

# Hydrogels Nanocomposites Based on Crystals, Whiskers and Fibrils Derived from Biopolymers

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**Abstract** The advent of nanotechnology has provided new insights of applications of well-known materials due to the exceptional properties owing to the nanoscale. As an example, nanocomposites based on polymer matrix and nanoscale fillers have appeared as good candidates in a broad range of applications. Such scenery can be credited to the use of new and multifunctional fillers that provide distinct and substantial features to the nanocomposites. Recent trends on the nanocomposites field show that crystalline biopolymers, such as cellulose, chitin, and starch, are an excellent source of fillers, especially nanocrystals like fibrils, whiskers, and platelets. The incorporation of such fillers in different matrices (e.g., crosslinked polymeric network) has demonstrated outstanding improvement of several properties, such as mechanical, water uptake capacity, thermal, optical, etc. Furthermore, crystals, fibrils and whiskers can induce desirable properties in the final materials (e.g., solute retention or release, crystallinity, biodegradability, biocompatibility, antibacterial activity, etc.). This chapter condenses the relevant works regarding the preparation of polysaccharide-based crystals, whiskers, and fibrils, their application in the development of hydrogel nanocomposites as well as the future trends of this area.

**Keywords** Nanocomposites • Hydrogels nanocomposites • Biopolymers • Crystals • Whiskers • Fibrils

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## 1 Introduction

The first Industrial Revolution, at the end of eighteenth century, has triggered the development of technological research and the obtention of novel materials. The challenges today are focused on adapting the available technology to produce desirable responses from a material or a process with the minor onus (e.g., low cost and high efficiency). One of the most brilliant methods created to answer such condition is the nanotechnology. Nanotechnology, in general lines, is the science that treats the matter at the molecular level. It means that new materials; substances, and products are formulated in this field with atomic accuracy [97, 98]. The direct results are the obtention of a wide range of desirable properties and unlimited possible applications. For example, the materials prepared or obtained in nanosized scale (particles, aggregates, or agglomerates where at least or more than 50 % show size dimension between 1 to 100 nm) have been utilized in hundreds applications. Nanomaterials have been included in various commercial products (e.g., dentifrices, batteries, paints, clothes, etc.) in order to increase, modify or even create new features [18, 154, 155]. Several fields, such as medical, optics, electronic, biotechnology, energy, and environmental have benefited a lot from nanomaterials [18]. The association of different classes of materials, such as polymers (synthetic or natural), ceramics, and metals and nanosized fillers allows preparing high-performance nanocomposites materials [54, 141, 153]. The term nanocomposite defines a multiphase solid material with one of the phases in the nanosized dimension [165]. In other words, it is the combination of a solid bulk matrix and nanodimensional phases differing in properties due to dissimilarities in structure (morphological, chemical, and dimensional) and physicochemical features. As a consequence, the nanocomposite properties will markedly differ from the individual components. For instance, in mechanical terms, nanocomposites could present better performance than traditional composite materials due to the outstanding high aspect ratio presented by the nanomaterials (also known as “filler”) incorporated into the bulk matrix [27, 68]. Another aspect is that the interface area between the matrix and the filler phase(s) is typically an order of magnitude greater than that for conventional composite materials.

Taking into account that nanosized fillers can be prepared/obtained from numerous organic (polymer) and inorganic (metals, oxides) sources [68, 82, 119, 155, 191, 199], they vary in relation to the size, chemical composition, shape, surface area, production cost, and toxicity. Crucial aspects that must be considered are the (bio)availability of the source and the toxicity and cost of chemicals involved in the preparation of the fillers. Biopolymers are quoted currently as potential candidates to extract fillers to form nanocomposites due to issues such as biodegradability, low cost, nontoxicity, relatively reactive surface, etc.

## 1.1 Biopolymers

Biopolymers are polymeric macromolecules produced by living organisms. Polysaccharides (e.g., cellulose, starch, and chitin), proteins and peptides, and nucleic acids (DNA and RNA) are examples of biopolymers [105, 108]. Some of them, such as cellulose and chitin, are the most abundant biopolymers on earth [166–170]. The main difference between the conventional polymers and biopolymers can be credited to their structure [181–183]. Repeating units form both polymer and biopolymers; however in most of the cases, biopolymers show a well-defined three-dimensional structure, while the conventional polymers do not [173–177]). The exact chemical composition and well-defined sequence in which the repeating units are organized are characteristic of the primary structure of the polymer. Many biopolymers show a complex structure, which defines biologic activity for instance [105]. Biopolymers can show very complex folding patterns, included secondary and tertiary structures, both based on the properties of the primary structure [163]. On the other hand, the conventional polymers, such as the synthetic ones, show a simple and random (stochastic) structure [19]. Therefore, such class of polymers shows a typical molar weight distribution, which is not observed for the biopolymers. However, a well-defined structure presented by biopolymers contributes to decreasing their range of molar weight distribution, which results in higher monodispersity. Such characteristic is contrasting with synthetic polymers, which can present high polydispersity [19].

Biopolymers have been extracted and purified for several finalities (food, commercial, industrial, etc.) and at the same time some of them are studied in different areas. These studies include the development/obtention of novel materials to replace the oil-based ones (e.g., synthetic polymers, elastomers, etc.), which show, in general, high-cost production, low availability, environmental problems, etc. [178–180]. The main drawback to replace the oil-based materials is to develop materials with similar, interesting properties. Several efforts in this sense have been done. The novel nanocomposites, especially those based on biopolymers, are suitable candidates to this challenge. Biopolymers have replaced synthetic polymers in some application and also have been associated to them, resulting in composites materials [101, 156, 204]. This last strategy is convenient and highly reliable to enhance or induce some specific properties (e.g., thermal, mechanic, absorbing, etc.) [9, 14]. The incorporation of biopolymers in synthetic polymeric matrices, generating a polymer blend, may improve biodegradability and biocompatibility [126, 136]. Such attractive profile has attracted the interest of several researchers, and as a consequence the number of manuscripts published in this field has grown considerably in the last years.

Currently, biopolymers are being used as a source of nanofillers to be included in distinct bulk matrices [74, 114]. For example, biopolymers with fibrous characteristics have been incorporated with exceptional success in thermoplastic resins as polyvinyl chloride or polyethylene [106]. Such reinforcing fibers lead to two significant improvements: lighter final material because the filler density is, in general,

lower than the matrix density; and the enhancement of mechanical properties [186]. Despite this favorable scenery, sometimes a good dispersion of biopolymer fillers in the polymeric matrix is not achieved. The fillers proceeding from biopolymers have hydrophilic features due to their polar functional groups (charge density), while the polymeric matrix is hydrophobic, as consequence of their nonpolar groups [96–99]. Innovative strategies to overcome this undesirable effect have been described by several authors. Among those strategies, the controlled chemical modification of the fillers surface has been performed, in order to increase the interfacial compatibility between the polymeric matrix and filler [104, 158].

The good results presented by the use of fibers and short coir fibers, as reinforcement fillers, have encouraged today their use to produce alternative low-cost composite materials for structural and nonstructural applications (i.e., automotive, packaging, and building applications, rubber technology, furniture and consumer goods) [12, 141, 152]. In the last decades, the fibers have received massive support from others nanomaterials, also proceeding from biopolymers, to form suitable composite materials [178–180]. Nanocrystals, nanofibrils, and nanowhiskers have been extensively used to prepare nanocomposites with excellent thermal, mechanical, barrier properties, and reactive surface compared with conventional materials and composites [34, 87, 100]. Outstanding data about these superior properties are related in the literature even when low levels of such nanomaterials are utilized. Additionally, promising researches show that the incorporation of nanomaterials like fibrils, crystals, and whiskers, increases the levels of recyclability, transparency, and low weight of the final composite materials [178–180]. All these desirable aspects, associated with all the above-mentioned advantages allow inferring that biopolymers are the most exciting and encouraging source for nanomaterials to act as fillers in composite materials.

## **2 Crystals, Whiskers and Fibrils Derived from Biopolymers**

Biopolymers can be separated into three main classes according to the monomeric units that build their structure: polynucleotides (i.e., nucleic acids); polypeptides (i.e., short polymers based on amino acids); and polysaccharides. Polysaccharides are polymeric carbohydrate macromolecules composed of long chains of mono- or disaccharide units bound together by glycosidic linkages [105, 108]. In general, the hydrolysis of polysaccharides gives their mono-, di-, or oligosaccharides constituents units. From the structural aspect, polysaccharides range from linear to highly branched structures and their quite heterogeneous characteristics (with slight modification on the repeating units) can drive to crystalline or amorphous arrangements [56, 79]. Such modifications can promote even the insolubility of some polysaccharides in water. When all repeating units in a polysaccharide backbone are the same residue, it is classified as homopolysaccharide or

homoglycan; however when more than one residue are present they are called heteropolysaccharides or heteroglycans [56, 79]. The most important and abundant polysaccharides are starch, cellulose, chitin, and chitosan.

