

Characterization and Properties of Biopolymer Reinforced Bamboo Composites



Laila El Foujji, Khadija El Bourakadi, Abou el kacem Qaiss, and Rachid Bouhfid

Abstract The development of novel sustainable eco-friendly materials gained increasing attention, in order to minimize the dependency on fossil fuels. Biopolymers and derivatives are among the chosen materials due to their natural origin, diversity and abundant character as well as being environmentally friendly thanks to their biodegradability. Biopolymers are complex biochemical units that vary due to their structures, they are synthesized from plants or living organisms. The advantages of these natural polymers are biodegradability and renewability, but used alone, they have low mechanical properties. To overcome this drawback, using composite materials which have a wide spectrum activity in industrial and engineering fields seems as an interesting choice. Recently, for composite manufacturing, interest shifted towards using fibers stemming from natural resources as reinforcements, because of their environmental benefits. Using a biodegradable matrix and a bio-resourced filler would result in a completely biodegradable composite. The available naturally occurring reinforcements are based upon jute, sisal, flax, hemp, and kenaf etc. We will be interested in the use of bamboo fibers as reinforcing fillers for biopolymer composites. Bamboo fibers own one of the most desirable combinations of low density (1.4 g/cm^3) and good mechanical properties allowing them to compete with glass fibers in terms of specific stiffness and strength at similar volume fractions. In this chapter, we will present the latest biopolymers used in composite and nanocomposite materials and their main properties and characterization screening their combination to various types of bamboo fillers, starting from the raw materials to nanoscale dimensions and, we will show some main applications in interesting domains.

Keywords Bamboo · Biopolymers · Composites · Nanocomposites · Characterization

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1 Introduction

Each year, the development progresses in science and technologies led to a huge number of polymers and polymer by-products. However, the main majority of the synthesized polymers are from fossil fuel origins, which make them non-biodegradable materials, and with the absence of the best treatment methods, they become environmentally harmful wastes [1]. In addition, the shortage of oil and fossil fuels has been a problem for many years and raises concerns all around the globe. It also greatly affects the field of chemical industry. For example, a 2012 statistic study showed that the annual plastics production is around 200 million tons [2]. Therefore, it is necessary to find new renewable and environmentally friendly raw material alternatives to replace fossil fuel resourced ones. An interesting good approach is to produce polymers from agricultural sources [3], polymers issued from renewable resources, biomass in particular, have received a rising attention lately due to their environment friendly impact. This class of polymers have two important properties, which are biodegradability and biocompatibility, that are mostly investigated regarding several applications such as medical issues [4]. Through the previous two decades, major advances have been done on developing biodegradable polymer materials for several applications [5], some applications of biodegradable polymers include food packaging, packing foams, disposable food service items and health care products, at the present, most of these products are produced from polystyrene or polyethylene. They also become wide ranging vital materials in the implantable applications, such as dental and orthopedic devices, drug delivery systems and tissue engineering scaffolds [6]. The use of biopolymers (such as starch, chitin, cellulose...) with other components is an interesting choice in order to bring them new properties or at least, improve their intrinsic properties. Composites and nanocomposite materials the strategy to be followed to reach the previous goal. The mix between biopolymers and fibers to improve some properties, should not alter the biopolymers' biodegradable and environment safety properties. The advantage of natural bio-sourced fibers over inorganic ones (such as glass fibers...) is their reduced cost. Other properties also include low density, high specific density/resistance ratio, low abrasiveness, along with biodegradability and renewable origin [7]. Bamboo is an interesting source of fibers, it's a fast growing tree, and has an abundant global production of about 30,000 kt each year, the stiffness and strength of bamboo fibers are closely similar to this property of glass fibers and hard woods [8]. Bamboo fibers present favorable physical and mechanical properties compared to natural fibers and have been proposed for reinforcing different polymer matrices including polylactic acid [9]. The cellulose is the main constituent of bamboo fibers, about 57%, followed by the lignin content by approximatively 25% and the humidity is present at 8.5%. Nanocellulose is gaining a great deal of attention, it typically has a 5 to 50 nm width and an important specific surface area. Enormous advancements and considerable interest on cellulose nanofiber were seen in the last decade owing that to renewable character, low density, advantageous mechanical properties, availability, and diversity of sources. The use of cellulose nanofibers from bamboo pulp as a

reinforcing phase in natural rubber have been studied and proven to have superior values of tensile strength compared to early reports on natural rubber [10]. Cellulose whiskers or nanocrystals extracted from bamboo are another important type of reinforcements, an improved yield of 88% of cellulose nanocrystals extraction was established by simultaneous mechanochemical activation and phosphotungstic acid hydrolysis, Short rod-like cellulose nanocrystals were elaborated and showed higher thermal stability and displayed a web-like network structure that could provide higher reinforcing capability for composite materials [11].

2 Polymers and Biopolymers

The polymer is a word that descends from the Greek term “many parts”, it’s the main constituent of plastic and elastomer materials. Large molecules or macromolecules that are made and composed of repeated monomers chemically joined and bonded into long chains result in obtaining polymers [12]. Thanks to their numerous properties, natural polymers, and synthesized ones play a ubiquitous role in everyday life [13]. The chemical industry produces enormous quantities of synthetic polymers in order to assure the material needs for product diversity, including coatings, films, paints, and structural plastics. Yet, in the previous several decades, the development of eco-friendly and sustainable products to lessen the dependence on the attenuated fossil fuels, which is the source of most plastics, knew a major increase. The rapid growth of the demand for removing petroleum-derived plastics from our eco-system has been an impetus to the research on bio-friendly polymers [14]. Biopolymers are the alternative solution for this problematic issue, currently considered as a potential class of materials and among the most investigated ones [15]. Biopolymers are extracted from various natural resources. A summarize of biopolymer classification is shown in Fig. 1.

2.1 *Classification and Characterization of Natural Biodegradable Biopolymers*

The classification of biodegradable polymers is not usually an easy task. They can be sorted according to many criteria. Starting from their chemical composition, synthesis and processing methods, their economic importance and application. These classifications provide useful and different information [17]. To categorize biodegradable polymers called biopolymers based on their origin, we can find two groups: natural polymers issued from natural resources and synthetic polymers.

