Review

An Overview of Natural Polymers as Reinforcing Agents for 3D Printing

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Abstract: Three-dimensional (3D) printing, or additive manufacturing, is a group of innovative technologies that are increasingly employed for the production of 3D objects in different fields, including pharmaceutics, engineering, agri-food and medicines. The most processed materials by 3D printing techniques (e.g., fused deposition modelling, FDM; selective laser sintering, SLS; stereolithography, SLA) are polymeric materials since they offer chemical resistance, are low cost and have easy processability. However, one main drawback of using these materials alone (e.g., polylactic acid, PLA) in the manufacturing process is related to the poor mechanical and tensile properties of the final product. To overcome these limitations, fillers can be added to the polymeric matrix during the manufacturing to act as reinforcing agents. These include inorganic or organic materials such as glass, carbon fibers, silicon, ceramic or metals. One emerging approach is the employment of natural polymers (polysaccharides and proteins) as reinforcing agents, which are extracted from plants or obtained from biomasses or agricultural/industrial wastes. The advantages of using these natural materials as fillers for 3D printing are related to their availability together with the possibility of producing printed specimens with a smaller environmental impact and higher biodegradability. Therefore, they represent a “green option” for 3D printing processing, and many studies have been published in the last year to evaluate their ability to improve the mechanical properties of 3D printed objects. The present review provides an overview of the recent literature regarding natural polymers as reinforcing agents for 3D printing.

Keywords: cellulose; lignin; chitosan; wood; keratin; hemp; soybean; coffee waste; flax; bamboo

1. Introduction

Three-dimensional (3D) printing, or additive manufacturing, is an innovative method to produce a three-dimensional object using different processes and raw materials, such as resins and powder grains, generally building a product layer by layer [1]. The invention of 3D printers in 1986 has marked a turning point in different fields, including pharmaceutics [2], engineering [3], agri-food [4,5] and medicines [6,7]. The rapid manufacturing times and the easy process with the computer-assisted design (CAD) are key to 3D printing’s increasing success [8]. There are three methods mainly used by a 3D printer to produce the objects: fused deposition modelling (FDM), selective laser sintering (SLS) and stereolithography (SLA) (Figure 1). Selective laser sintering (SLS) is a production method in which the radiation of a laser heats a powder just above the softening temperature of the material. Then, particles are fused together mechanically and solid is deposited layer by layer, thereby producing the object [8]. The stereolithography (SLA) method consists of the solidification of a liquid resin thanks to the photopolymerization. The manufacturing proceeds by curing the liquid resins layer by layer until the three-dimensional object is obtained [9]. The starting material for FDM is usually a thermoplastic filament that is fed into the printer. The following phase consists of an extrusion process of melted materials.
that are subsequently layer-by-layer deposited onto a surface to build a specific 3D object (Figure 1). Among the different 3D printing techniques, FDM is the most common and widespread, and its success depends on the availability of materials that can be processed with it. Specifically, these materials are represented by thermoplastic polymers characterized by a glass transition temperature in the range of 50 °C up to around 230 °C. Two other very important features are represented by the rheological melting behavior and the mechanical properties of the selected polymers [10]. To date, the most common polymeric materials used are represented by polyolefins (i.e., polyethylene PE and polypropylene PP), acrylonitrile–butadiene–styrene (ABS), polycarbonate (PC), polysulfone (PSU) and biodegradable materials such as polylactic acid (PLA) [11,12]. The use of polymers as matrices for 3D printing is strongly recommended because they offer good chemical resistance, low cost and easy processability, but one of their main limitations in the manufacturing process is the low functionality and low mechanical and tensile properties, namely, the modulus, strength and impact resistance of the final product [13]. Among the different strategies suggested to overcome these issues, the use of reinforcing materials is one of the most promising. The reinforcement is obtained by mixing the polymeric matrix with fillers, characterized by an extraordinary mechanical performance and an excellent functionality [14]. In this way, composite materials, commonly used to perform 3D printing, are obtained. The different reinforcing agents are usually classified according to their morphology (e.g., fibers, particles, flakes and laminates) or length and dimension (micro- or nanomaterials). In addition, the kind of reinforcement defines the composite characteristics according to the concentration, the shape, the size, the distribution and the orientation of the fillers [15]. 3D printed polymeric matrices can be reinforced in terms of mechanical properties (e.g., tensile strength and modulus, flexural strength and modulus, hardness, elongation) through particle-based (e.g., glass beads, iron or copper microparticles), fiber-based (e.g., short glass or carbon fibers) and nanomaterial-based (e.g., carbon nanotubes, titanium dioxide nanoparticles) approaches. Among all the materials, glass and carbon fillers are the most employed reinforcing agents [14]. In this regard, the use of natural materials, including biopolymers, as reinforcement agents for 3D printing, is an emerging strategy, configuring as an attractive alternative to all synthetic and non-renewable source-derived fillers [15]. The aim of this review is to provide a general overview about natural polymers ( polysaccharides and proteins) recently employed for 3D printing processes.

Figure 1. Graphical schemes of 3D printing techniques. (A). Fused deposition method (FDM). (B). Digital light processing (DLP). (C). Stereolithography (SLA). (D). Selective laser sintering (SLS).
Polysaccharides as reinforcement agents were employed as pure fibers (e.g., most representative components of this class are cellulose, lignin, chitosan, starch and alginate [7]). Polysaccharides are macromolecules that are constituted by repeated units of sugars interconnected through glycosidic linkages to form a crystalline and amorphous material. They are abundant in nature and many of them have a complex structure made up of numerous intramolecular and intermolecular hydrogen bonds. The most representative components of this class are cellulose, lignin, chitosan, starch and alginate [7].

Proteins [17] are complex macromolecules built by amino acids joined together via peptide bonds. They are abundant in nature and have favorable properties as biodegradability and biocompatibility. However, they are mainly employed in a 3D process for the construction of soft materials as hydrogels or scaffolds for tissue engineering. The protein used for 3D printing are gelatin, keratin, collagen, silk and soy proteins [18].