## 2.1 Starch

Starch, the energetic reserve of the most part of green plants, is probably the second most abundant polysaccharide next to cellulose in nature [117]. The word “starch” derives from sterchen, meaning to stiffen. Starch grains from the rhizomes of Typha (cattails, bulrushes) as flour have been identified from grinding stones in Europe dating back to 30,000 years ago [143]. Starch grains from sorghum were found on grindstones in caves in Ngalue, Mozambique dating up to 100,000 years ago. Pure extracted wheat starch paste was used in Ancient Egypt possibly to glue papyrus. The extraction of starch is first described in the history around AD 77–79. Romans used it also in cosmetic creams, to powder the hair and to thicken sauces. Persians and Indians used it to make dishes similar to gothumai wheat halva. Rice starch as surface treatment of paper was used in paper production in China, from AD 700 onwards.

All the potentialities of this useful polysaccharide have been explored for years by food industries and the technological fields. Starch presents very attractive properties such as good nutrition facts, natural abundance, nontoxicity, biocompatibility, and biodegradability. Nowadays, the primary sources of starch are the cereal and root crops (rice, maize, wheat, potato, and cassava). Starch is mainly composed of two homopolysaccharides: amylose and amylopectin [58, 107]. These homopolysaccharides have the same repeating units that are linked in linear and branched fashion [201].

Amylose is a linear homopolysaccharide composed of  $\alpha$ -(1,4)-D-glucopyranosyl units, in which slightly branched points may occur. Due to its simpler polymeric structure, amylose has tendency to assemble into a regular pattern forming crystals. On the other hand, amylopectin is the highly branched component of starch formed mainly by D-glucopyranosyl units joined together through  $\alpha$ -(1,4) linkages. However, 5–6 % of  $\alpha$ -(1,6) linkages can be found at the branching points [16]. The high branching structure confers to amylopectin a molecular weight that is ca. 1000 times greater than those presented by amylose. Besides these two main components, starch could present in some particulate material (i.e., cell wall fragments) and surface and internal components (i.e., proteins, enzymes, lipids, amine, and nucleic acids) [8, 16].

Both homopolysaccharides that form starch has large number of hydroxyl groups on their backbones, which drive to a high number of hydrogen bonds. Such bonds keep the starch chains hold together in an ordered manner that results in crystalline regions alternated by less-ordered amorphous starch chains. The presence of the crystalline regions is also credited to the intertwining of amylopectin side-chains, which is affected by amylose distribution in the starch granules [125].

Depending on the botanical origin of starch, the amylose chains can occur in the granule as individual molecules (amorphous regions), randomly interspersed among or in bundles between amylopectin clusters (amorphous and crystalline regions). Additionally, amylose can occur co-crystallized with amylopectin chains. Depending on their X-ray diffraction pattern, reflecting long-range ordering in the granule, starches are categorized in three crystalline types (polymorphs) called A, B, and C [90]. Such characteristics allow developing very attractive nanomaterials from starch like starch nanocrystals, which are crystalline platelets, prepared by the acid or enzymatic hydrolysis of amorphous moieties of the starch backbone. Some studies showed that despite the influence of the botanical origin on the starch final properties, different sources could provide nanocrystals with similar size and crystallinity [88, 89]. The acid hydrolysis carried out in the amorphous moieties, composed majorly of amylose, results in particles with square-like morphology about 10 nm thick and 50-100 nm equivalent diameters. This morphology is predominant when the initial amylopectin content and A-type crystallinity increase. However, it is worthy to say that although the nanocrystals crystallinity is higher than that of their corresponding native starches, they are not fully crystalline [90].

Starch nanocrystals are currently applied in bio-based nanocomposites formulation, in order to improve the mechanical, thermal, swelling, and barrier properties of different polymeric matrices, especially those that fit the actual environmental concerns [69, 71, 96–99]. The inclusion of starch nanocrystals in the polymeric matrix has been done basically by: (i) mixing an aqueous suspension of starch nanocrystals and the polymer solution; (ii) vacuum degassing; (iii) water evaporation (casting process); and (iv) film formation [96–99]. Various works indicate that the starch nanocrystals content in the resultant composites ranged from 2 to 50 wt% [96–99]. Inside the polymeric matrix, the starch nanocrystals can form three-dimensional networks through hydrogen linkages between the starch nanoparticles cluster and also to favorable interactions between the matrix and filler. Such particulars promote miscibility and dispersion of the starch nanocrystals in the polymeric matrix. Additionally, the incorporation of starch nanocrystals into polymer matrices with some shortcomings (i.e., high cost, non-biodegradability, non-bio-compatibility, etc.) should ameliorate them to some degree. Some works report the chemical modification of starch nanocrystals surface in order to enhance their use as filler materials in different synthetic or natural polymeric matrices [30, 87, 114]. The success of starch nanocrystals as filler can be credited to its intrinsic rigidity, morphology, strong interfacial interactions, ability to organize percolated networks, and simple preparation method.

## 2.2 Cellulose

Cellulose, the most abundant polysaccharide on earth, has been exhaustively studied as a source of fillers for developing novel nanocomposites. Cellulose was discovered in 1838 by the French chemist Anselme Payen, who isolated it from

plant material and determined its chemical formula. Payen also established the word “cellulose,” derived from the latin word “*cella*” (from *celare* that means to hide;). It was used to denote a small compartment, such as the cell of a honeycomb or a storeroom. The diminutive of “*cella*” is *cellula*, which is a frequent prefix (*cellulo*) in English scientific words, and gives us cellulose, full of little cells. Hermann Staudinger determined the structure of cellulose in 1920 [78]. Kobayashi et al. chemically synthesized cellulose without the use of any biologically derived enzymes in 1992 [80].

Cellulose is composed of D-glucopyranose units held together by  $\beta$ -(1,4) glycosidic linkages, which contrasts with the  $\alpha$ -(1,4) glycosidic linkages present in the most part of the polysaccharides. Cellulose presents linear chains, unlike starch, with average molar mass ranging from 104 to 106 g/mol, depending on the source. Such chains adopt an extended and stiff rod-like structure, aided by the equatorial conformation of the glycosidic units. Many properties of cellulose depend on its degree of polymerization. Cellulose from wood pulp, for example, has typical chain lengths between 300 to 1,700 glycosidic units; cotton and other plant fiber as well as bacterial cellulose have chain lengths ranging from 800 to 10,000 glycosidic units [78]. Chains with small lengths result from the breakdown of cellulose and are known as cellodextrins. In contrast to the long chain of cellulose, cellodextrins are typically soluble in water and organic solvents.

Cellulose is found in nature as a structural component in the primary cell wall of plants, algae, and bacteria [164]. In plants, the primary cell wall consists of three central regions, and each region has lignin, hemicellulose, and cellulose microfibrils (30–90 %, according to the source) as the principal components [149] (see Table 1). In plants, cellulose gives rigidity to the cells. It is estimated that 1012 tons of cellulose are photosynthesized every year [78].

As a natural polymer, cellulose is biodegradable, biocompatible, renewable, and affordable. Therefore, it has been used in many different fields including paper industry and fabrics [70], gunpowder and propellants [11] and food additives (anticaking agent, emulsifier, stabilizer, dispersing agent, thickener, and gelling agent) [17] for decades. More recently, cellulose found applications in the nanomaterials field [51] and in the production of bioethanol [24].