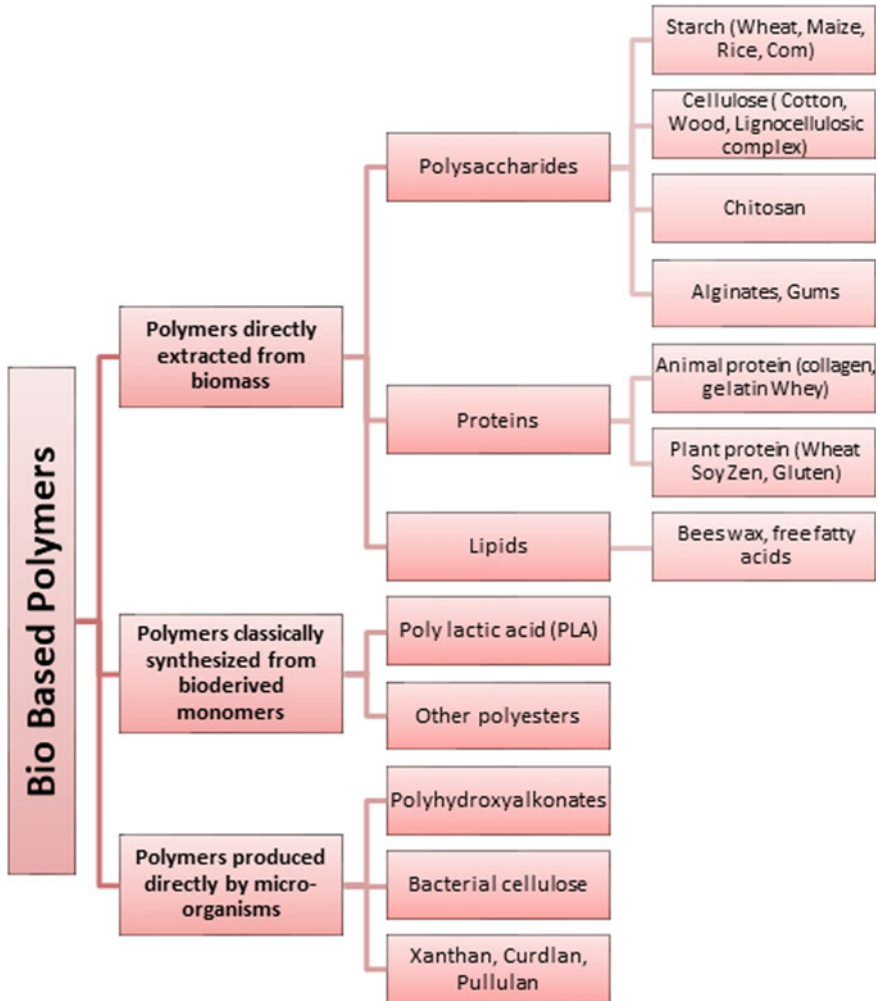


Fig. 1 Classifications of bio based polymers [16]

2.1.1 Carbohydrate Polysaccharides

Polysaccharides are made of several monosaccharides linked together via glycosidic bonds. It's the largest component of the biomass, its value is expected to exceed 90% of the carbohydrate mass in nature [18].

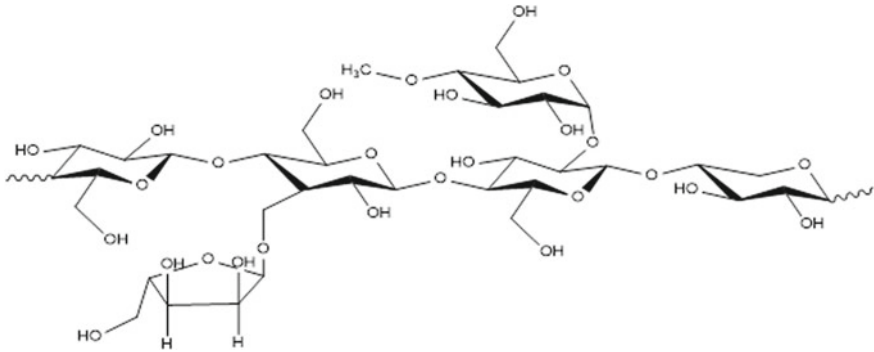


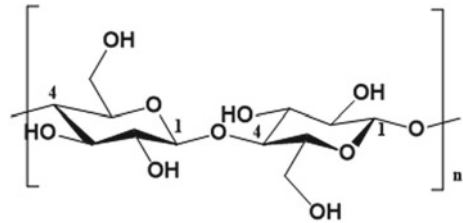
Fig. 2 Hemicellulose structure

Microbial and Animal Polysaccharides

Microbial polysaccharides are renewable resources materials made by microorganisms, and they have both characteristic of biocompatibility and biodegradability, such as alginates/alginate acid. Thanks to their high properties for thickening, stabilizing, emulsifying, and gelatinization, they are used in many industrial fields as additives, such as the synergic effect seen between polysaccharides and particle gel on the thickening and oil recovery [19]. Many potential natural polysaccharides are used in the drug delivery systems, the widely used one is chitin and its derivative. Chitin is a widespread biopolymer, located in large quantities in marine animals, especially on the animals' outer skeleton such as insects and crustaceans [20]. Chitosan have gained important attention thanks to the fact of being biodegradable, biocompatible and to their non-immunogenicity and non-toxicity [21].

Hemicellulose

In general, hemicellulose is a pentose-based polysaccharide [22], that forms the cellulose-hemicellulose network thanks to its attachment by hydrogen bonds to the cellulose microfibrils, which guarantees the rigidity and strength of the plant tissues [23]. The hemicellulose structure was first elucidated as arabinoxylan oligosaccharides with diferulic acid cross-linkage in moso bamboo shoots, the thermal degradation was observed to occur at 200–300 °C for 4-year-old moso bamboo. Figure 2 shows the hemicellulose structure. The hemicellulose includes xylans, xyloglucans, glucomannans and mannans, and it plays an important role in plant tissue configuration [24].

Fig. 3 Structure of cellulose

Cellulose

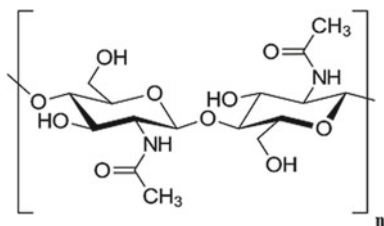
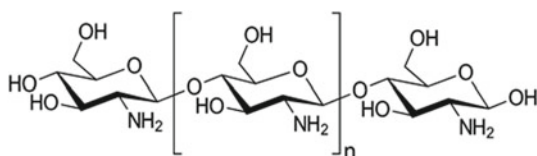
One of the top polysaccharides contributing at a fast rate to engineer multifunctional bio-based materials, is the cellulose, especially at its nanoscale forms. Cellulose is a linear chain of glucose molecules having a flat ribbon-like conformation, its repeat unit consists of two anhydroglucose moieties joined together 1–4 glycosidic bond as shown in Fig. 3, n is the polymerization degree which found to vary between 10,000 and 15,000 depending on cellulose source [25]. Cellulose is extracted from plant using chemical, mechanical or enzymatic methodologies, we will focus later on, on some important applications of this polysaccharide, but as a first important application, we can cite the manufacture of a fully bio-based conductive separator made from cellulose polysaccharide for application as a separator in electrolyte polymers in fuel cells [26]. The pretreatment of bamboo with cold sodium hydroxide and urea lead to some structural and morphological changes, providing high reactive cellulose that found and important application in the bioethanol production [27].

Starch

Starch is ranked among the three more abundant polysaccharides on earth, along with cellulose and chitin. But it is the only used material as main carbohydrate storing system of green plants, while chitin and cellulose are structural polysaccharides. Starch is collected in amyloplasts organelles and can be stored for a long period of time, and it's used generally in food [28].