The natural polymers (polysaccharides and proteins) discussed in this review for 3D printing includes different kinds of chemical species derived from plants, animals and minerals. For instance, many plant-based natural fillers are extracted from agricultural by-products made up of a mixture of different biopolymers, such as cellulose, lignin, and hemicellulose, which are components of parts of the plant (e.g., leaves, seed, fruit, grass) [15]. Among all plants and animal-derived biopolymers, the most represented groups are polysaccharides and proteins. Polysaccharides are macromolecules that are constituted by repeated units of sugars interconnected through glycosidic linkages to form a crystalline and amorphous material. They are abundant in nature and many of them have a complex structure made up of numerous intramolecular and intermolecular hydrogen bonds. The most representative components of this class are cellulose, lignin, chitosan, starch and alginate [7]. Polysaccharides as reinforcement agents were employed as pure fibers (e.g., cellulose, lignin or hemicellulose) or as a mixtures extracted from plants (e.g., flax, bamboo, hemp) in which they are the main constituents. Another source of polysaccharide is represented by process wastes of vegetal matrices such as those from coffee.

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3. Natural Materials Used as Fillers in 3D Printing

3.1. Cellulose

Cellulose is the most abundant natural biopolymer that can be found mainly in plants but also in animals, fungi, bacteria and algae. From a chemical point of view, cellulose is a natural homopolymer made up by repeated units of glucose bonded with α-1,4 glycosidic bonds. Furthermore, it is a semi-crystalline polymer with a high molecular weight that is assembled thanks to the intra-and intermolecular Van der Waals forces [19]. The importance of cellulose has been well known for at least 150 years, since it has been used in many fields for daily life applications, but only in the last two decades it has been used as biopolymer for biocomposites. The morphology of the cellulose represents one of the main criteria for classification; in 3D printing, different shapes of cellulose materials were used as reinforcement for polymers: cellulose nanocrystals (CNCs), cellulose nanowhiskers (CNWs), microcrystalline cellulose (MCC), cellulose nanofibers (CNFs). The first is represented by cellulose nanocrystals (CNCs) [20,21], which are the final product obtained after the acid hydrolysis of cellulose fibers. CNCs are defect-free fibers with a rod-shape. Different studies support the thesis that the addition of only 0.5% w/w CNCs improves the mechanical properties and the thermal stability of the biocomposites and this is also proved by the analysis conducted by Wang et al. [22]. An element of novelty is brought by the work conducted by Shariatnia et al. [23], where a solution of water and CNCs was sprayed between polymer layers during 3D printing with the FDM method. This marked a real innovation, since with the FDM technique problems related to the aggregation of the composite during the extrusion, which causes a clogging of the nozzle, are often present due to the water evaporation and the deposition of CNCs. This novel method results in an increased interlayer shear strength (44%) and an improvement in tensile modulus and tensile strength (20% and 33%, respectively), when the CNC amount in the water dispersion is between 0.5% and 1% w/w. Another application of cellulose as reinforcement...
in biocomposites is represented by the use of cellulose nanowhiskers (CNWs). They bring a good enhancement of the dynamic mechanical and thermal properties of the polymers, the tensile strength, the toughness and the elongation at break of the composite [24], despite the fact that they also have some drawbacks: their incorporation into the polymer matrix is difficult and not homogeneous, and their aggregation makes them less easy to handle (to solve this issue the freeze-drying is performed in order to dry CNWs) [25]. Furthermore, the presence of strong hydrogen bonds and the hydrophilic surface allow one to use them only with water-based systems [26]. Many efforts were conducted to chemically modify the structure of CNWs by silylation [27], acetylation [28], use of surfactants [29] and polyethylene glycol (PEG) grafting [30], with the aim to make them compatible with other solvents. However, despite the fact that these modifications are possible, the reinforcing ability of the chemically modified CNW is less efficient than that of the untreated CNWs, resulting in lower mechanical properties of the produced composites. In this regard, the work of Petersson et al. [26] compared the untreated CNWs with the whiskers treated with tert-butanol (B-CNWs) and the whiskers treated with a polyalkoxylated alkylphenol phosphate ester surfactant (Beycostat E A B09, also known as BNA), which is the same as that used in the study by Heux et al. [29]. The structural observation showed that the treatment with the surfactant resulted in a better distribution of the CNWs in the polymer matrix, followed by the B-CNWs composites, and the worst distributed in the PLA matrix was the PLA-CNWs. All the samples were stable at a temperature between 25 and 200 °C, and they also were able to enhance the storage modulus of the PLA in the plastic zone, while the S-CNWs also enhanced the storage modulus of the PLA/s elastic zone. Bondeson and Oksman [24] proposed a different approach because they treated CNWs with polyvinyl alcohol (PVOH) as a compatibilizer to improve their dispersion into the PLA. The TEM analysis showed that there was no homogeneous dispersion of the CNWs in the polymer matrix, and the whiskers were better dispersed in the PVOH than the PLA phase, resulting in very small improvements in terms of mechanical properties. Thus, CNWs acted as a reinforcement for the PVOH phase but not to the PLA. Microcrystalline cellulose (MCC) has been used as reinforcement in order to produce biocomposites intended for 3D printing [31]. Murphy and Collins decided to modify the MCC with a titanate coupling agent to obtain a better interaction between MCC and PLA. The addition of 3% w/w titanate-modified MCC guaranteed the dispersion in the PLA matrix and the production of the filament. Moreover, the composite characterization showed that the addition of MCC caused an increase in crystallinity and in the storage modulus. The treatment with the titanate coupling agent reduces the cellulose hydrophilicity, while the biocomposites can absorb a higher quantity of water from the environment.