**Table 1** Percentage of cellulose, hemicellulose, and lignin from different botanic sources [47]

Source	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Wheat straw	35.80	26.80	16.70
Sweet sorghum	44.60	25.30	18.00
Alamo wood	48.80	17.30	27.70
Corn stover	36.40	22.60	16.60
Corn ears	38.50	32.80	18.70
Rice straw	35.62	11.96	15.38
Bean straw	30.64	23.14	9.35

Cellulose presents three hydroxyl groups in each sugar residue and, as a linear polymer, the interchains H-bond interactions occur at high level and, as a consequence, cellulose is found in nature as a highly crystalline polymer with crystallinity index as much as 80 % [131]. Differently to starch, cellulose is much more crystalline. Whereas, starch undergoes a crystalline to amorphous transition in water in the temperature range of 60–70 °C, cellulose undergoes the same transition in water close to 320 °C and high pressure. Cellulose possesses several different crystalline structures, which can be assigned to the location of hydrogen bonds between and within strands. Natural cellulose is denoted as cellulose I, with structures I $\alpha$  and I $\beta$  [121, 122]. These two structures have the same fiber repeating distance (1.043 nm for the repeat dimer interior to the crystal, 1.03 nm on the surface but differing displacements of the sheets) relative to one another. Cellulose produced by bacteria and algae is enriched in I $\alpha$  while cellulose of higher plants consists mainly of I $\beta$ . Cellulose from regenerated cellulose fibers is denoted as cellulose II. In this case, the structure shows an antiparallel arrangement of the strands and intermolecular and both intra and intersheet hydrogen bonding. The conversion of cellulose I to cellulose II is irreversible, suggesting that cellulose I is metastable and cellulose II is stable. With various chemical treatments, it is possible to produce the structures cellulose III and cellulose IV [135]. The high crystallinity renders cellulose insoluble in most common solvents, and therefore prevents many of its potential applications [6]. Water cannot penetrate crystalline cellulose but dry amorphous cellulose absorbs water becoming soft and flexible. Some of this water is nonfreezing, but most is just trapped. Less water is bound by direct hydrogen bonding if the cellulose has high crystallinity but some fibrous cellulose products can hold a considerable amount of water in the pores and its typically straw-like cavities; water-holding ability correlating well with the amorphous (surface area effect) and void fraction (that is, the porosity). The preparation of nanofibrils and nanowhiskers from cellulose, which are easily dispersed in water, is an interesting way to overcome the solubility restrictions [57]. Cellulose micro- and nanofibrils are substructural elements of cellulosic fibers that can be mechanically disintegrated from the cell wall matrix. Recent enzymatic or chemical pretreatments combined with mechanical disintegration process of the fibers produce stable and homogeneous nanofibrils, which show outstanding potential for many technological applications [74]. Noteworthy, the size and nature of these native cellulose nanofibrils make these structures amenable to the manufacture of robust thin films and bio-based nanocomposites [74, 203].

The most crystalline form of cellulose is the nanowhiskers, which are shorter than the nanofibrils. Cellulose nanowhiskers are isolated from microcrystalline cellulose using acid hydrolysis or sonication process [34]. So, it is usual to submit cellulose to a previous delignification process. Cotton, bamboo, and wood are the most usual sources of cellulose to produce nanowhiskers. As a result, nanowhiskers crystallinity and size dimension are dependent of the botanical source of cellulose and preparation method. In the last decade, several research groups have focused efforts on developing new methodologies to prepare cellulose nanowhiskers from different botanic sources. Additionally, a huge number of works have been



published in literature regarding the incorporation of cellulose nanowhiskers in polymeric and composites matrices [32, 160, 189]. Such enthusiasm is due to the innumerous advantages that cellulose nanowhiskers show in relation to the conventional inorganic nanosized materials. Simple methodology, low-cost cellulosic feedstock, and mechanical properties compared to those presented by the carbon nanotubes and inorganic nanofibers, fact that allows cellulose nanowhiskers to be a promising filler material.

2.3 Chitin and Chitosan

Further starch and cellulose, chitin and its derivative chitosan have been extensively utilized to prepare nanosized fillers [134]. Chitin was the first polysaccharide discovered and after cellulose is the second most abundant biopolymer in nature being found among the kingdoms of Fungi, Plantae (plants), and Animalia (animals). Some chitin sources are shown in Table 2.

Chitin (first called as *fungine*) was first isolated in 1811 by Henry Braconnot, a French scientist during his experiments with mushrooms had found an insoluble fraction in acid and bases on their cell walls. Afterward, on 1823 August Odier found the same compound in the cuticles of insects and called it chitin [76]. The word chitin derives from French “*chitine*” that in your turn is from the Greek “*khiton*” or “*chiton*”, which means protection or wrapping. Although it had been found in 1811, the chitin structure was described only in 1929, almost one century after, by the Swiss chemistry, Albert Hofmann. Chitin is a linear polysaccharide formed by N-acetyl-D-glucosamine units hold together by  $\beta$ -(1,4) glycosidic linkages. In nature, it occurs as ordered crystalline microfibrils forming structural components in the exoskeleton of crustaceans, mollusks, and insects or in the cell walls of fungi and yeast [26, 146]. The chitin content in a living organism can vary from 3 to 40 % according to the specimen. Table 3 shows some data about the composition of different sources utilized to extract the chitin [83].

Table 2 Chitin main sources [146]

Sea animals	Insects	Microorganisms
Annelida	Scorpions	Green algae
Mollusca	Spiders	Yeast ( $\beta$ -type)
Coelenterata	Brachiopods	Fungi (cell walls)
Crustaceans	Ants	Mycelia penicillium
Lobster	Cockroaches	Brown algae
Crab	Beetles	Spores
Shrimp		Chytridiaceae
Krill		Blastocladiaceae
		Ascomydes

**Table 3** Composition of different sources of chitin [83]

Source	Chitin (%)	CaCO <sub>3</sub> (%)	Proteins (%)	Lipids (%)
Crab	15–30	40–50	15	2–5
Shrimp	30–40	20–30	35	5–10
Krill	20–30	20–25	–	–
Squid pen	20–40	<i>Insignificant</i>	–	–
Clams	3–6	85–90	–	–
Insect	5–25	<i>Insignificant</i>	–	–
Fungi	10–25	<i>Insignificant</i>	5–10	5–10

\*Values referent to the dry mass

The structure of chitin is comparable to cellulose because both polysaccharides have the same supporting function in the organism in which they are present. The difference between these two polysaccharides is the acetamide group attached at C2 carbon of the chitin.

Among several properties of chitin, its nontoxicity, biodegradability, and biocompatibility are the most relevant [146]. Due to these features, this polysaccharide has been widely used in biomedical and pharmacological applications. Chitin shows a rigid crystalline structure and depending on the source (crabs or shrimps, for instance) it can occur as two allomorphs, namely the  $\alpha$  and  $\beta$  forms, which can be differentiated by infrared and solid-state NMR spectroscopy together with X-ray diffraction analysis [150]. Both  $\alpha$  and  $\beta$  forms of chitin are insoluble in water or the usual organic solvents. Despite natural crystallinity variations, the insolubility is the major problem preventing further development of processing and uses of such a polysaccharide. Besides this limitation, the crystallinity of chitin allows preparing nanofibers from prawn shell by a simple grinding treatment after the removal of protein and minerals under neutral pH conditions. Chitin nanofibers are highly uniform and the width ranges from 10 to 20 nm [65].

Several derivatives are synthesized from chitin; among them the most important is chitosan. Despite the occurrence in nature of partially deacetylated chitin (with a small content of glucosamine units), chitosan is obtained by partial (or total) deacetylation of chitin in the solid-state under alkaline conditions (concentrated NaOH) or by enzymatic hydrolysis in the presence of chitin deacetylase [42, 146]. The main parameters that influence all the chitosan properties are the molecular weight and deacetylation degree [75]. Such parameters are straightly determined by the conditions used in the chitosan preparation. Chitosan is insoluble in water as chitin; however, its solubilization can be obtained at acidic conditions. At low pH, the amino groups of chitosan are protonated, which increases the electrostatic repulsion among the chains allowing their solvation by water molecules [36]. In the solid state, chitosan is a semi-crystalline polysaccharide with many polymorphs according to the literature [20, 146]. Single crystals of chitosan have been obtained using fully deacetylated chitin of low molecular weight, for instance. Chitosan shows similarly as chitin, nontoxicity, biocompatibility, biodegradability, hemostatic potential, antibacterial and antitumoral activity, and good film-forming

properties [137]. Furthermore, the amino and hydroxyl groups of chitosan are placed in adjacent positions, which confer a chelating feature to this polysaccharide. The use of chitosan to formulate materials to remove metals, ionic compounds and dyes from contaminated wastewater is encouraged [28, 35].

For decades, both chitin and chitosan have been used to design the most sorts of materials for applications ranging from environmental treatments to tissue engineering [137, 146]. Recently, these polysaccharides have attracted attention as significant sources of nanosized fillers for innumerable polymeric matrices [30, 65, 114]. Nanofibrils and nanowhiskers can be prepared from chitin or chitosan by breaking down their structures in crystalline nanofragments [65, 114]. Such fillers can be obtained with specific shapes or self-assembling of basic building blocks due to chain cleavage, which occurs at random location. This forms rod-like or spindle-like particles that tend to align cooperatively and to develop rigid structures [94, 114]. A brief research in the literature shows that chitin and chitosan nanowhiskers have been used as reinforcing additives for high-performance environment-friendly biodegradable nanocomposite materials. For example, as biomedical composites for drug and gene delivery, nanoscaffolds in tissue engineering, nanostructures for medical and veterinary applications, cosmetic, and orthodontics [114, 118]; Zeng et al. 2012. According to the biological source of chitin and taking into account the methodology used to prepare chitosan, the resultant nanowhiskers can be use in antitumor application and immune-modulating activity [62, 114].

The next sections present the most popular methodologies that have been used to prepare nanosized fillers from cellulose and their main applications as well as the cut-edging technologies that are being developed.