Chitin

Chitin is the second largest carbohydrate resource for the production of fuels issued from bio-sourced origin and of some chemicals, the sustainable and efficient conversion of chitin makes it an attractive material [29]. Chitin is constituted by sequences of *N*-Acetyl-*D*-glucosamine through a β linkage, its structure is shown in Fig. 4 it is the second abundant biopolymer in nature after the cellulose. Among the applications of chitin is its use in the manufacture of films used on board surfaces to prevent the bacterial growth in perishable food packed in starch-based treated board [30].

Fig. 4 Chitin structure**Fig. 5** Chitosan structure

Chitosan

Chitosan is a linear cationic biopolymer, ranked in the second position of the most abundant natural biopolymer after cellulose. It has a similar structure to cellulose; the only difference is the type of attached group to carbon 2 [31]. The chemical structure of chitosan is shown in Fig. 5. This polysaccharide is built from 4-linked-β-2-amino-2-deoxy-glucopyranose residues, some of which are *N*-acetylated as shown in Fig. 5.

Chitosan biopolymer have a wide spectrum of use, an important application is its use as a coating agent of several nanoparticle materials, such as polymer, lipid and metal nanoparticles. An efficient coating process is confirmed, as well as, many physicochemical and biological advantages that were brought by the chitosan-coating, like physicochemical stability, improvement of tissue/cells interaction, controlled releasing time and increase in the bioavailability and efficacy of drugs [32].

2.1.2 Animal and Plant Sourced Proteins

Many proteins extracted from animals exist, for example gelatin, collagen and whey. The collagen, another abundant and natural biopolymer that has many applications in the biomedical and non-biomedical fields, this biopolymer can be extracted from fish waste using ionic liquid as a green pretreatment route [33]. Gelatin is another biopolymer with interesting properties, it can for example be applied as a coating layer to stabilize surfaces by increasing the steric barrier and it shows interesting anti-angiogenic and antibacterial activity [34]. Many plant proteins are used in chemistry fields (wheat gluten, soya, zein, caesin...), for example functional commercial soy proteins are often affected due to their natural high molecular weight but a controlled

enzymatic hydrolysis reaction of these proteins can improve both the technical functionality of these proteins and numerous of their bioactive properties like providing good emulsion activity and gelling ability [35].

2.2 Synthesis and Properties of Synthetic Biopolymers.

Synthetic biopolymers have been developed, primarily in response to perceived uncertainty in the continuing supply of fossil raw materials from the 1970s oil crisis, they are mostly developed for biomedical and agricultural applications, Among these synthetic biopolymers, we cite polylactic acids or polylactide, that indicates the same biodegradable aliphatic polyester, polyhydroxyalkanoates, polyhydroxybutyrate, polyglycolide, polydioxanone, polyvinyl alcohol.... Synthetic biodegradable biopolymers have been developed, typically for biomedical and agricultural applications [36]. The biopolymer production capacity in 2011 sorted by type is presented in Fig. 6.

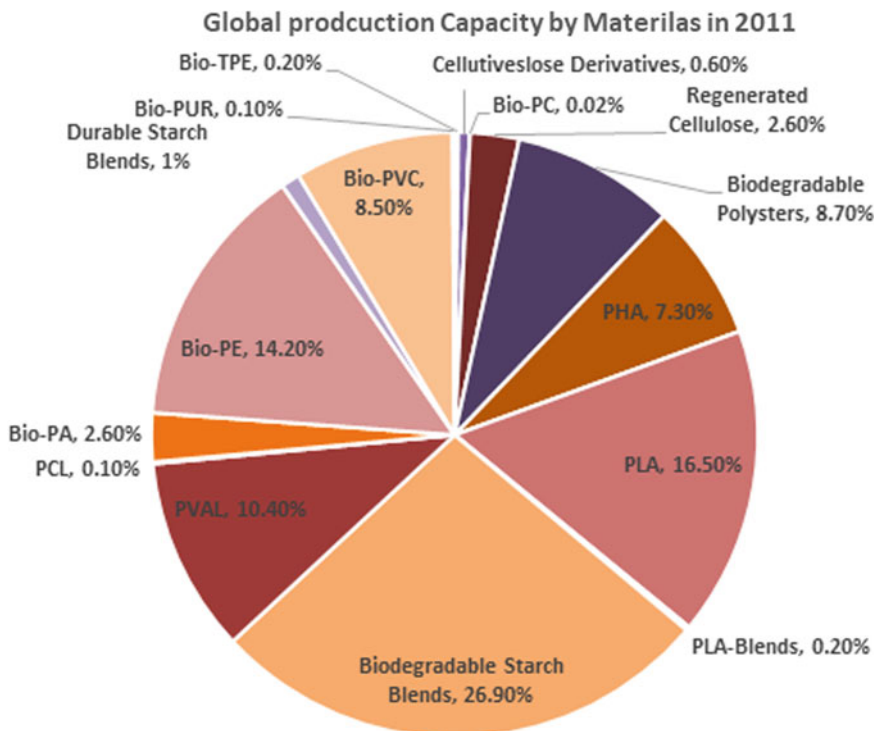


Fig. 6 Biopolymer production capacity in 2011 by type [37]

3 Bamboo and Bamboo Fibers

Bamboo received expanding attention in the previous two decades thanks to its economic and environmental values [38]. Bamboo (*Bambusa arundinacea*) is a woody, perennial, evergreen plant that belongs to the Poaceae-Graminae, considered to be the fifth-largest known ubiquitous family of monocotyledonous flowering plants, containing all lower grasses along with some giant members. Numerous chemical compounds are found in the leaves of bamboo and have an important therapeutic activity against a number of diseases and play a vital role as antioxidants. Leaves mainly consist of benzoic acid, hydrocyanic acid, glutelin protein, flavonoids, proteolytic enzymes [39]. The general composition of bamboo culm is shown in Fig. 7.

3.1 Sources of Bamboo

Bamboo is one of the most important and substantial green renewable resources, it is an easily flourishing plant, a cursory obtainable fibrous plant that can be used as an alternate for the unsustainable synthetic fibers in the biodegradable polymer, it offers a great potential alternative to wood [41]. Globally, bamboo is widely available in about 1662 species and 121 genera, and it is distributed over a large number of biogeographic regions, commonly found in Africa, Asia, some parts of Europe and America [39].