Besides CNCs, CNWs and MCC, Cellulose Nanofibers (CNFs) are also used with the purpose of reinforcing polymer matrices. The major problem with the use of the nanocellulose is the difficulty to disperse them since they tend to aggregate when dried because of their high surface area; a possible solution to solve this drawback is to perform a preliminary treatment of the CNFs. Among the different chemical agents used for that purpose, the 2,2,6,6-Tetramethylpiperidine 1-oxyl (TEMPO)-oxidation of the bacterial cellulose is the method chosen by Li et al. [32]. The use of TEMPO is a highly studied method to improve the dispersion of the CNFs in the polymer matrices, such as the PLA, but also to provide a shear-thinning behavior to the composites and to enhance their printability [33] (Figure 3). Li et al. produced a biodegradable TEMPO-oxidized bacterial cellulose (TOBC)/PLA composite starting from a homogeneous dispersion of TOBC around the microspheres of PLA and by producing the filament for 3D printing with a single screw extruder [32]. The advantage in the use of bacterial cellulose is that it is a raw material considered ‘purified cellulose’ because it lacks hemicellulose and lignin, elements that are often responsible for the unequal distribution of the cellulose in the polymer matrix. The characterization of the composites showed an improvement in mechanical properties with the addition of TOBC: there was an increasing in tensile strength (+9.2%), elongation at break (+202%), bending strength (+45%) and elastic modulus (+49%) in the PLA-1.5%
w/w TOBC nanocomposites. The work of Jonoobi et al. studied the reinforcement of the PLA with cellulose nanofibers (CNFs) obtained by the Kenaf pulp (Hibiscus cannabinus L.) [34]. A good dispersion was obtained with 1% and 3% w/w of CNFs in the PLA matrix and only with 5% w/w of CNFs. From a mechanical point of view, the tensile properties increased with the increased amount of CNFs: tensile modulus and strength in the composites were higher than the pure PLA, 24% and 21%, respectively, with the addition of 5% w/w CNFs. It was also observed that there was a large standard deviation that suggested the unequal dispersion of the CNFs in the matrix. A recent study conducted by Dong et al. evaluated the influence of the annealing treatment on the flexural properties of the biocomposites of PLA and PLA-grafted cellulose nanofibers (PLA-g-CNFs) [35,36]. A preliminary addition of CNFs to the PLA via ring-opening polymerization resulted in the PLA-g-CNFs. This product is then added to pure PLA in chloroform and then dried in order to proceed through extrusion and then 3D printing the composite. The analysis carried out showed an increased crystallinity of the composites (between 6% and 12%), and this led to better mechanical properties in the glass state, such as the storage modulus and tensile modulus. A subsequent study [35] involves the same PLA/PLA-g-CNFs composites, and the mechanical tests confirmed the improvement in elastic and viscous properties and the reinforcement effect due to the action of PLA-g-CNFs in restricting the mobility of PLA. The annealing treatment was performed above the glass transition temperature (Tg) of PLA. The three-point bending test at 70 °C showed a better performance in the annealed sample that maintained the original structure layer by layer; on the contrary, the unannealed samples were partially damaged. The flexural modulus was 90 times higher than the unannealed samples. The authors concluded that the annealing treatment coupled with the reinforcement given by the PLA-g-CNFs gave to the polymer a good resistance to temperature and an enhancement in flexural and mechanical properties. An interesting point of view is offered by the study of Tekinalp et al. in which the authors suggested that the role of the CNFs was similar to a microsponge, when added to a polymer such as PLA and intended for 3D printing [37]. Even if there was not a homogeneous dispersion of the CNFs into the PLA matrix, it was still possible to observe the microsponge effect of the nanofibers. Indeed, the CNFs stayed in fiber bundles and the PLA matrix penetrated through the bundles to keep in contact with the cellulose, creating the effect of a ‘microsponge’. This peculiar distribution contributed to marked improvements in mechanical properties of the composite, in particular the increasing of the tensile strength (+80%), the elastic modulus (+200%), the strain at break (+76%) and the toughness (+220%) compared to the pure PLA resin; all those accomplishments in the manufacturing process suggested that it is possible to use such a composite for 3D printing. In conclusion, the wide availability of the cellulose in nature, the low cost of the raw material and the promising studies carried out on different forms of the cellulose (nanofibers, nanowhiskers, microcrystalline cellulose, nanocrystals) configure this material as an excellent candidate for the reinforcement of polymer matrices intended for 3D printing application in biomedicine, food packaging, pharmaceutical and many other fields.
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Figure 3. Pectin reinforced with the carboxylated cellulose nanofibrils for the production of bio-based inks for 3D printing of scaffolds. Reprinted with permission from ref. [33]. Copyright 2019 Elsevier.

3.2. Hemicellulose

Hemicellulose is a type of hetero-polysaccharide found in the plant cell wall together with cellulose. It is formed by linear or branched chains of pentose (e.g., xylose) or hexose sugar (e.g., mannose, galactose), which provide different kinds of hemicellulose polymers known as xylans, glucomannans, arabinans, galactans and glucans. Hemicellulose has a lower molecular weight than cellulose since it consists of 50–3000 sugar units (cellulose has instead 7000–15,000 glucose molecules) [38,39]. Since 2018, the application for the 3D printing of hemicellulose was explored both mixed with cellulose nanofibers or cellulose nanocrystals [40,41] and alone [42] (Figure 4). However, these polysaccharides have lower properties in terms of mechanical reinforcement in comparison to cellulose, lignin and wood fibers, and they have not been employed as fillers except in the work of Xu et al., in which the elastic modulus of the composite filament was increased by the addition of 25% w/w of hemicellulose [43].
3.3. Lignin