### 3 Hydrogels Nanocomposites

Nature has found many different ways to overcome structural limitations during the history of evolution from early prokaryotes to the complex living systems that are found nowadays. This fact is supported by the knowledge of very rigid and tough natural materials, such as; the stiff exoskeleton that protects the fragile internal structures of arthropods [138], or the plant cell walls [124] that provide enough strength for giant trees from North America like sequoia (*sequoias sempervirens*) to grow as high as 115 meters or the bones that compose the internal skeleton of vertebrates from the tiny frog (*paedophryne amauensis*) of only 7.7 mm found in Papua New Guinea [147] to the extinct predator Tyrannosaurus Rex having ca. 13 m in length [61] and to the robust Blue whales (*balaenoptera musculus*) having incredible average size of 26 m [15]. Under detailed scrutiny, researchers have discovered that although composed of different substances, all these supporting materials (exoskeletons, bones, and plant cell walls) are naturally constructed based on the same principles. About them, the crystalline phases or mineralized particles are dispersed (or chemically bound) into a polymer matrix, and are considered nanocomposites [73, 145, 187]. The term nanocomposite was defined in earlier

sections, and it is considered as a multiphase material in which one of the phases has at least one of the dimensions ranging from 1 to 100 nm.

Understanding structure/properties relationship of such high-performance natural materials is a rational pathway to develop biologically inspired nanocomposites to the most diverse ends. Nature provides inestimable sorts of resources, and it is an excellent platform for nanomaterials. Taking into account healthy and environmental concerns that have risen in the last years from non-biodegradable synthetic polymers or the conventional inorganic fillers owing to the fact that many precursors are toxic and expensive [172], biopolymers such as cellulose, chitin, and starch are promising candidates for preparing crystalline biocompatible and biodegradable nanofillers that could replace the use of inorganic nanoparticles in some applications for preparing nanocomposites [41]. However, the reader should have in mind that polysaccharide nanocrystals have broader applications than replacing inorganic nanofillers as it is pointed out in this chapter.

More recently, there has been an increasingly interest in the development of hydrogel nanocomposites, in which the reinforcement phase is composed of polysaccharide nanocrystals since such nanofillers can improve mechanical, thermal, and optical properties [10, 132] as well as the water uptake response to external stimuli. Hydrogels are regarded as physically or chemically crosslinked polymeric chains capable of absorb and retain water and/or other aqueous fluids without dissolving, and are still considered one of the most important branches of the polymer science field. This status is supported by the fact that hydrogels may find application in ordinary utensils like a diaper [123] or soil conditioner beads for plants [120] as well as in more sophisticated technologies such as in drug delivery systems [81, 133], in gene delivery [93, 95], in tissue engineering [91], in separation science [205], in wound dressing [113], in sensors [184], among others. Reports focusing on the different aspects of development and application of hydrogel and hydrogel composites can be found in the scientific literature [2, 13, 23, 67, 84, 128, 148]. Therefore, this chapter condenses the most relevant works regarding the preparation of polysaccharide nanocrystals, their application in the development of hydrogel nanocomposites as well as the future trends of the area.

### ***3.1 Based on Cellulose Nanocrystals***

The recent development of nanotechnology has offered new possibilities of cellulose exploitation such as the preparation of cellulose nanoparticles; e.g., cellulose nanocrystals (CNC) and cellulose nanofibers (CNF), or both. A quick search at Web of Science © database under the topic “cellulose nanocrystals” revealed more than 1,000 published papers (164 paper only in the first half of 2014) illustrating the importance of such a topic in academia and industry.

Both CNC and CNF could be derived from botanical, animal, or bacterial cellulosic sources [45, 63, 190]. In general, the extraction of cellulose from the biomass may involve the use of organic solvents for removing waxes, alkali treatment

for removing hemicellulose, and other soluble polysaccharides followed by bleaching to eliminate lignin and polyphenols [109]. CNC are obtained by removing the amorphous phase, usually by acid hydrolysis in which  $\text{H}_2\text{SO}_4$  is the most common acid, resulting in highly crystalline nanoparticles. On the other hand, CNF are obtained by different methodologies (e.g., mechanical disintegration, 2,2,6,6-tetramethylpiperidine-1-oxyl radical-mediated oxidation, enzymatic hydrolysis, etc.) as a mixture or both crystalline and amorphous domains [64, 195]. CNC and CNF have been prepared by different sources and the most common are cotton [115], wood pulp [66], and tunicates (sea animals) [4]. However, many other sources have been reported as basis for preparing CNC and CNF such as sugarcane bagasse [171], algae [59], sisal fibers [157], banana plant [116], jute fibers [139], straw [142], and bamboo [188], among many others. CNC is derived as slender rods of few nanometers wide ( $\sim 10\text{--}50\text{ nm}$ ) and hundreds of nanometers long, but shorter than CNF, which can reach a few micrometers in length. It has been reported that CNC isolated from chardonnay grape skins presented as spherical nanoparticles (up to 100 nm) composed of a core-shell structure of self-assembled 50 nm long cellulose nanorods surrounded by cellulose nanofragments of less than 5 nm formed due to strong interfacial hydrogen bonds [102]. As the native cellulose fibrils dimensions and amount vary, the source and method of isolation have a substantial effect on the size of nanocrystals. For instance, cellulose nanocrystals from tunicates were found to have up to 2  $\mu\text{m}$  in length and are significantly longer than those obtained from different sources such as cotton or wood pulp which may vary between 100 and 300 nm in length [4]. Table 4 shows dimensional aspects of CNC obtained by acid hydrolysis from various sources and exemplifies the effect of source and reaction conditions on nanocrystals size. Controlling reaction time and temperature are paramount to obtain consistent hydrolysis of amorphous regions or less-ordered chains without promoting damage to the crystalline phase.

CNC and CNF have been used in the preparation of nanocomposites in the most diverse fields. Many review papers referring to methodologies, issues involved for preparing CNC and CNF, chemical modification of nanocellulose and applications of both CNC and CNF can be found in the literature [21, 29, 31–33, 51, 63, 85, 86, 109, 158]. Therefore, the development and the chemical modification aspects of CNC and CNF are not discussed in details in this chapter, which will be devoted to the main features of hydrogel nanocomposites based on CNC and CNF as reinforcement.

CNC have been incorporated into hydrogels aiming at improved mechanical properties due to its low density, to its excellent axial and transverse elastic moduli (150 and 10–50 GPa, respectively) and to the ability of forming a network into the matrix through hydrogen bonding, also known as percolation effect. Han et al. [52, 53] prepared hydrogels based on poly(vinyl alcohol) and borax reinforced with nanocellulose. Alkaline (20 wt% NaOH, 4 h) pretreated wood fibers were acid hydrolyzed (64 wt%  $\text{H}_2\text{SO}_4$ , fiber-to-acid ratio of 1:20, 45  $^\circ\text{C}$ , 1 h) followed by high-pressure (207 MPa) homogenization (at a rate of 135 mL/min for five passes) to generate CNC (length:  $149 \pm 40\text{ nm}$ ; width:  $9 \pm 2\text{ nm}$ ; 66 % crystalline). CNF (length:  $732 \pm 208\text{ nm}$ ; width:  $21 \pm 7\text{ nm}$ ; 58 % crystalline) were prepared using all

**Table 4** CNC obtained by acid hydrolysis from different botanic sources

Source	Methodology	Length (nm)	Width (nm)	Reference
Sisal fibers	Acid hydrolysis (40 min, 60 wt% H <sub>2</sub> SO <sub>4</sub> , 50 °C)	215 ± 67	5 ± 1.5	[157]
Sisal fibers	Acid hydrolysis (15 min, 65 wt% H <sub>2</sub> SO <sub>4</sub> , 60 °C)	250 ± 100	4 ± 1	[44]
Sisal fibers	Acid hydrolysis (50 min, 65 wt% H <sub>2</sub> SO <sub>4</sub> , 50 °C)	195	15	[1]
Sugarcane bagasse	Acid hydrolysis (30 min, 60 wt% H <sub>2</sub> SO <sub>4</sub> , 45 °C)	255 ± 55	4 ± 2	[171]
Sugarcane bagasse	Acid hydrolysis (180 min, 64 wt% H <sub>2</sub> SO <sub>4</sub> , 40 °C)	247 ± 32	10 ± 3	[159]
Sugarcane bagasse	Enzymatic hydrolysis followed by sonication	84–300	2–12	[25]
Cotton	Acid hydrolysis (300 min, 64 wt% H <sub>2</sub> SO <sub>4</sub> , 50 °C)	248	–	[37]
Cotton	Acid hydrolysis (45 min, 60 wt% H <sub>2</sub> SO <sub>4</sub> , 45 °C)	94 ± 31.6	21 ± 5.5	[194]
Alamo switchgrass	Acid hydrolysis (45 min, 60 wt% H <sub>2</sub> SO <sub>4</sub> , 45 °C)	148 ± 42.1	21 ± 4.3	
Maize Straw	Acid hydrolysis (150 min, 60 wt% H <sub>2</sub> SO <sub>4</sub> , 25 °C)	388 ± 43	19 ± 2	[142]
Banana plant	Acid hydrolysis (30 min, 11 M H <sub>2</sub> SO <sub>4</sub> , 50 °C)	466 ± 159	19 ± 6	[116]
	Acid hydrolysis (60 min, 11 M H <sub>2</sub> SO <sub>4</sub> , 50 °C)	441 ± 116	17 ± 5	
	Acid hydrolysis (90 min, 11 M H <sub>2</sub> SO <sub>4</sub> , 50 °C)	375 ± 100	13 ± 4	
	Acid hydrolysis (120 min, 11 M H <sub>2</sub> SO <sub>4</sub> , 50 °C)	361 ± 61	17 ± 4	
	Acid hydrolysis (180 min, 11 M H <sub>2</sub> SO <sub>4</sub> , 50 °C)	378 ± 66	17 ± 4	
	Acid hydrolysis (240 min, 11 M H <sub>2</sub> SO <sub>4</sub> , 50 °C)	319 ± 68	15 ± 4	