3.2 Bamboo Fibers Extraction

Bamboo fibers are extracted mainly by mechanical methods to avoid much black liquid release [42]. The bamboo fibers extraction methods are important to maintaining particular properties of bamboo fibers, the use of a machining center to

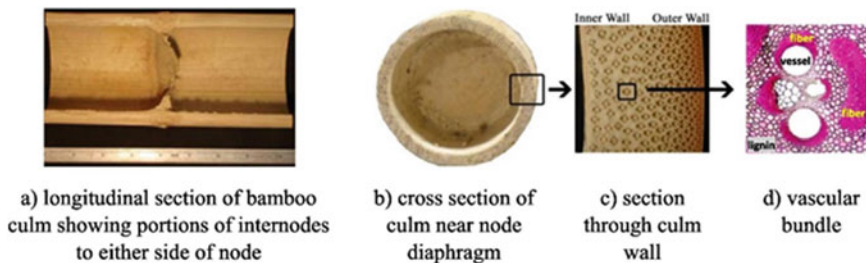


Fig. 7 Anatomy of bamboo culm showing functionally graded distribution of fiber in culm wall [40]

end-mill the bamboo culm, for example, results in obtaining high-quality, straight bamboo fibers without any thermal damage [43]. The treated bamboo may be made into huge durable structural elements that will have the potential ability to become transformative large-scale building materials. Laminated bamboo, for example, is a promising structural engineered material, generally made by improving the material's durability [44]. Raw bamboo fibers can be used as microscopic reinforcement agents, these fiber bundles of 125–210 μm in diameter were used as reinforcement agents of a polymer matrix made of maleic anhydride polypropylene. Commercialized bamboo chips ($3 \times 2 \text{ cm}$) using were filtrated and were the source of the bamboo bundles, using a mesh sifter machine. The tensile strength of the bamboo bundles was as high as that of the jute fiber [45]. In another case, using untreated and alkali-treated continuous bamboo fibers were studied to compare their properties, these fibers were incorporated into an epoxy matrix. The characterization showed that the strength of bamboo fibers was reduced with the alkaline treatment, however, the alkali-treated fiber-reinforced composites acquired better tensile strength than those with untreated bamboo fibers [46]. Bleached bamboo fibers are another branch of fibers that have some important characteristic, for instance, a comparative study on the compatibility of unbleached and bleached bamboo-fibers with the Linear low-density polyethylene matrix, showed better properties of the bleached fibers in terms of tensile strength and less water uptake, which assure an improved compatibility of these fibers conjointly with a better wettability with the apolar matrix [47].

3.3 Mechanical and Morphological Properties of Bamboo Fibers

3.3.1 Tensile Strength

The usual longitudinal tensile strength of Moso bamboo single fibers ranges from 1.43 to 1.69 GPa, what makes it significantly higher than nearly all the previously published data. High-strength bamboo strip used to reinforce composite materials with a maximum tensile capacity of approximately 180 MPa were fabricated using the hot press method [48]. Table 1 shows some physical properties of some natural fibers [49].

Table 1 Physical properties of some natural fibers

Sl. No.	Fiber name	Density g/m^3	Tensile strength (MPa)	Young's Modulus (GPa)	Specific strength MPa/g m^{-3}	Specific modulus GPa/g m^{-3}	Failure strain (%)
1	Bamboo	800	441	35.9	551	44.9	1.3
2	Jute	1300	370	22.7	281.6	17.5	1.4
3	E-glass	2500	2400	70	900	28	–

3.3.2 Scanning Electron Microscopy

The morphologies of untreated bamboo fibers and alkali-treated bamboo fibers are shown in a and b of Fig. 8, respectively. Alkali treatment leads to a more open or uneven rough fiber surface which results probably in an increased fiber-material bonding due to a larger fiber surface area [50].

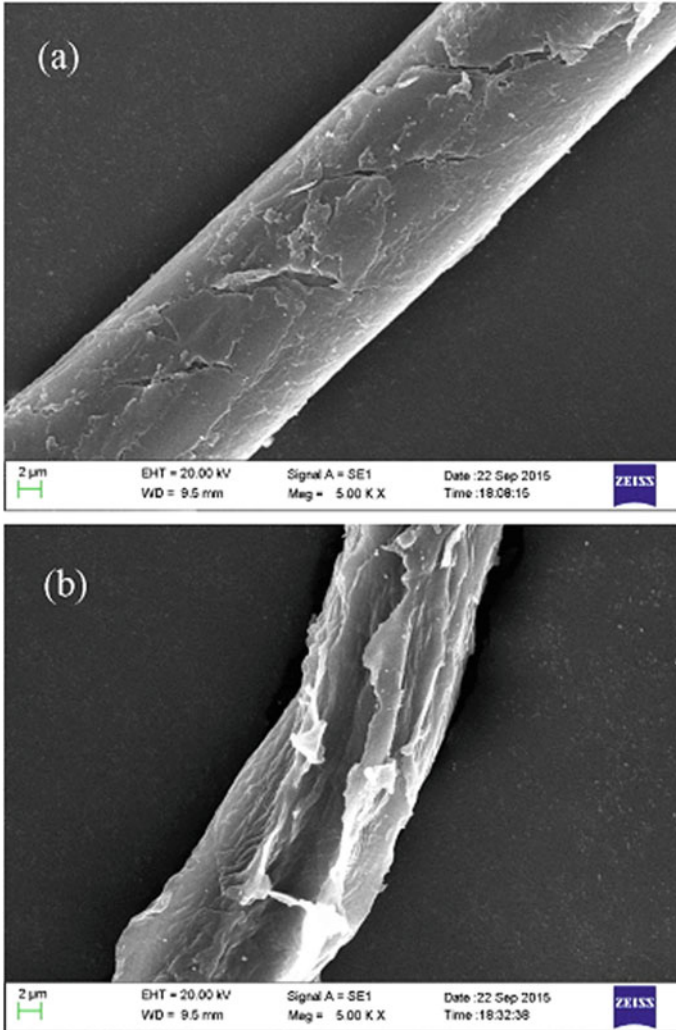


Fig. 8 SEM micrographs of the bamboo fibers: **a** untreated bamboo fibers; and **b** 10% alkali treated bamboo fibers

3.3.3 Fourier Transform Infrared Spectroscopy

The Fourier transform infrared spectroscopy (FTIR) is a powerful technical tool that is used to recognize and confirm the presence of certain functional groups belonging to the modifying agent used during the modification and also the mechanisms of interaction between materials [51]. Fourier transform infrared spectrums of treated samples that were presented elsewhere [52] comparing raw to bleached and caramelized fiber have only some subtle differences that exist between these treated sample and the raw one, observed shifts in the bleached material compared to the raw Moso bamboo were attributed to the bleaching process oxidizing the aromatic rings of the phenolic groups in the lignin (1230 cm^{-1}) and to hydroxyl groups in the polysaccharides (1047 cm^{-1}). The FTIR spectra from another study [53] of original bamboo, microwave liquefied residue, bleached residue, alkali treated residue, and cellulose nanofiber are presented in Fig. 9. They are showing the important absorbance peaks that distinguish the original bamboo which have characteristic bands such as 1735 cm^{-1} for hemicellulose and 1230 cm^{-1} for lignin, from the liquefied one, where an absorbance band appears at 1203 cm^{-1} and attributed to S=O vibration revealing the introduced sulphate groups during the microwave process because of the use of sulfuric acid as the catalyst. The other characteristic absorbance bands of lignin (1596 , 1506 , 1456 , and 1230 cm^{-1}) were absent in the spectrum of the bleached residues.