Lignin is the second most abundant biopolymer after cellulose on earth, mainly derived from plants. Chemically, it is a hetero-polymer derived from the cross-linking of three different substituted phenols (lignols): coniferyl, sinapyl, and p-coumaryl alcohols. From wood pulping, three types of industrial lignin can be obtained, such as kraft lignin, organosolv lignin and lignosulfonate, which are materials exploited for different applications, including 3D printing [44]. The interest in lignin has been growing in recent years since its availability has been markedly increased as a consequence of the development of more efficient processes for isolation and purification on an industrial scale. Therefore, nowadays, lignin can be obtained from different biomasses with a high yield and at a low cost [45]. Thanks to its abundance, biodegradability, high carbon content, aromaticity and low cost, lignin is widely used as a reinforcement agent for manufacturing composites [46]. Moreover, its intrinsic antioxidant, antibacterial and antimutagenic properties, related to the polyphenol structure, can also confer biological properties to the composite [47]. Only recently has lignin been investigated as an additive for 3D printing; however, its properties and potential use in the production of biocomposites are known. Indeed, lignin can be employed without or with modification (e.g., acetylation), despite the fact that the best performances in terms of improved material properties have been achieved in its acetylated form [48]. Nguyen, Bowland and Naskar for the first time reported the use of lignin with acrylonitrile–butadiene rubber and acrylonitrile–butadiene–styrene (ABS) polymer for the preparation of materials with an improved 3D printability. Physical and chemical crosslinks can form between lignin and acrylonitrile–butadiene rubber, allowing for a lignin loading of up to 40% w/w with an excellent printability, and the obtained 3D printed composites showed mechanical properties comparable to those obtained with a petroleum-based thermoplastic (discontinuous carbon fibers) [49].

The performances of the different types of technical lignin, such as Kraft lignin, organosolv lignin, and lignosulfonate in PLA 3D printed bars using the FDM technique,
were evaluated without the addition of any compatibilizer. This study highlighted the high compatibility of organosolv lignin and lignosulfonate for PLA, resulting in lower mechanical properties of the composites prepared with kraft lignin [30]. In another study, up to 20% \( \text{w/w} \) of organosolv lignin was incorporated in PLA filaments intended for 3D printing by FDM. Because of the poor mechanical properties of the obtained composite filament, a plasticizer as polyethylene glycol-(PEG) 2000 was added (0.25–5% \( \text{w/w} \)). The addition of PEG-2000 at a concentration of 2% \( \text{w/w} \) resulted in an enhancing of both tensile stress and elongation at maximum load by 19% and 35%, respectively, for the filament containing 20% \( \text{w/w} \) of lignin [51]. To achieve a better adhesion to the PLA matrix and improve the mechanical properties of the composites, a chemically modified lignin with maleic anhydride was prepared. The introduction of carboxyl groups on lignin increases the surface polarity and the hydrogen bonding interaction ability with PLA chains. In this way, a suitable filament for FDM 3D printing was obtained with good thermal and mechanical properties [52]. PLA composites containing lignin displaying antibacterial and antioxidant properties and intended for healthcare applications were prepared by the FDM technique. The composite filaments were prepared starting from PLA pellets coated with kraft lignin with the aid of castor oil. This procedure allows for the production of the filaments using a single screw extruder, which is in contrast to other works in which a double screw extruder was necessary. The obtained 3D printed grid showed good antioxidant properties (the concentration of 2,2-diphenyl-1-picrylhydrazyl was reduced by 80% after 5 h, despite possessing a lower resistance to fracture) [53]. Lignin-coated cellulose nanocrystals (L-CNC) were instead employed as mechanical reinforcement for methacrylate resin to obtain nanocomposites through the SLA technique. Specifically, mechanical properties in terms of tensile strength and modulus have enhanced with the addition of 0.1% and 0.5% of L-CNC [54].

3.4. Chitosan

Chitosan, the most abundant natural biopolymer after cellulose and lignin, is a natural polysaccharide obtained by the deacetylation of chitin, and it consists of glucosamine and N-acetyl-glucosamine monomers linked through \( \beta (1–4) \) glycosidic bonds. It is nontoxic, biodegradable and biocompatible, and it has important activities such as antimicrobial, anti-inflammatory and antioxidant effects. Chitosan has a polymeric structure that improves the adhesion, proliferation and differentiation of cells. Its production is low-cost and eco-friendly, and it is used for applications in the biomedical, food, cosmetics and pharmaceutical fields [55]. The main application of chitosan biopolymer in 3D printing is the development of bio-ink suitable for the production of hydrogels or scaffolds, mimicking the extracellular matrix (ECM) of different tissues (bone, cartilage, vascular, skin and neuronal) and supporting cell attachment, proliferation and differentiation for tissue repairing [56]. Despite the favorable biological properties, chitosan has some limitations in terms of mechanical properties, degradation rates and 3D-printability [57]. Three methods have been reported for chitosan 3D printing, namely, extrusion-based, fused-deposition and solvent-dispensing methodologies [58,59]. For all the techniques, the 3D printability of chitosan is affected by viscosity that, in most of the cases, requires an adjustment by adding other materials, such as PEG, pectin and gelatin, to assure an easy extrusion, to avoid clogging of the device and to retain the shape of the construct before drying. Pectin has been widely employed since it can form polyelectrolytes by physically crosslinking its carboxylic groups with the amino groups of chitosan at pH 3–6 and, as a function of its concentration, can provide 3D printable bio-inks with a suitable viscosity (between 400 and 4000 Pa·s). Indeed, in some cases, the achievement of a satisfactory printability is not the only factor limiting the use of chitosan for 3D printing since the obtained specimen have a low stiffness and compressive strength. Therefore, shrinkage and collapse of the material can occur after printing. To overcome this issue and assure shape fidelity after printing, other reinforcing materials are used to improve the characteristics of composites based on chitosan. One example is offered by the use of rigid particles as filler material, to improve
mechanical properties. For this purpose, milled silk particles (SP) were investigated to prepare mixed 3D printable composites with chitosan. The addition of SP not only ameliorated the mechanical strength of the hydrogel but also supported cell adhesion and growth by providing a rough surface. Overall, the presence of SP gives a greater stability to the bioink. [56,60]. Regarding the fabrication of the PLA/chitosan scaffold, chitosan is at first dried in vacuum and then mixed with PLA. The mixtures are extruded using a twin-screw extruder, so it is possible to produce composite polymeric filaments. The mechanical analysis shows a decrease in tensile strength due to an increase in chitosan content because a higher amount causes discontinuities in polymeric chains. Instead, higher infill density leads to increased tensile strength. The further addition of more chitosan increases the density of the composite material so that the compressive strength increased. The study of these parameters makes it possible to fabricate chitosan-reinforced PLA scaffold using fused filament fabrication (FFF) 3D printed technology [61].