the same conditions for CNC, but at 48 wt% H<sub>2</sub>SO<sub>4</sub>. Nanocellulose-PVA-Borax hydrogels (2 wt% PVA; 0.4 wt% borax; 1 wt% CNC or CNF) were prepared by dissolving 0.1 g of borax in 1 wt% nanocellulose aqueous suspension followed by addition of 0.5 g of PVA. The reaction remained at 90 °C for 2 h and then cooled to room temperature. The incorporation of nanocellulose enhanced the compressive strength and viscoelasticity of the hybrid hydrogels. In this case, the crystalline nanocellulose can act as a multifunctional crosslinking agent acting both physically or chemically. It was demonstrated that crosslinking density, viscoelasticity, and stiffness of hydrogels were improved as the aspect ratio (length/width ratio) increased at a cost of loss of transparency (mean transparency of 51.0 % for CNC). The free-standing, high elasticity, and moldable hydrogels exhibited self-recovery under continuous step strain, and thermo-reversibility under temperature sweep have potential of applications including artificial muscles, bioactuators, soft machines, tissue scaffolds, and drug delivery devices.

McKee [110, 111] prepared thermo responsive hydrogels based on methylcellulose (Mn = 86 kg/mol, DS of 1.78) physically crosslinked by cellulose nanocrystals with tunable mechanical properties. CNC (dimensions not informed) were isolated from ground Whatman ashless filter paper by acid hydrolysis (64 wt%

H<sub>2</sub>SO<sub>4</sub>, 45 °C, 45 min). It was showed that the elastic modulus ( $G'$ ) of the viscoelastic solution at 20 °C could be tuned from 1 to 75 Pa by increasing the CNC concentration from 0 to 3.5 wt% at 1 wt% methylcellulose while at 60 °C the  $G'$  values varied from 110 to 900 Pa for the same increasing CNC concentration. Yang et al. [197, 198] also reported the reinforcement effect of cellulose nanocrystals from acid hydrolyzed (60 wt% H<sub>2</sub>SO<sub>4</sub>, 55 °C, 2 h) pulp fibers in acrylate-modified poly(ethylene glycol) hydrogels. Homogeneous composites were formed for CNC volume fraction lower than 1.5 %. At 1.2 v/v-% modulus, fracture stress, and fracture strain enhanced by a factor of 3.48, 5, and 3.28, respectively. Oscillatory shear data indicated the CNC—PEG nanocomposite hydrogels were more viscous than the neat PEG hydrogels and were efficient at energy dissipation due to the reversible interactions between CNC and PEG polymer chains.

Yang et al. [197, 198] investigated the relation of CNC aspect ratio and the mechanical behavior of nanocrystal/poly(acrylic acid) hydrogels. Acid hydrolyzed (55 wt% H<sub>2</sub>SO<sub>4</sub>, 50 °C, 2 h) microcrystalline cellulose and wood pulp generated CNC having aspect ratio ( $L/d$ ) of 31 and 14, respectively. The fracture strength of hydrogels increased from 157 to 229 kPa as the aspect ratio of CNC increased from 14 to 22, and then the strength further increased to 254 kPa at  $L/d$  of 31. It was also demonstrated the polymer chains rearrange on the CNC surfaces according to the stretched state of hydrogel changing both pore size and pore wall during deformation.

Osorio-Madrado et al. [129] demonstrated the reorganization of cellulose nanocrystals (width:  $30 \pm 12$  nm; length: 200 nm to 4  $\mu$ m), isolated from green algae *Cladophora sp* (50 wt% H<sub>2</sub>SO<sub>4</sub>, 40 °C, 8 h), into agarose hydrogels under tensile loading. In other words, uniaxial stretching under controlled humidity conditions induced anisotropy. The drying process was essential for specific filler/matrix interactions allowing a stress transference while stretching and promoting crystals alignment. This process would allow tuning the mechanical features of the hydrogel.

It has been reported that CNC played a role in the water absorption capacity of hydrogels. Spagnol et al. [160–162] prepared hydrogel composites composed of different polymeric matrices, e.g., chitosan-*graft*-poly(acrylic acid), starch-*graft*-poly(sodium acrylate), and poly(acrylamide-*co*-acrylate) reinforced with CNC isolated from cotton fibers by acid hydrolysis (36.5 % HCl, of 1/20 g/mL cellulose/HCl ratio, 45 °C, 1 h). It was showed that independently on polymer matrix, the addition of CNC up to 10 wt% substantially increases the water uptake due to the extra hydrophilic groups of cellobiose unit, but at higher concentrations the hydroxyl groups from CNC took place in the crosslinking reaction increasing the crosslinking density and, as a result, decreasing the absorption of water. Through surface response methodology and analysis of variance (ANOVA) it was demonstrated that CNC contributed 30 % to the swelling degree.

Mckee et al. [110, 111] prepared supramolecular stable and stiff hydrogel composites with healable features based on brush-modified cellulose nanocrystals crosslinked with soft polymeric chains by dynamic host–guest interactions using cucurbit[8]uril as supramolecular crosslinker. The hydrogels combined high storage



modulus, fast sol-gel transition ( $<6$  s) and self-healing ability as fast as 30 s. Besides, the self-healing capacity was also observed for hydrogel samples aged for 4 months. This work suggests robust strategies to combine highly dynamic supramolecular interactions with mechanically active colloidal reinforcements for the preparation of the next generation of advanced materials from renewable resources.

Nanocellulose can present a chiral nematic phase in water, in which the CNC self-assemble in the helical configuration. If the helical pitches of nanocrystals assemble, have the same order of the visible light wavelength the system can exhibit photonic color. In this sense, Kelly et al. developed photonic hydrogels by controlling the polymerization condition to ensure the CNC nematic phase was preserved [72]. That was possible by previous evaporation-induced self-assembly (EISA) followed by UV-photo-polymerization. It was showed that any change in the helical pitch due to variations of external media (such as salt, pH, etc.) the reflected color of the hydrogel could be tuned.

CNC and CNF have been incorporated in hydrogels or other polymeric matrices seeking improvement of drug release behavior for delivery systems, swelling features, improved mechanical properties for materials with potential application in bone and tissue repair, and in the preparation of hydrophobic-absorbing matrix based on functionalized CNF aerogels, as summarized in a recent review paper [148].

### 3.2 Based on Chitin Nanocrystals

Chitin can be derived from innumerable sources, but from the commercial point of view, the most important are shrimp, lobster and crab shells, which are residue from food industry. Chemical [151], physical [77], enzymatic and microbiological [46] methodologies have been explored to isolate chitin. In general, the extraction process involves several steps for removing bound proteins, minerals, lipids, and pigments.

Chitin nanowhiskers (CtNW) and chitin nanofibers (CtNF) can be isolated by 2,2,6,6-tetramethylpiperidine-1-oxyl radical-mediated oxidation (TEMPO-oxidation) surface cationization followed by mechanical disintegration and acid hydrolysis, [200]. Similarly, to the obtention of CNC, the acid hydrolysis of chitin is the most common procedure for isolating CtNW, and it is based on the faster hydrolysis kinetics of the amorphous phases. However, in the case of chitin, HCl is used instead of the  $\text{H}_2\text{SO}_4$  used for cellulose. Although different reaction conditions have been reported (Table 5), the most used is 3 N HCl, for 90 min at boiling, as described elsewhere [130, 134], which in general, generates 50–300 nm long and 10–50 nm wide CtNW.