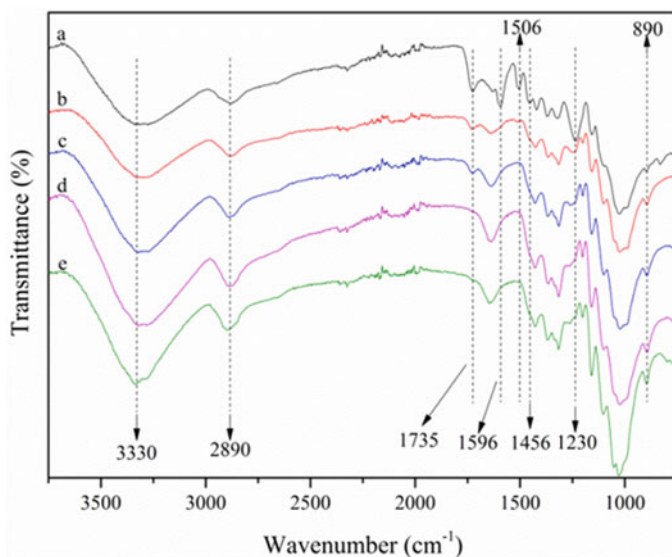


Fig. 9 FTIR spectra of **a** original bamboo, **b** microwave liquefied residue, **c** bleached residue, **d** alkali treated residue, and **e** cellulose nanofiber [53]

4 Properties of Bamboo and Cellulosic Bamboo Fibers

4.1 Bamboo Based Nanofibrillated Cellulose

The bamboo was studied as micro and nano reinforcement agent in polymeric matrices, including thermoplastics such as polyethylene, polypropylene, different polyesters, and other semicrystalline polymers, hybrid composites such as that of polypropylene and polylactic acid, macro reinforcement in thermosets and polyester resins [55]. The hierarchical structure of bamboo fibers is described in Fig. 10. Nanofibrillated Cellulose is the cellulose fibers that have been fibrillated to reach the agglomeration stage of many cellulose microfibril units, nanofibrillated cellulose has a nanoscale diameter (at least one dimension should be less than 100 nm) and a typical length of several micrometers [56]. Cellulose nanofibrils can be derived from the bamboo plant using eco-friendly ultrasonic treatment process, which provides a high aspect ratio of isolated nanofibrils [57]. Appropriate pretreatments of cellulosic fibers are important parameters to consider for promoting hydroxyl groups accessibility, increasing inner surface, alter crystallinity, and break cellulose hydrogen bonds and therefore, boost the reactivity of the fibers, among the mechanical processes used to isolate nanofibrillated cellulose, we can cite: High pressure homogenization, grinding, cryo-crushing, micro-fluidization, steam explosion, ball milling and high intensity ultrasonication [56, 58].

Chemical modification on cellulose fibers is mainly used to facilitate cellulose nanofibers production and decrease energy consumption, among the first used strategies of introducing negative charges on the cellulose fibers surface is the oxidation, using 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) [59], the newest research on TEMPO oxidation for cellulose nanofibrillation focused on coexisting salts, where a

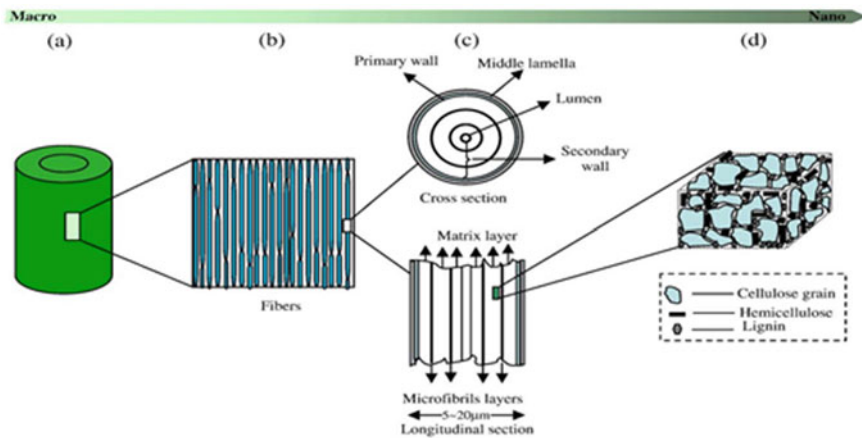


Fig. 10 Hierarchical organization of bamboo fibers over different length scales [54]

portion of NaBr was replaced by Na_2SO_4 , providing both cheaper cost and leads to the same carboxylic content. Phosphorylation is another way of introducing negative charges on cellulose fibers, it's a new emerging chemical pretreatment. Many other chemical modification processes exist (enzymatic, sulfoethylation, cationization, ozonation...) [60].

4.2 *Bamboo Cellulose Nanowhiskers*

Cellulose microfibril is a semicrystalline polymer, it is constituted of a disordered region called amorphous region and a highly ordered called crystalline region [61]. While acid hydrolysis treatment is applied to cellulosic microfibrils, it allows the dissolution of cellulose amorphous domains. During this process, hydronium ions pierce the cellulose chains in the amorphous domains promoting the hydrolytic cleavage of the glycosidic bonds and liberating individual crystallites. The resulting material is called cellulose whiskers, but other terminologies are used such as cellulose nanocrystals, cellulose nanowhiskers, or nanocrystalline cellulose [62]. A mechanochemical approach of manufacturing bamboo cellulose whiskers via the dissolving action of phosphoric acid on cellulose microfibrils was applied, this leads to high yields bamboo cellulose nanocrystals thanks to the swelling effect of phosphoric acid on microfibrils, allowing them a better disintegration [63]. Decreasing the size of a material from the microscale to the nanoscale have a major effect on its properties, they change and they are expected to drive new potential applications. The main impacted properties by this change are reported below:

4.2.1 **Specific Surface Area**

The specific surface area is a property of solids defined as the total surface area of a material per unit of mass, since the nano-dimensions of the structural elements leads to a high surface area, the reported large specific surface area of cellulose nanocrystals is estimated to be more than $100 \text{ m}^2 \text{ g}^{-1}$ and even up to several hundreds of $\text{m}^2 \text{ g}^{-1}$ [64]. The addition of sulfuric acid to bamboo fibrils separated the cellulose whiskers instantly. After a 3 h treatment using a 65 wt% sulfuric acid, bamboo whiskers showed the maximum specific surface area of $14.225 \text{ m}^2 \text{ g}^{-1}$, while after a 4 h treatment with a 55 wt% sulfuric acid treatment, the specific surface area of the whiskers reached $13.355 \text{ m}^2 \text{ g}^{-1}$. Cellulosic hydrolysis degree varied in acid concentration and processing time, more pores led to a larger specific surface area, but an excessive treatment dissolved the cellulose and the specific surface area may decrease [65].