3.5. Wood Fibers/Flour

Several experimental studies were conducted using unpurified materials from plant wood as reinforcement, generally referred as wood fibers or wood flour. They can be obtained from the raw materials through grinding processes able to reduce the size in the micrometric range without further purification. Wood flour is lightweight, renewable, and widely available. The effect of the wood on composite properties depends on several factors: wood particle properties, size distribution and compatibility with the matrix. A particle size of $\leq 100$ µm is necessary to avoid the debonding of wood particles from the polymeric matrix and the possible fracture of the composites. Recently, poplar wood flour (1–10% w/w) was employed to reinforce composites based on metacrylated prepared using SLA 3D printing. This is the first work reporting the ability of wood flour at a low concentration to improve the mechanical properties of plastic prepared by the SLA technique [62]. At a low concentration (up to 10% w/w), wood flour is also a good reinforcing agent for FDM 3D printing [63]. Specifically, wood flour has been claimed to be an environmentally friendly and a low-cost filler, even compared to the other natural material available, therefore reducing the production costs of 3D printed composites [64,65]. As for pure cellulose, one of the main limitations in using wood flours as filler is its scarce adhesion to the polymeric matrix, which negatively affects its ability to impart improved mechanical properties. To overcome this issue, one possibility is to functionalize the polymer to increase the interfacial adhesion with wood flour [66]. In a study, PLA was modified using a silane coupling agent and then teak wood flour was added at two different particle sizes in the micrometric range to produce by FMD composite filaments with improved mechanical strength [67]. Other reactive coupling agents such as N, N-(1,3-phenylene dimaleimide) (BMI) and 1,1-(methylene-4,1-phenylene)bismaleimide (DBMI) can also be employed to ameliorate the interfacial adhesion between PLA and wood flour for the preparation of 3D printed composites. The mechanical properties of the composites were improved in terms of stiffness, strength and deformability. DBMI resulted to be a more efficient coupling agent than BMI because of the flexibility of the molecule [68]. The presence of wood flour worsens the mechanical properties of the composites prepared from unmodified PLA. Therefore, it is necessary to add a compatibilizer or modifier. For the FDM process, generally thermoplastic polymers are used as compatibilizers and toughening agents such as polyurethane (TPU), polycaprolactone (PCL) and poly (ethylene-co-octene) (POE). Among these, TPU is the most commonly employed as a toughening agent for PLA-based composites. TPU has a great influence on the performances of the composites; in fact, it increases the impact strength, the tensile and flexural strength, and the viscosity, favorable for the extrusion process [65]. Moreover, TPU can also be used as the polymeric matrix in the presence of wood flour to fabricate composites with good tensile properties without any further surface treatment or addition of a compatibilizer [64].
3.6. Flax/Bamboo Fibers