Similarly to CNC, the majority of applications described in the literature are employing CtNW as the reinforcement phase in the preparation of nanocomposites due to attractive features, e.g., derived from renewable sources, biodegradable, nontoxic, and excellent transversal and longitudinal moduli (15 and 150 GPa,



**Table 5** CtNW and CtNF obtained by different reaction conditions [39, 40, 48, 55, 103, 144, 192, 193, 196]

Source	Methodology	Length (nm)	Width (nm)
Crab	Acid hydrolysis (HCl 3 N, 60 min)	50–300 (150)	10
Crab	Acid hydrolysis (HCl 3 N, 90 min)	100–600 (240)	4–40 (15)
Crab	Acid hydrolysis (HCl 3 N, 90 min)	100–650 (500 ± 50)	10–80 (50 ± 10)
Crab	Acid hydrolysis (HCl 3 N, 90 min)	200–500	5–20
Crab	Acid hydrolysis (HCl 3 N, 360 min)	255	31
Crab	TEMPO-oxidation	340	8
Crab	Surface cationization	250	6
Shrimp	Acid hydrolysis (HCl 3 N, 360 min)	230–970	31
Shrimp	Acid hydrolysis (HCl 3 N, 360 min)	180–820 (427)	43
Shrimp	Acid hydrolysis (HCl 3 N, 360 min)	110–975 (343)	46

respectively). CtNW have been introduced into polymeric films for reducing O<sub>2</sub> permeability [38], into fibers to improve mechanical properties [185], in lithium battery electrolytes for improved thermal and mechanical stability as well as ionic conductive [5], in membranes to enhance cell compatibility [60], among others.

CtNW have been far less studied than CNC and only a few papers report on the preparation of hydrogel nanocomposites based on CtNW as reinforcement. Even though, it has been shown significant effects on swelling capacity and drug release behavior caused by the incorporation of CtNW. Lin et al. [96] acid hydrolyzed (3 N HCl, 90 min, at boil) shrimp chitin to prepare 300–400 nm long and 10–20 nm wide CtNW to be further incorporated into alginate microspheres (900 ± 20 µm) hydrogels crosslinked by calcium ions. It was demonstrated the addition of 50 wt% CtNW increased the swelling capacity from 1.815 to 2.329 % due to the inhibition of crosslinking points caused by the presence of CtNW, which provided a less rigid matrix allowing more fluid (pH 7.4 phosphate buffer solution) intake. The presence of CtNW also promoted an increase in the encapsulation efficiency of theophylline from 33 % (standard hydrogel without CtNW) to 55 % at 50 wt% CtNW, which acted as a barrier to prevent drug leaking. Besides, CtNW-loaded microspheres showed sustained releasing profile, in which the drug releasing mechanism was found to occurs by diffusional transport ( $n = 0.419$ ) contrasting the anomalous transport ( $n = 0.716$ ) presented by the pristine alginate microspheres.

Hybrid hemicellulose-based hydrogels prepared by freeze (10 h, −20 °C)-thawing (1 h, 80 °C) cycles nanoreinforced with CtNW has been recently reported [49]. CtNW (length: 200 ± 10 nm; width: 40 ± 10 nm) were prepared by acid hydrolysis (3 N HCl, 90 min, 90 °C) and incorporated into hydrogels at different volume ratio (0–2) at the constant (1:1) hemicellulose/poly(vinyl alcohol) ratio of 2 wt% solutions (each). The presence of CtNW (up to ratio 1:1:1) induced larger and more numerous porous to the hydrogel structure, while at higher concentration (e.g., 1:1:2) the result observed was opposite. The samples absorbed 10–20 g of water by gram of dry hydrogel, and statistically no significant effect on swelling

was verified by the introduction of CtNW. On the other hand, the mechanical features were dependent on CtNW loading, but no linear tendency with concentration was observed: e.g., at 0.5 CtNW the fracture stress was maximum (9.6 MPa), but at 0.75 CtNW the value was lower (8.1 MPa) than the standard (9.3 MPa). It was suggested the prepared samples present potential to be applied in the tissue engineering field.

CtNW has also been chemically bound to silane-modified magnetic nanoparticles for DNA extraction [22] from *E. coli* and *S. aureus* microorganisms. CtNW (dimensions not explicitly informed) were isolated by acid hydrolysis (3 N HCl, 3 h, 105 °C). The CtNW-Magnetic nanoparticles formed a stable colloidal suspension in both water and DMSO. Furthermore, the magnetic nanoparticles could be aligned by the application of a magnetic field. It was showed that the size of nanoparticles depends on the surface charges on CtNW, which are controlled by adjusting the pH of the media.

Araki et al. [7] reported chitosan hydrogels filled with CtNW (6–8 nm wide, 100–200 nm long, 3 N HCl, 3 h, at boil) using isocyanate hexamethylene-1,6-di-(aminocarboxysulfonate) (HDS) as crosslinker. The addition of CtNW promoted an increasing in the hydrogel stiffness as showed by the Young's modulus that changed from 2.53 kPa at 0 wt% CtNW to ~170 kPa at 13 wt% that represents about 67-folds increase. Similarly, the stress at break increased 41-fold for the same variation of composition. However, the improved mechanical properties were accompanied by a loss in the swelling capacity of ca. ten-folds, which was attributed to the suppression of chitosan chains mobility caused by the presence of the rigid CtNW.

### ***3.3 Based on Starch Nanocrystals***

Starch nanocrystals (SNC), unlike CNC and CtNW, are platelet-shaped nanoparticles with much shorter length of 20–40 nm, width of 15–30 nm, and a few nanometers of thickness [29, 87]. Preparation of SNC by acid hydrolysis of native starch has the time-consuming process, which can take up to 30 days, and the low yield as the major drawbacks. The choice of starch source, acid type and concentration, reaction conditions (temperature and time) and pretreatment (e.g., enzymatic, mechanical treatment, etc.) are paramount to reduce hydrolysis time and improve yield [88, 90]. Most reports on SNC preparation follows the procedure described by Angellier et al. [3], in which the hydrolysis is conducted using 3.16 M H<sub>2</sub>SO<sub>4</sub> solution for 5 days at 40 °C.

Although SNC are much shorter and less crystalline (~45 %) than other polysaccharide nanocrystals (>90 %), the reinforcing effect due to the percolation of SNC into different polymeric matrix (natural rubber, polyurethane, starch, pullulan, PVA, among others) has been reported [43, 87, 112, 140]. SNC have also been studied as stabilizing agents in emulsions (also denoted as pickering emulsion) with potential applications in food, cosmetics and pharmaceuticals [50, 92, 93].

Up to date, only few works report on the incorporation of SNC into hydrogels. For instance, SNC (40–60 nm long, 15–30 nm wide) hydrolyzed (3.16 M H<sub>2</sub>SO<sub>4</sub>, 5 days, 40 °C) from pea starch were used to form hydrogel nanocomposites based on Ca<sup>+2</sup>-crosslinked alginate polymer matrix [96–99]. The composites presented pH-dependent swelling behavior, where the fluid uptake at pH 1 and at 50 wt% SNC was less than 30 % whereas at pH 6.8 and 7.4 the swelling was higher than the noncomposite hydrogels reaching about 2000 %. The efficiency of theophylline encapsulation was 55 % in the composite contrasting the lower efficiency of only 34 % of the standard hydrogel. The releasing behavior of theophylline-loaded hydrogel nanocomposites microspheres was investigated under different pH conditions (1 and 7.4). It was showed the composite samples could sustain the release for a longer time, and the equilibrium was reached at ~400 min, more than the double period observed for the noncomposite hydrogel. Besides, the mechanism by which the drug is released changed from anomalous transport ( $n = 0.716$ ) to diffusional transport (0.424) with the addition of SNC. Therefore, SNC could prevent the drug release burst at the first minutes of releasing, allowing the composite to be applied as carriers for drug delivery systems.

Zhang et al. [202] prepared supramolecular hydrogel based on cyclodextrin inclusion filled with SNC with potential for injection-implantation drug delivery. SNC (10–20 nm wide, 40–70 nm long) were made by hydrolyzing pea starch in 3.16 M H<sub>2</sub>SO<sub>4</sub> solution for 5 days at 40 °C. The presence of polysaccharide nanocrystals increased the stability of the hydrogel framework and inhibited the diffusion of bovine serum albumin, which served as a model protein drug in the nanocomposite hydrogels and showed prominent sustained release profiles. The shear-thinning property of the nanocomposite allows it to be applied as injectable material.