4.2.2 Aspect Ratio

Aspect ratio is defined to be the length to width (L/W) ratio, it is a predominant factor in the morphological characterization of cellulose nanowhiskers, usually, spherulitic nanoparticles exhibit a low aspect ratio value (≥ 1), but close to 1. A study on cellulose nanocrystal prepared by using sulfuric, hydrochloric, phosphoric, and a mixture of acetic and nitric acid solutions showed good aspect ratios ranging from 1 to 28 [66].

4.2.3 Mechanical Properties

The mechanical modulus of cellulose nanomaterials is doubtlessly their main asset.

The cellulose is a ubiquitous structural polymer that gives its mechanical properties to higher plant cells. The tensile modulus of native cellulose crystals for example can be estimated to range between 56 and 220 GPa, with an average value of 130 GPa [67].

4.2.4 Thermal Properties

The thermal properties of cellulose nanoscale materials are low because of its low thermal stability, and this might affect their use, especially sulfuric acid-hydrolyzed nanocrystals [62].

4.2.5 Morphological Properties

Bamboo cellulose nanocrystals exhibited a large length-to-diameter ratio (L/D) and had rod-like shapes (Fig. 11), the fibrillated bamboo cellulose nanocrystals had a higher surface area and better cross-linking characteristics when used as nanofillers. The bamboo cellulose nanocrystals had an average length, diameter and L/D ratio of 455 nm, 12 nm and 37, respectively [68].

5 Composites and Nanocomposites Based on Bamboo

A composite material is a multiphase material formed from a combination blend of materials which vary in the composition or in the form and remain bonded together, and retain their identities and properties. Composites maintain an interface between components and act in concert to provide improved specific or synergistic characteristics that cannot be obtainable by any of the original components acting alone [69].

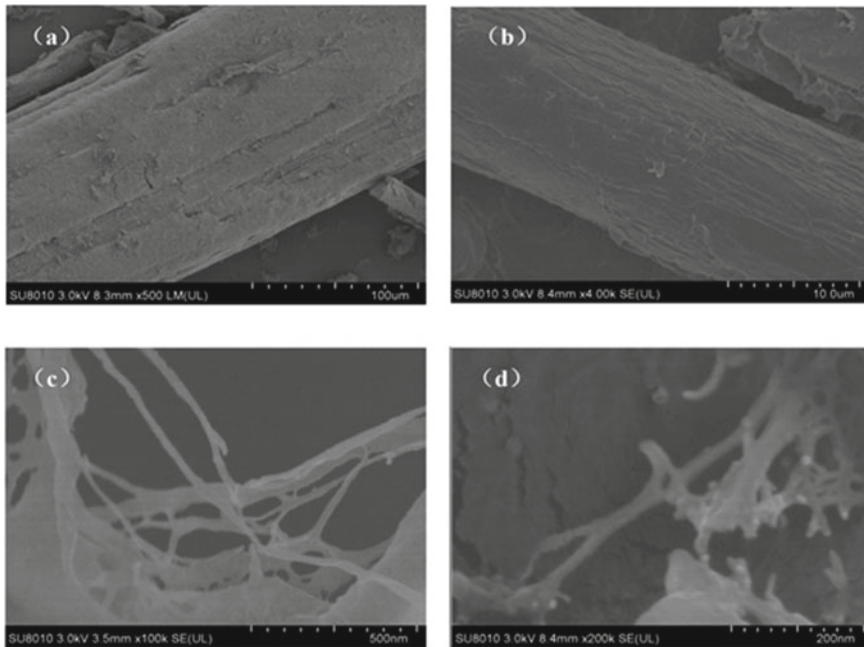


Fig. 11 SEM Micrographs of bamboo cellulose with different treatment: **a** raw bamboo particles; **b** alkali treated; **c** 55 wt% H_2SO_4 4 h; **d** 65 wt% H_2SO_4 3 h [68]

In the present era, researchers cannot think about the development without developing new materials with exciting properties to meet the increasing and diverse demand of both industry and society [70]. Composite materials are materials consisting of a fibrous phase generally a reinforcing fiber providing high mechanical properties for example, incorporated in a continuous phase (matrix). Depending on the type of matrix, composites are classified as polymeric, metallic, or ceramic [71]. Nanocomposites show great promise as they can provide the necessary stability and processability for important application.

5.1 Characterization of Composite Materials

5.2 Physicochemical Properties of Composites and Nanocomposites

Dramatic changes in the physicochemical properties of composites and nanocomposites can occur, due to the fillers or reinforcement agents, physical and thermal properties can increase or decrease according to the amount and nature of the fillers,

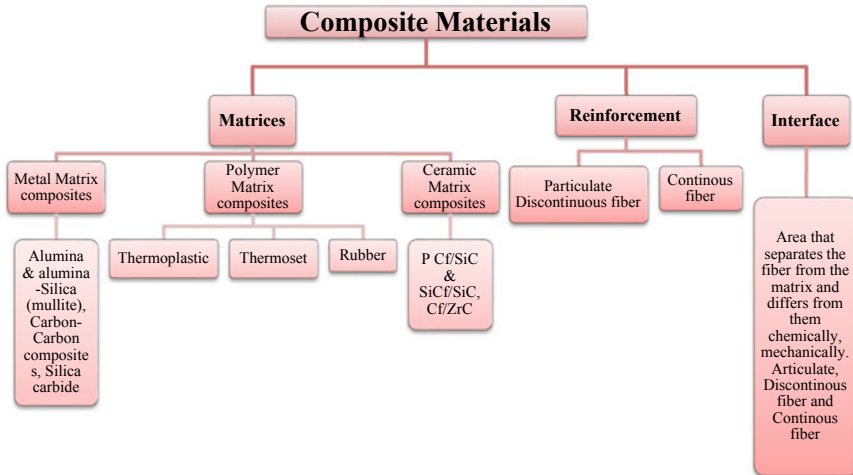


Fig. 12 Composite materials and types of constituents [69]

as well as many other properties such as mechanical behavior, along with some critical issues like the poor bonding, poor wettability, and the degradation at the interface between fiber/matrix which is usually caused by a hydrophilic and hydrophobic effect [72]. Some main components of composite materials are described in the Fig. 12.

5.3 Manufacturing Processes

Manufacturing processes of composites and nanocomposites are crucial steps to consider in the materials elaboration process. For instance, the damage of the fiber during manufacturing present a main reason of the decrease of the composites’ strength, as well as other properties, The suitable manufacturing processes must be utilized to transform the materials to the final shape without causing any defect of products, for example the injection moulding of composites is a process where a measured amount of mixture which contains the molten polymer and fiber is forced into mould cavities [73]. Another process is the Compression moulding, many studies were conducted on the possibility of using natural fibers as filler mixed with renewable polymers to form a new class of biocomposites through compression moulding process, it’s the preferred process thanks to its simplicity and fast processing cycle [74]. Hot processing favorable for simple flat samples because only two hot plates are needed to compress all fiber and matrix together simultaneously, then heat was applied, and the last process is resin transfer moulding [72].