Flax and bamboo are largely known natural fibers used as a cheap alternative to wood. They have been used both alone or in combination to prepare new biodegradable composites because such fibers are abundant in nature and they have mechanical properties similar to that of the wood, without needing many years to grow and be ready for use [69]. Among the different natural fibers, flax and bamboo are the most used because of their good properties; bamboo is characterized by a low density, good mechanical properties, abundance in nature (particularly in some areas of the world such as Asia) and low cost (Figure 5) [70]. The flax fiber (Linum usitassisimum L.) is chosen because of its tensile properties that are among the best in the natural fiber variety [71], and its ease of availability. A flax fiber stem is divided in two different layers: the inner layer contains lignin and pectin, and the secondary layer is made up of cellulose microfibrils intercalated by pectin and hemicellulose [72]. Numerous studies were performed in order to enhance the binding between the polymer and the reinforcement fibers, most of which involved the preliminary treatment with alkali, but other treatments were also performed to obtain a better polymer–fiber adhesion. As such, Qian and Sheng [73] carried out a study in which the bamboo cellulose nanowhiskers (BCNW) was treated with a coupling agent, (3-mercaptopropyl)trimethoxysilane (A-189), at five different concentrations. The SEM observation of the silane-treated BCNW indicated that the proper amount of coupling agent is 4% w/w because a minor quantity did not cover all the surface area and a higher quantity led to a self-polycondensation of the coupling agent itself. This quantity also led to a better adhesion between BCNW and PLA, and this is demonstrated by the FT-IR analysis. Tensile strength and tensile modulus of the BCNW-PLA composites were lower when the fibers received the preliminary treatment with the coupling agent and reached the best performance with 4% w/w of A-189. Another relevant parameter is the elongation at break, which represents the capacity of the natural fibers to resist without breaking to a change of shape [74]. Despite the fact that, generally, the addition of a natural fiber to a thermoplastic material causes the reduction in the elongation at break, Qian and Sheng found that the addition of the silane-treated BNCW to the PLA led to a huge increase, from 12.35% of the untreated fibers to 250.8% of the treated fibers with 4% of coupling agents. Furthermore, the SEM images showed the typical brittle fracture of the pure PLA, demonstrating its high tensile strength. The addition of BCNW to the PLA without preliminary treatment increased the toughness of the composites but the best performance was offered by the addition of the silane-treated BCNW to the PLA. Numerous studies involved only the use of flax fiber as reinforcement for biocomposites. Despite the fact that most of the studies in the literature focused on discontinuous fibers (i.e., fibers with short aspect ratios), Le Duigou et al. conducted a study with the novel use of continuous flax fibers/PLA for the manufacturing of biocomposites for 3D printing [71]. The preparation of the continuous fibers was made by selecting flax fiber yarns and coating them with a PLA polymer matrix. The observation of the biocomposites revealed irregularities on the surface and a larger diameter of the filament respect to the commercial ones. Also observed was an irregular dispersion of the flax fibers in the matrix and a low level of adhesion between polymer and fibers, represented by the presence of numerous pull-outs of flax fibers. With regard to the tensile mechanical properties, an increasing of stiffness and strength of the flax/PLA composites with respect to the pure PLA was observed, probably due to the higher content of the fibers (>30% w/w). The mechanical properties were also comparable to those of the synthetic fibers (e.g., carbon or glass fibers). Another study focuses on the feasibility of continuous flax fiber-reinforced plastic (CFFRP) for 3D printing [75]. The filament was produced as follows: firstly, the pure PLA filament was heated and extruded through a single screw extruder, then the flax fiber was added, and the final composite filament was collected into rolls. The tensile tests did not show a reinforcing effect such as that of the synthetic carbon fibers, but there are numerous advantages in the use of the CFFRP because it is biodegradable, environmentally friendly and it has low costs. For all these reasons, the use of CFFRP gives a better performance with respect to the pure PLA, but
more investigations shall be carried out to improve its use as a substitute for synthetic fibers. Badouard et al. [76] published a promising work concerning the production of flax biocomposites with three different biodegradable polymer matrices: Poly-(L-lactide) (PLLA), Poly-(butyl-adipate-terephthalate) (PBAT) and Poly-(butylene-succinate) (PBS). The addition of flax fibers caused an increase in Young’s modulus, independently from the polymeric matric used. Also studied was the influence of the fiber content (maximum concentration of 30% for PBAT composites) and the use of flax shives, which have a shorter length than fibers and have been evaluated since they can have some advantages in terms of better distribution in the polymer matrix during the extrusion of the filament. The scientific literature concerning natural fiber reinforcement mostly refers to the polylactic acid (PLA) or the polyolefins plastics, but there are also some studies involving the use of flax fibers to reinforce plastics such as Nylon 6 (also called PA6 or Polyamide 6) and polybutylene terephthalate (PBT) [77]. The reinforcement of this kind of polymer represents a challenge because PA6 and PBT need a higher melting temperature, 230 and 250 °C, respectively, that can bring about the degradation of hemicellulose and cellulose of the fibers. Flax fibers were chosen because of their thermal stability, in fact, they have lost at 225 °C only 2% of their weight and a loss weight of 4% occurs at 250 °C. For the preparation of composites, the flax fibers were treated with a preliminary alkalinization to prepare the surface for the adhesion to the polymer. The mechanical tensile strength of the obtained filament was 20% higher and the elastic modulus was almost three time higher in the presence of a fiber concentration of 40–50% wt. The authors concluded that it is possible to produce a composite made by mixing plastics and flax fibers by keeping the processing temperature lower than the melting point of the material. A comparison study was also conducted in which polylactic acid (PLA) was reinforced with bamboo or flax fibers and two different plasticizers [78]. The aim of the work was to understand the influence of the length and diameter of the fibers on the composite properties. Two plasticizers were used, cPLA1 and cPLA2, with the aim of reducing the brittleness of the PLA. Four different composites were reinforced with bamboo (B1, B2, B3 and B4) and two composites with flax fibers (F1 and F2). Tensile tests were conducted, and it was found that, among the two plasticizers, the cPLA1 has only 30% of the pure PLA stiffness, while cPLA2 has 19%, suggesting that the first one has to be preferred. Furthermore, the best performance as reinforcement is attributed to the longer bamboo fibers, with an increase of 215% in the modulus with respect to the short bamboo (only 39%) and the flax fibers. More studies are needed to obtain complete information about the use of flax and bamboo fibers as reinforcement, although at the moment they are already used and a great deal of research is being carried out on them.
Figure 5. Schematic illustration of preparation and characterization of sustainable composites produced from PLA and flax/jute fibers. Reprinted from [79].

