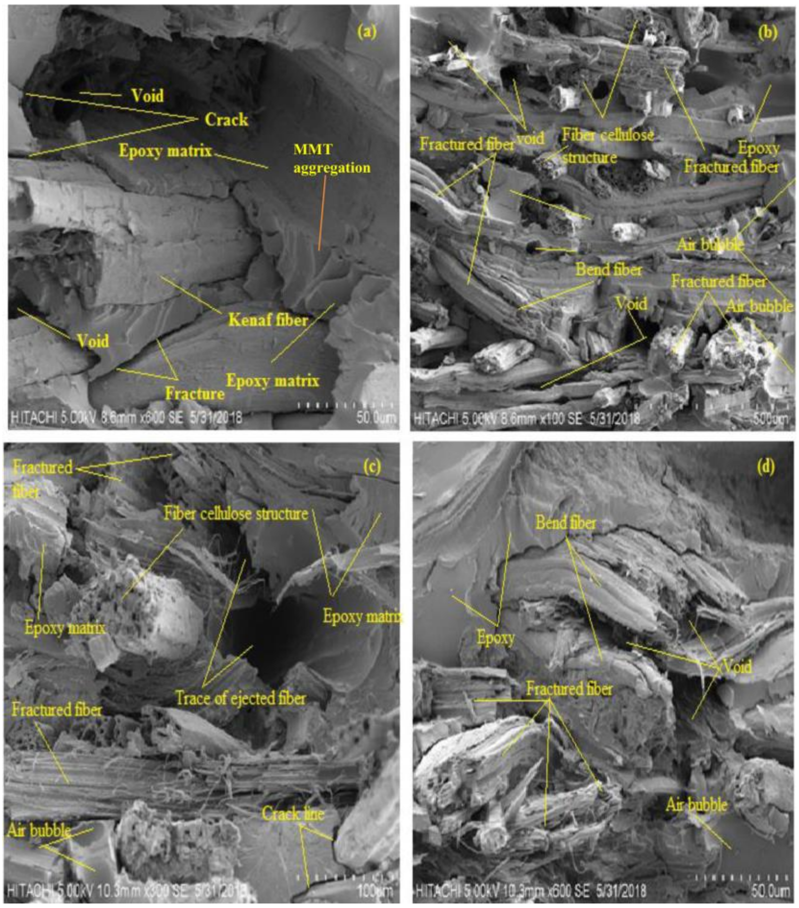

Figure 13.5 SEM micrographs of kenaf/epoxy (a) nanoclay/kenaf/epoxy (b) CNFs/kenaf/epoxy (c) and (d) organically modified nano clay/kenaf/epoxy[29].

For the enhancement of various performances including mechanical properties of nano clay hybriddised nanocomposites, achieving suitable morphological structures with larger d-spacing of nano clay particles (intercalated and exfoliated structures) is very important[30].

13. 4 Concluding Remarks

Cellulose are naturally abundant versatile biopolymer with many attractive attributes for composite reinforcements and for wide range of applications with more sustainable features. Renewability and biodegradability are key material properties expected from sustainable composites, as a new generation of eco-friendly materials. As far as their manufacturing using 3D printing is concerned, there are still many challenges ahead. One of them is hydrophilic nature of cellulose, limiting compatibility with hydrophobic matrices when making composite reinforcements, needing further treatments and modifications, limiting their full exploitation. Enhancement in improving the mechanical performance of CNPs reinforced nanocomposites, but equally, other functional properties are equally important to explore for wider applications of 3D printed components. Considering several reports reviewed in this chapter, 3D printing techniques are new advanced manufacturing methods suitable for CNPs towards enhanced properties for various applications.

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