6 Bio-based Polymers Matrices Reinforced Bamboo Composites

Chitosan is an exciting biodegradable, biocompatible and non-toxic polymer, it is commercially available and indeed widely used in composites as a matrix, in a recent study, the manufacturing and characterization of bio-nanocomposite films using chitosan as matrix, which was reinforced with bamboo or montmorillonite nanofibers was done. The solutions were prepared by dissolving crab shell chitosan in a glacial aqueous acetic acid following the described specific concentration and under the described conditions, the prepared films were elaborated by the casting technique. A comparison of cassava starch and chitosan as matrix polymers was established, showing some better response to nanostructure process of cassava starch, while in another hand the use of bamboo nanofibers showed a good interaction between the polymer matrix and the nanofibers, and the use of montmorillonite nanoparticles and bamboo nanofibers improved the low mechanical resistance of chitosan films and improved also its poor barrier properties [75]. In another study poly lactic-co-glycolic and nanohydroxyapatite and bamboo fibers were combined as a ternary composite by solution mixing method, the effect of the bamboo fibers content was investigated, it has an important impact on crystallization behavior, interface structure and mechanical and thermal properties. 5 wt% of the bamboo fibers showed the ultimate benefits for both crystallization and mechanical properties [76]. Another study investigated the mechanical and thermal properties of an aged composites based on polypropylene, ethylene-propylene-diene monomer and talc reinforced with bamboo fibers. Again, adding bamboo fibers increased significantly flexural and tensile modulus and the fatigue life, while decreased the elongation at break and impact strength. A compatibilizer was also used and it influences positively only tensile and flexural strength, but it has a negative effect on tensile elongation at break and impact strength of the material [77].

6.1 Morphological and Structural Characterization of Nanocomposites

Nanocomposite materials can be characterized using several tools, in the following part examples of nanocomposites materials characterization studies will be presented. A research paper on poly(lactic acid) (PLA)/bamboo cellulose nanowhiskers (BCNW) bionanocomposite material exhibits improved high toughness but a low modulus, in order to surpass this drawback, new fillers of silane surface-modified based ultrafine bamboo-char were used. The elaborated materials were films made by solution casting method using different amount of reinforcements ranging from 0.25 to 4 wt%.

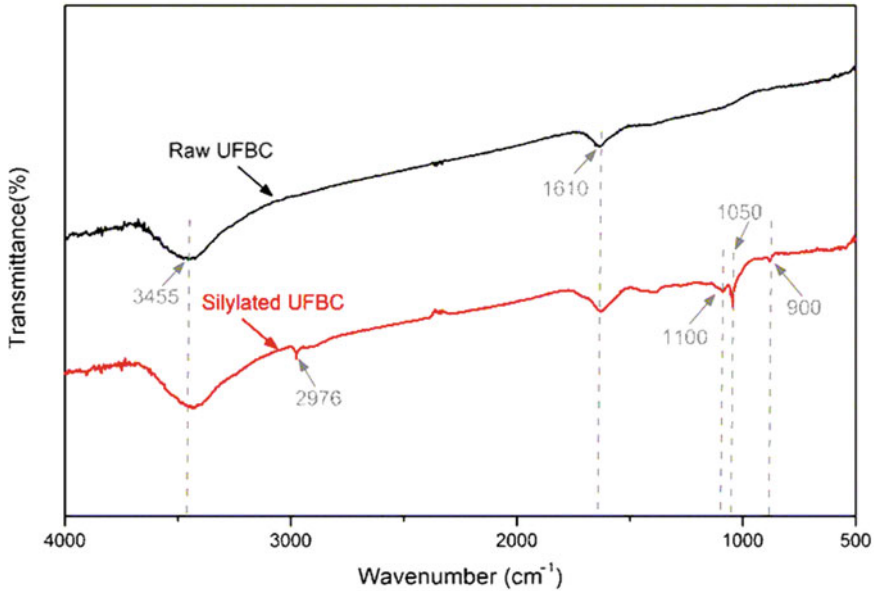


Fig. 13 FT-IR spectra of raw ultrafine bamboo-char (UFBC) and silylated UFBC

6.1.1 Fourier Transform Infrared Spectroscopy

At first, an important technical characterization tool to be used is the Fourier transform infrared spectroscopy, in this example, and in order to assure the surface modification of the ultrafine bamboo-char using silane, Fig. 13 makes a clear statement of that modification by the appearance of an absorption band at 2976 cm^{-1} equivalent to the silane group [78].

6.1.2 Scanning Electron Microscopy

Scanning electron microscopy (SEM) is used in order to observe the uniform dispersion of the fillers, confirmed again in the Fig. 14, the micrographs of bionanocomposite surface exhibited more pits and cavities than the binary system of PLA/BCNW. Which is due to the presence of UFBC/PLA around the biochar particles and formed small cavities all around the particles resulting in a core-shell dispersion structure, UFBC were dispersed uniformly in the PLA matrix and the two phases had a good interface effect [78].

After proving the modification and the incorporation of the fillers, mechanical properties of the composites were evaluated, the surface modified UFBC did successfully reinforce the PLA/BCNW bionanocomposites, a higher tensile strength was reached (18.87 MPa) along with improved tensile modulus (272.24 MPa), the ideal UFBC content was 0.25 wt% assuring an elongation at break value of 165.8% [78].

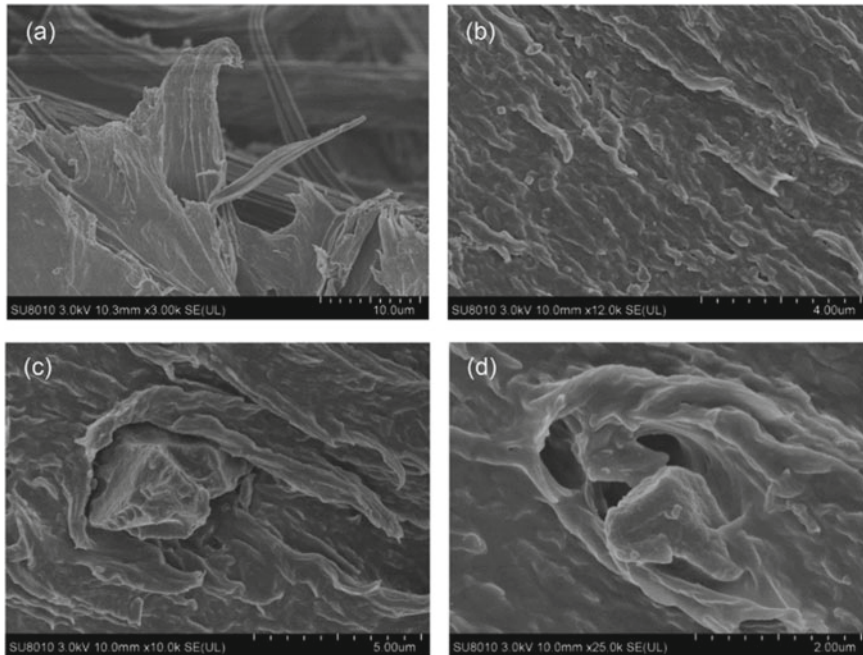


Fig. 14 Fractural surface of PLA/BCNW/UFBC bionanocomposites, **a** 0.25%, **b** 0.5%, **c** and **d** 0.5% UFBC in PLA

Another study was focused on the borer powder of bamboo which can be considered as an excellent starting material for manufacturing cellulose nanocrystals in both a low-cost and using an environmental-friendly way, the chemical composition of uninfected bamboo powder and borer powder has not been changed significantly, so cellulose nanocrystals (CNC) and carboxylated cellulose nanocrystals (CCN) were prepared, the crystallinity of the CNC and the CCN nanofibers are significantly improved after a series of chemical treatments, that is up to 69.84 and 62.75%, respectively [79].