3.7. Hemp Fibers

Hemp (Cannabis sativa L.) is one of the oldest plants used from the Neolithic age to our days for many applications in different fields, such as pharmaceutical, agri-food, cosmetic, textile, paper and building construction, but also for its recreational properties [80]. The Cannabis sativa L. plant can easily grow in every climate, and it offers a variety of raw sources (leaves, flowers, stem, plant fiber and fruit—also known as ‘achene’) that can be used for many applications, from oil and soap to building materials [81]. The growing interest in hemp has led to explore a possible application as reinforcement for the polymeric matrices in 3D printing in accordance with the need to have “green” and fully biodegradable materials. In the study conducted by Coppola et al., the powder obtained from hemp shives was employed, at increasing volume percentages (i.e., 1%, 3%, 5% w/w), for the preparation of different blends with polylactic acid (PLA) [82]. The hemp powder was derived from the waste product of hemp fiber extraction and is mainly composed of cellulose, lignin and pectin. The mixing of hemp powder and PLA is carried out without any previous chemical or physical treatment to improve the adhesion and homogeneity of the final blend and hemp/PLA composite filaments were obtained by extrusion at 160–180 °C. The DMA analysis on composite filaments shows that the blends with 1% and 3% hemp have a low storage modulus compared to the pure PLA, because of the low adhesion between PLA and hemp powder, while the blend containing 5% hemp powder shows a higher storage modulus. The production of specimens from the different blends with a 3D printer using FDM techniques demonstrates an advantage in the PLA/hemp composite materials in terms of elastic modulus and tensile strength. Coppola et al. concluded that hemp powder is suitable as reinforcing for polymers in 3D printing, but further studies are required to understand if some chemical or thermal treatments could result in an enhanced bond between PLA and hemp powder. In a subsequent study, the possibility of using preliminary treatments to improve the interaction between hemp fibers with PLA was evaluated. Overall, the most common involves the treatment of hemp with alkali to obtain a better interface between fibers and polymer, and to remove, at the same time, lignin, hemicellulose, waxes and oils. Sometimes, this process is not sufficient, despite
the fact that alkali treatment helps in exposing the hydroxyl groups of cellulose in the fibers. Mazzanti et al. carried out a study using a percentage of hemp fiber of 3% and 6% w/w in PLA. The observation with the SEM microscopy shows that the fiber–polymer interface is only slightly affected by the alkali treatment. Irrespective of this, a larger increase in stiffness and strength that results in a lower ductility of the composites is achieved by adding alkali-treated hemp fibers with the respect to the untreated ones. The author’s conclusion is that the major difference made by the alkali treatment involves the fibers’ morphology and the better mechanical performances are related to the reduction in the amount of fiber bundles in the composite and the consequently more distributed isolated elementary fibers [83]. Another application in the 3D printing field involves the use of hemp hurd (HH), which is the inner core of the plant stem, containing cellulose, hemicellulose and lignin. Xiao et al. prepared HH/PLA biocomposites to evaluate the hemp use as filler for FDM 3D printing. In this case, the blend was prepared by mixing, via melt-compounding, the PLA with poly (butylene adipate-co-terephthalate) (PBAT) as a toughening agent and ethylene–methyl acrylate–glycidyl methacrylate terpolymer (EGMA) as interfacial compatibilizer. Four different blends with increasing percentages of HH (10–40% w/w) were prepared. The addition of hemp did not affect the thermal behavior of the biocomposites, but it increased their crystallinity. Despite this, a slight decrease in tensile and flexural strength occurs by increasing the HH concentration related to the high porosity and low interfacial bonding between PLA and HH. FDM printed specimens show a greater dimensional accuracy by increasing HH loading [84]. Not only PLA but also silicone was reinforced with Hemp fibers. Among the different treatments proposed in the literature, Koushki et al. decided to compare the untreated hemp fibers with NaOH-treated fibers and NaOH-silane-treated fibers. All the tests confirmed that the treatment improved the adhesion between fibers and polymer since treated fibers have a greater availability of functional groups that can easily bond with the polymer. Both the tensile strength and the modulus increased by 27% and 54%, respectively, compared to the values of untreated fibers, with a 15% w/w loading of hemp, assuring a good printability by direct ink writing (DIW) [85]. The treatment with coupling agents such as maleic anhydride grafted polypropylene (MAPP) and maleic anhydride grafted poly (ethylene octane) (MAPOE) leads to a better resistance to temperature and also to an improvement in interfacial bonding. The higher content of short hemp fibers improved the higher mechanical properties (e.g., storage modulus) [86]. In conclusion, the use of hemp fibers can be helpful for the production of more convenient 3D printed specimens, despite the fact that, as for the other natural fibers, more experimental studies are necessary.

3.8. Soybean

The soybean (Glycine max L.) is a crop plant originating from China, but is now widely spread and cultivated in different areas of the world [87]. The soybean represents an important source of seed protein, oil and hull fibers, and its importance from a food and technological point of view has increased over time, also thanks to numerous studies that demonstrated its real value. The soybean seed contains 40% proteins and 20% oil, both of which are used in different fields, such as food, industry and technology [88]. The increasing attention to the green economy and the reuse of waste materials led the scientific community to carry out numerous studies to give a second life to industrial production waste, as in the case of oils and fibers derived from the soybean. Indeed, numerous works were recently carried out to study the feasibility of exploiting epoxidized soybean oil (ESO) as a reactive compatibilizer [89] or plasticizing agent for PLA-based materials intended for 3D printing [90]. Moreover, ESO can be also employed for the preparation of temperature or UV-curable resins for SLA 3D printing or digital light processing (DLP) [91]. Cui et al. developed a hybrid resin based on ESO and acrylates for SLA 3D printing. After printing, the thermal curing at 100 °C promoted the formation of interpenetrating networks, leading in the improvement of the mechanical strength of the printed object without affecting its flexural properties and the surface finishing [92].
Voet and coworkers prepared UV-curable resins based on meta-acrylate oligomers functionalized with ESO. Specifically, photoresins were generated when 80% of the photosensitive oligomers were mixed with bio-based diluents and a photoinitiator. The authors demonstrated the applicability of their resin in SLA 3D printing and the maintaining of suitable mechanical properties of the 3D printed objects in comparison to using a fossil-based commercial resin, with the advantage of a bio-based product, thereby reducing the environmental impact [93]. Soybean Hull Fibers (SHF) are instead largely investigated as reinforcement agents for thermoplastic polymers mainly intended for FDM 3D printing. Balla et al. conducted a study to understand the feasibility of the soybean hull fiber as reinforcement for a thermoplastic co-polyester (TPC) to manufacture composites intended for 3D printing [94]. A preliminary study was carried out to prepare and characterize different composites mixed with chemically treated soybean hull fibers (CT-SHF) and untreated fibers (UT-SHF) [95]. UT-SHF were crushed to reduce their size and then they were added to the TPC; on the contrary, CT-SHF have been subjected to single or double acid chemical treatment, then washed, dried, reduced to fine powder and at the end added to the TPC. The SEM observation revealed that the treated hull fibers were more porous and had a smaller size after the acid treatment, probably due to the removal of superficial impurities, waxes and hemicellulose, but no morphological differences were found between the fibers treated with single or double acid hydrolysis. The soybean hull fibers were well distributed in the TPC matrix, and the mechanical analysis showed that the tensile modulus increased up to 90% with the double chemical treatment, but there was no significant improvement in strength. The addition of CT-SHF also exhibited a toughness 29% higher than the UT-SHF, and the analysis of the interface adhesion confirmed that the chemical treatment allows for an improved bonding between TPC and soybean fibers. For all these reasons, this work demonstrates the promising use of soybean hull fibers as reinforcement for the production of TPC composites, for 3D printing, using the fused deposition modelling (FDM) technique [94]. In conclusion, these studies demonstrate that the application of soybean hull fibers as reinforcement for matrices intended for 3D printing is possible, even if some chemical and physical treatments are necessary to obtain their best performance in terms of mechanical properties and printability. The application of soybean hull fibers as reinforcement is still novel, and further studies are needed to improve their use and avoid some common problems with the FDM 3D printing process, such as nozzle clogging, agglomeration of fibers (due to the non-homogeneous distribution in the composite) and variation of viscosity after the addition of soybean hull fibers.