## 4 Conclusions and Future Trends

This chapter demonstrates that polysaccharide nanocrystals (PN) derived from well-known biopolymers such as cellulose, chitin, and starch can be versatile nanoparticles to be applied in different fields, especially in the preparation of hydrogel nanocomposites. Interestingly, by using nanotechnology one can take advantage from the same features that once prevented cellulose and chitin to be largely explored by industry (specially due to high crystallinity and lack of solubility in common solvents) to produce highly crystalline and high-performance rod-shaped nanoparticles (also called nanowhiskers, nanocrystals or nanofibrils). It also should be pointed out that such nanocrystals are excellent candidates to replace traditional inorganic fillers (metal oxides, noble metals, carbon, etc.) in the preparation of many nanocomposites. The natural abundance, renewability, low cost, biodegradability, biocompatibility, low density, and outstanding elastic modulus of such polymers, as well as the absence of expensive and toxic precursors, stimulate their use.

Although polysaccharide nanocrystals have been proved to be promising materials, some challenges are still to be overcome. For instance, most researches on PN are conducted by academic groups purely by scientific curiosity and commercial or industrial production of PN is restricted to a few companies and mostly to CNC.

So far, CNC have been more explored than CtNW or SNC in the preparation of hydrogel nanocomposites, but it has been demonstrated that any of those particles can strongly influence either the mechanical properties or swelling/release features of hydrogel composites.

More comprehensive studies on the concepts that drive the properties of such soft-hard combined composite hydrogels will broaden the understanding of structure-properties relationship allowing new materials and new applications.

## References

1. Ahmad EEM, Luyt AS (2012) Morphology, thermal, and dynamic mechanical properties of poly(lactic acid)/sisal whisker nanocomposites. *Polym Compo* 33(6):1025–1032
2. Alarcon CDLH, Pennadam S, Alexander C (2005) Stimuli responsive polymers for biomedical applications. *Chem Soc Rev* 34(3):276–285
3. Angellier H, Choisnard L, Molina-Boisseau S, Ozil P, Dufresne A (2004) Optimization of the preparation of aqueous suspensions of waxy maize starch nanocrystals using a response surface methodology. *Biomacromolecules* 5(4):1545–1551
4. Anglès MN, Dufresne A (2000) Plasticized starch/tunicin whiskers nanocomposites. 1. Structural analysis. *Macromolecules* 33(22):8344–8353
5. Angulakhsmi N, Thomas S, Nair JR, Bongiovanni R, Gerbaldi C, Stephan AM (2013) Cycling profile of innovative nanochitin-incorporated poly (ethylene oxide) based electrolytes for lithium batteries. *J Power Source* 228:294–299
6. Araki J (2013) Electrostatic or steric?—preparations and characterizations of well-dispersed systems containing rod-like nanowhiskers of crystalline polysaccharides. *Soft Matter* 9(16):4125–4141
7. Araki J, Yamanaka Y, Ohkawa K (2012) Chitin-chitosan nanocomposite gels: reinforcement of chitosan hydrogels with rod-like chitin nanowhiskers. *Polym J* 44(7):713–717
8. Araujo MA, Cunha AM, Mota M (2004) Enzymatic degradation of starch-based thermoplastic compounds used in protheses: Identification of the degradation products in solution. *Biomaterials* 25(13):2687–2693
9. Arora A, Padua GW (2010) Review: Nanocomposites in food packaging. *J Food Sci* 75(1): R43–R49
10. Azizi S, Ahmad MB, Hussein MZ, Ibrahim NA, Namvar F (2014) Preparation and properties of poly(vinyl alcohol)/chitosan blend bionanocomposites reinforced with cellulose nanocrystals/ZnO-Ag. *Int J Nanomed* 9:1909–1917
11. Barbosa IVM, Merquior DA, Peixoto FC (2006) Estimation of kinetic and mass-transfer parameters for cellulose nitration. *AIChE J* 52(10):3549–3554
12. Bensadoun F, Kchit N, Billotte C, Bickerton S, Trochu F, Ruiz E (2011) A study of nanoclay reinforcement of biocomposites made by liquid composite molding. *Int J Polym Sci*
13. Berger J, Reist M, Mayer JM, Felt O, Peppas NA, Gurny R (2004) Structure and interactions in covalently and ionically crosslinked chitosan hydrogels for biomedical applications. *Eur J Pharm Biopharm* 57(1):19–34

14. Bhardwaj R, Mohanty AK (2007) Advances in the properties of polylactides based materials: a review. *J Biobased Mater Bio* 1(2):191–209
15. Branch TA, Abubaker EMN, Mkango S, Butterworth DS (2007) Separating southern blue whale subspecies based on length frequencies of sexually mature females. *Mar Mammal Sci* 23(4):803–833
16. Buléon A, Colonna P, Planchot V, Ball S (1998) Starch granules: Structure and biosynthesis. *Int J Biol Macromol* 23(2):85–112
17. Burdock GA (2007) Safety assessment of hydroxypropyl methylcellulose as a food ingredient. *Food Chem Toxicol* 45(12):2341–2351
18. Buzea C, Pacheco II, Robbie K (2007) Nanomaterials and nanoparticles: sources and toxicity. *Biointerphases* 2(4):MR17–MR71
19. Campbell IM (2003) Introduction to synthetic polymers. London, Oxford
20. Cartier N, Mazeau K, Domard A, Chanzy H (1992) Single-crystals of chitosan. *Adv Chitin Chitosan*, 155–164
21. Charreau H, Foresti ML, Vázquez A (2013) Nanocellulose patents trends: a comprehensive review on patents on cellulose nanocrystals, microfibrillated and bacterial cellulose. *Recent Pat Nanotec* 7(1):56–80
22. Chatrabhuti S, Chirachanchai S (2013) Single step coupling for multi-responsive water-based chitin/chitosan magnetic nanoparticles. *Carbohydr Polym* 97(2):441–450
23. Chawla P, Ranjan A, Pandey P, Chawla V (2014) Hydrogels: A journey from diapers to gene delivery. *Mini-Rev Med Chem* 14(2):160–173
24. Chen Y, Dong B, Qin W, Xiao D (2010) Xylose and cellulose fractionation from corncob with three different strategies and separate fermentation of them to bioethanol. *Bioresour Technol* 101(18):6994–6999
25. De Campos A, Correa A, Cannella D, De M Teixeira E, Marconcini J, Dufresne A, Mattoso LC, Cassland P, Sanadi A (2013) Obtaining nanofibers from curauá and sugarcane bagasse fibers using enzymatic hydrolysis followed by sonication. *Cellulose*, 20(3): 1491–1500
26. Dean J, Dixon B (1992) Advances in Chitin and Chitosan. Elsevier, London
27. Diez-Pascual AM, Naffakh M, Marco C, Ellis G, Gomez-Fatou MA (2012) High-performance nanocomposites based on polyetherketones. *Prog Mater Sci* 57(7):1106–1190
28. Ding P, Huang KL, Li GY, Zeng WW (2007) Mechanisms and kinetics of chelating reaction between novel chitosan derivatives and Zn(II). *J Hazard Mater* 146(1–2):58–64
29. Dufresne A (2008) Polysaccharide nano crystal reinforced nanocomposites. *Canad J Chem* 86(6):484–494
30. Dufresne A (2010) Processing of polymer nanocomposites reinforced with polysaccharide nanocrystals. *Molecules* 15(6):4111–4128
31. Dufresne A (2012) Processing of polymer nanocomposites reinforced with cellulose nanocrystals: a challenge. *Int Polym Proc* 27(5):557–564
32. Dugan JM, Gough JE, Eichhorn SJ (2013) Bacterial cellulose scaffolds and cellulose nanowhiskers for tissue engineering. *Nanomedicine* 8(2):287–298
33. Durán N, Lemes AP, Seabra AB (2012) Review of cellulose nanocrystals patents: preparation, composites and general applications. *Recent Pat Nanotechnol* 6:16–28
34. Eichhorn SJ (2011) Cellulose nanowhiskers: promising materials for advanced applications. *Soft Matter* 7(2):303–315
35. Fajardo AR, Lopes LC, Rubira AF, Muniz EC (2012) Development and application of chitosan/poly(vinyl alcohol) films for removal and recovery of Pb(II). *Chem Eng J* 183:253–260
36. Fajardo AR, Piai JF, Rubira AF, Muniz EC (2010) Time- and pH-dependent self-rearrangement of a swollen polymer network based on polyelectrolytes complexes of chitosan/chondroitin sulfate. *Carbohydr Polym* 80(3):934–943
37. Fan J-S, Li Y-H (2012) Maximizing the yield of nanocrystalline cellulose from cotton pulp fiber. *Carbohydr Polym* 88(4):1184–1188