6.1.3 X-Ray Diffraction Analysis

The crystallinity improvement of the nanofibers (CCN or CNC) compared to the borer powder is also shown in the same study [79], this property of CCN and CNC makes them eventually used to improve mechanical properties of composite materials, based on the fact that mechanical properties, especially the tensile strength modulus is massively dependent on the crystallinity property. Another study [11] presented the X-Ray diffraction analysis (XRD) of other bamboo based cellulose samples. All the cellulose samples present four diffraction peaks at $2\theta = 15^\circ$, 16.5° , 22.7° , and 34.8° , corresponding to the (110), (110), (200), and (004) crystallographic planes of the

monoclinic cellulose demonstrating that the crystalline type of CNCs is remained after the nanocrystallization process. Compared to bamboo pulp, an increase of the crystallinity index for CNCs is seen and which is explained by the degradation of amorphous regions and disordered regions of cellulose. As mentioned previously, a higher crystallinity index in CNCs is associated with higher tensile strength and thermal stability, which is expected to be beneficial for producing high strength composite materials.

6.1.4 Thermal Analysis of Nanocomposites

To characterize the thermal properties of bamboo pulp and of its derivative cellulose nanocrystals (CNCs), The initial thermal decomposition of bamboo pulp is 313 °C compared to 322 °C for CNCs, the maximum degradation temperature follows the same path, where for CNCs the temperature is increased to 348 °C compared to 338 °C for the pulp. All of these results indicate that the thermal stability of CNCs is higher than that of cellulose raw material, due to the fact that the thermal stability of cellulose is affected by crystalline order [11].

7 Applications of Bamboo Cellulose Nanocrystals

The use of bamboo cellulose nanocrystals as alternate to bacterial cellulose for wound dressings seems to be an interesting application of these materials, a prior study highlighted interesting properties of cellulose nanocrystals, such as their ability and capacity of absorbing water along with their strong antibacterial activity. The *in-situ* single approach was adopted for the elaboration of this bionanocomposites, where the formation and simultaneous impregnation of silver nanoparticles onto cellulose nanocrystals matrix were carried out. The elaborated bionanocomposite was found to significantly enhance the *in-vivo* skin tissue repair by decreasing the production of inflammatory cytokines and increasing fibroblast proliferation, angiogenesis, and finally tissue neopithelization and regeneration in less than 14 days by favoring collagen deposition [80].

Hybrid materials made of bamboo cellulose nanocrystals and zinc oxide were elaborated. Using solely water solvent in mild temperature (80 °C), this facile green-route one step synthesis provided materials with various morphologies (nearly spherical, thin sheet and flower-like shapes) depending on pH values. These materials were subjected to several applications, they were used to absorb methylene blue and malachite green dyes, they showed high removal capacity (93.5 and 99.0% respectively) reaching 91.5% and 97.8% respectively withing the first 5 min. These materials were also tested to investigate their antibacterial activity. The spherical like hybrid materials actually showed high ratios reaching 91.4–99.8% against *Escherichia coli* (gram positive) and *Staphylococcus aureus* (gram negative) as shown in Fig. 15 [81].

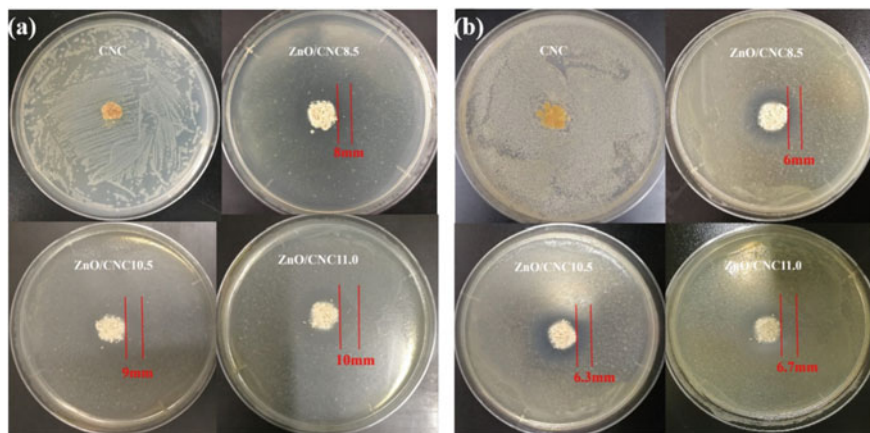


Fig. 15 Antibacterial ability of CNC and ZnO/CNC hybrids against **a** *E. coli* and **b** *S. aureus*

Poly(3-hydroxybutyrate)/cellulose nanocrystal films were elaborated in order to test their barrier and migration ability while they are in contact with food products, the extraction source of cellulose source was bamboo stems, the nanocomposites were elaborated using the solvent exchange cum solution casting evaporation technique, the oxygen transmission rate of these films was dropped dramatically by 65% even at low cellulose nanocrystals loading of 2 wt% compared to neat poly(3-hydroxybutyrate). These materials seem to be promising materials for various applications in the field of food packaging [82].

Some other nanocomposites were elaborated based on glycerol plasticized starch, and in order to reinforce these materials, bamboo based cellulose nanocrystals were used, the latter material was prepared using a combination of sulfuric acid and HNO_3 - KClO_3 hydrolysis which led to several geometries depending on the concentration of the acidic media. Tensile strength and Young's modulus of these nanocomposites, was much higher than their counterparts for glycerol plasticized-starch without bamboo crystals, these results were due to the effect of the size of cellulose nanocrystals, and to the reduced water uptake.

8 Conclusion

The addition of bamboo fiber in biopolymeric materials represents a promising route, as it improves the overall properties of the composite and nanocomposite materials. The increase in mechanical properties was engendered by the high properties of the bamboo extracted nanofibrils and nanocrystals (modulus, tensile strength), but many other parameters must be taken into consideration, such as the fiber size, surface modification, fiber content, coupling additives, etc. because they also influence the

mechanical properties as well as other characteristics of the composite and nanocomposite (thermal stability, crystallinity, water absorption, etc.). The realization of a composite material with the best possible properties, thus passes through the control of all these parameters.

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