3.9. Coffee Waste

Coffee is one of the most important food commodities in the world. The coffee industry generates a large amount of residues, among which the most used are spent coffee grounds (SCG) and coffee silver skin (CS). Particularly, SCG is the residual material obtained during the treatment of coffee powder with hot water or steam for the instant coffee preparation. SCG consists of carbohydrates, proteins, mineral and almost 30% of cellulose fibers [96]. CS, instead, is a thin tegument of coffee that is removed during the roasting, representing the main by-product. It is mainly composed of dietary fibers and other polysaccharides or sugars [97]. Thanks to their abundance, biodegradability and almost zero cost, there is an increasing interest in the used of SCG and CS as natural fillers in polymer matrices in order to develop a series of economic and functional bio-composites for application in various fields, in particular for 3D printing [98]. Despite the fact that coffee waste has been used in recent years as an effective reinforcement filler in bio-composites prepared with different polymers (polylactic acid—PLA, polyhydroxybutyrate—PHB) [99–102], very few works were performed on 3D printed materials. Chang et al. prepared a 3D printable PLA filament containing up to 20% \( \text{w/w} \) of oil-extracted spent coffee (OS-SCG). The obtained 3D printed composites show a 418.7% increase in impact toughness compared to the pure PLA with a potential use for high-impact applications, such as personalized prosthesis [103]. Li et al. prepared 3D printed specimens from composites formed by
PLA and decolorized SCG. When the content of decolorized SCG was up to 10% w/w, the specimens maintained a tensile and flexural strength comparable to those of pure PLA. On the other side, the melt flow properties of the composite filament were better than pure PLA. The decolorized SCG can be further pigmented for the production of a series of colored 3D printed specimens [104]. Actually, there is a scarcity of information about the effective use of spent coffee ground for 3D printing. However, recent studies have claimed that it is an effective natural filler in polymeric bio-composites produced with other techniques (e.g., twin screw extruder), since it improves the mechanical properties, while being biodegradable and at a low cost. The interaction with other additives (e.g., compatibilizers, coupling agents) in different polymeric matrices should be deepened in further studies in order to develop better bio-composites for different applications [99,100,102].

3.10. Keratin

Keratin is a fibrous protein and one of the most abundant biopolymers. It is obtained from different common natural sources (wool, chicken feathers and horn) and it has numerous and favorable properties, including biocompatibility, biodegradability and mechanical endurance [105]. C. G. Flores-Hernandez et al. used ground rabbit hair [106] and the rachis of chicken feathers [107] to reinforce PLA-based composites. Both ground rabbit hair and rachis were pre-treated with NaOH 0.1M to improve interaction between fibers and matrix and extruded with PLA to obtain a filament for the FDM 3D printing processing. A different mechanical behavior of the obtained composites was observed. Thermo-mechanical analyses showed a lower storage modulus (E') for composites prepared with pre-treated keratin from rabbit hair than pure PLA. On the contrary, a large increment in E' with respect to pure PLA (195%) was observed for composites prepared with 1% of keratin from treated ground rachis. The authors explained such a difference by considering that rabbit hair is predominantly composed of α-keratin, while feathers of β-keratin provide more flexibility to the composites. The presence of α-keratin fibers determines an increase in the movement of polymeric chains, thereby providing more flexibility and resulting in a decrease in E’ modulus on the other side, β-keratin promotes rigidity in the prepared composites. PLA composites have been produced using not only keratin alone but also with the addition of chitosan. In L. E. Rojas-Martínez et al.’s work, the effect of keratin configuration (mainly α-helix for keratin from hair or β-sheet for keratin from feather) in the presence of chitosan and the morphology and size of the added reinforcement mixture (fiber-type with a size < 1 mm and particle-type with a size < 0.7 µm) was investigated. The storage modulus of PLA composites with reinforcement of chitosan and keratin as fibers decreases with respect to pure PLA, indicating a more plastic behavior of the materials. On the contrary, an increase in the storage modulus of around 15% with the respect to pure PLA occurred in composites prepared with the particle-type reinforcement, determining an increase in the rigidity of the composite. Particle-type reinforcement improves fibroblast growth and adhesion more than fibers with a moderate swelling ratio of the obtained scaffold both in water and in simulate body fluid (Figure 6) [108]. Keratin is also mixed with lignin in order to form novel copolymer materials intended for additive manufacturing. In W.J. Grigsby et al., keratin is complexed with lignin at a 4:1 ratio, and suitable filaments for FDM 3D printing were produced [109]. Keratin and keratin/polymer combinations were also processed by the SLS technique. Keratin composites prepared with polyamide and polyethylene were considered to be suitable for SLS processing, without relevantly improving the mechanical properties of the composites [110]. All these studies show that keratin can be a versatile reinforcement agent for 3D printing, and it can be used in association with polymers or other materials to develop scaffolds, which can be used for several applications, such as 3D printing and tissue engineering.
Three-dimensional printing of PLA composite scaffolds reinforced with keratin and chitosan. Reprinted with permission from ref. [108]. Copyright 2020 Elsevier.

Figure 6. Three-dimensional printing of PLA composite scaffolds reinforced with keratin and chitosan. Reprinted with permission from ref. [108]. Copyright 2020 Elsevier.

4. Conclusions

The employment of natural polymers derived from plants or biomasses as reinforcement agents represents a flourishing field of investigation in 3D printing processes, since it helps with cutting the costs of the final printed objects, by making, at the same time, a "greener choice" in terms of producing more biodegradable and less environmentally impactful materials. Moreover, the technological approach of improving the thermo-
mechanical properties of polymeric printed specimens using natural products promotes the re-use and provides a “second-life” to many agricultural and industrial wastes. Research is still ongoing and the current literature available suggests that pure polysaccharides (especially cellulose and lignin) and plant-based fibers are more efficient than protein-based materials in enhancing mechanical properties of 3D printed composites. However, more studies are required to better define the functionality of each biopolymer and its area of applicability.

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