38. Fan Y, Fukuzumi H, Saito T, Isogai A (2012) Comparative characterization of aqueous dispersions and cast films of different chitin nanowhiskers/nanofibers. *Int J Biol Macromol* 50(1):69–76
39. Fan Y, Saito T, Isogai A (2007) Chitin nanocrystals prepared by TEMPO-mediated oxidation of  $\alpha$ -chitin. *Biomacromolecules* 9(1):192–198
40. Fan Y, Saito T, Isogai A (2010) Individual chitin nano-whiskers prepared from partially deacetylated  $\alpha$ -chitin by fibril surface cationization. *Carbohydr Polym* 79(4):1046–1051
41. Faramarzi MA, Sadighi A (2013) Insights into biogenic and chemical production of inorganic nanomaterials and nanostructures. *Adv Colloid Interface Sci* 189:1–20
42. Felse PA, Panda T (1999) Studies on applications of chitin and its derivatives. *Bioprocess Eng* 20(6):505–512
43. Gao YJS, Zhao S, Liao SQ, Fang L, Wang ZF, Li LF (2014) Reinforcement of natural rubber latex film by starch nanocrystal. *Appl Mech Mater* 543–547:3886–3891
44. Garcia De Rodriguez NL, Thielemans W, Dufresne A (2006) Sisal cellulose whiskers reinforced polyvinyl acetate nanocomposites. *Cellulose* 13(3):261–270
45. George J, Ramana KV, Bawa AS, Siddaramaiah (2011) Bacterial cellulose nanocrystals exhibiting high thermal stability and their polymer nanocomposites. *Int J Biol Macromol* 48(1):50–57
46. Ghorbel-Bellaaj O, Jellouli K, Younes I, Manni L, Ouled Salem M, Nasri M (2011) A solvent-stable metalloprotease produced by *Pseudomonas aeruginosa* grown on shrimp shell waste and its application in chitin extraction. *Appl Biochem Biotechnol* 164(4):410–425
47. Gonzalez-Renteria SM, Soto-Cruz NO, Rutiaga-Quinones OM, Medrano-Roldan H, Rutiaga-Quinones JG, Lopez-Miranda J (2011) Optimization of the enzymatic hydrolysis process of four straw bean varieties. *Rev Mex Ing Quim* 10(1):17–28
48. Gopalan Nair K, Dufresne A (2003) Crab shell chitin whisker reinforced natural rubber nanocomposites. I process swelling behavior. *Biomacromol* 4(3):657–665
49. Guan Y, Zhang B, Bian J, Peng F, Sun R-C (2014) Nanoreinforced hemicellulose-based hydrogels prepared by freeze–thaw treatment. *Cellulose* 21(3):1709–1721
50. Haaj SB, Thielemans W, Magnin A, Boufi S (2014) Starch nanocrystal stabilized pickering emulsion polymerization for nanocomposites with improved performance. *ACS Appl Mater Interface* 6(11):8263–8273
51. Habibi Y, Lucia LA, Rojas OJ (2010) Cellulose nanocrystals: chemistry, self-assembly, and applications. *Chem Rev* 110(6):3479–3500
52. Han J, Lei T, Wu Q (2013) Facile preparation of mouldable polyvinyl alcohol-borax hydrogels reinforced by well-dispersed cellulose nanoparticles: physical, viscoelastic and mechanical properties. *Cellulose* 20(6):2947–2958
53. Han J, Lei T, Wu Q (2014) High-water-content mouldable polyvinyl alcohol-borax hydrogels reinforced by well-dispersed cellulose nanoparticles: dynamic rheological properties and hydrogel formation mechanism. *Carbohydr Polym* 102:306–316
54. Hanemann T, Szabo DV (2010) Polymer-nanoparticle composites: from synthesis to modern applications. *Materials* 3(6):3468–3517
55. Hariraksapitak P, Supaphol P (2010) Preparation and properties of  $\alpha$ -chitin-whisker-reinforced hyaluronan–gelatin nanocomposite scaffolds. *J Appl Polym Sci* 117(6):3406–3418
56. Heinz TE (2005) *Polysaccharides I*. Springer, New York
57. Hon DNS (1994) Cellulose—a random-walk along its historical path. *Cellulose* 1(1):1–25
58. Hovgaard L, Brondsted H (1996) Current applications of polysaccharides in colon targeting. *Crit Rev Ther Drug* 13(3–4):185–223
59. Hua K, Carlsson DO, Alander E, Lindstrom T, Stromme M, Mhraryan A, Ferraz N (2014) Translational study between structure and biological response of nanocellulose from wood and green alga. *RSC Adv* 4(6):2892–2903
60. Huang Y, Zhang L, Yang J, Zhang X, Xu M (2013) Structure and properties of cellulose films reinforced by chitin whiskers. *Macromol Mater Eng* 298(3):303–310

61. Hutchinson JR, Bates KT, Molnar J, Allen V, Makovicky PJ (2011) A computational analysis of limb and body dimensions in *tyrannosaurus rex* with implications for locomotion, ontogeny, and growth. *PLoS One* 6(10):E26037
62. Ifuku S, Saimoto H (2012) Chitin nanofibers: preparations, modifications, and applications. *Nanoscale* 4(11):3308–3318
63. Isogai A (2013) Wood nanocelluloses: fundamentals and applications as new bio-based nanomaterials. *J Wood Sci* 59(6):449–459
64. Isogai A, Saito T, Fukuzumi H (2011) TEMPO-oxidized cellulose nanofibers. *Nanoscale* 3(1):71–85
65. Jayakumar R, Menon D, Manzoor K, Nair SV, Tamura H (2010) Biomedical applications of chitin and chitosan based nanomaterials-a short review. *Carbohydr Polym* 82(2):227–232
66. Jin L, Wei Y, Xu Q, Yao W, Cheng Z (2014) Cellulose nanofibers prepared from TEMPO-oxidation of kraft pulp and its flocculation effect on kaolin clay. *J Appl Polym Sci* 131(12):2345–2353
67. Kabiri K, Omidian H, Zohuriaan-Mehr MJ, Doroudiani S (2011) Superabsorbent hydrogel composites and nanocomposites: a review. *Polym Composite* 32(2):277–289
68. Kalia S, Dufresne A, Cherian BM, Kaith BS, Averous L, Njuguna J, Nassiopoulous E (2011) Cellulose-based bio- and nanocomposites: a review. *Int J Polym Sci*, ID 837875
69. Karimi S, Dufresne A, Tahir PM, Karimi A, Abdulkhali A (2014) Biodegradable starch-based composites: effect of micro and nanoreinforcements on composite properties. *J Mater Sci* 49(13):4513–4521
70. Karmazsin E (1987) Thermal-analysis in the cellulose, paper and textile-industry. *Thermochim Acta* 110:471–475
71. Kaushik A, Kumra J (2014) Morphology, thermal and barrier properties of green nanocomposites based on tps and cellulose nanocrystals. *J Elastom Plast* 46(3):284–299
72. Kelly JA, Shukaliak AM, Cheung CCY, Shopsowitz KE, Hamad WY, Maclachlan MJ (2013) Responsive photonic hydrogels based on nanocrystalline cellulose. *Ang Chem Int Ed* 52(34):8912–8916
73. Kerstens S, Decraemer WF, Verbelen J-P (2001) Cell walls at the plant surface behave mechanically like fiber-reinforced composite materials. *Plant Physiol* 127(2):381–385
74. Khalil H, Bhat AH, Yusra AFI (2012) Green composites from sustainable cellulose nanofibrils: a review. *Carbohydr Polym* 87(2):963–979
75. Khan TA, Peh KK, Ching HS (2002) Reporting degree of deacetylation values of chitosan: The influence of analytical methods. *J Pharm Pharm Sci* 5(3):205–212
76. Khoushab F, Yamabhai M (2010) Chitin research revisited. *Mar Drug* 8(7):1988–2012
77. Kjartansson GT, Zivanovic S, Kristbergsson K, Weiss J (2006) Sonication-assisted extraction of chitin from north atlantic shrimps (*pandalus borealis*). *J Agr Food Chem* 54(16):5894–5902
78. Klemm D, Heublein B, Fink HP, Bohn A (2005) Cellulose: fascinating biopolymer and sustainable raw material. *Angew Chem Int Ed* 44(22):3358–3393
79. Klemm DE (2006) *Polysaccharides II*. Springer, New York
80. Kobayashi S, Kashiwa K, Shimada J, Kawasaki T, Shoda S (1992) Enzymatic polymerization—the 1st invitro synthesis of cellulose via nonbiosynthetic path catalyzed by cellulase. *Macromol Symp* 54–5:509–518
81. Kono H, Otaka F, Ozaki M (2014) Preparation and characterization of guar gum hydrogels as carrier materials for controlled protein drug delivery. *Carbohydr Polym* 111:830–840
82. Kuilla T, Bhadra S, Yao DH, Kim NH, Bose S, Lee JH (2010) Recent advances in graphene based polym composite. *Prog Polym Sci* 35(11):1350–1375
83. Kurita K (2006) Chitin and chitosan: Functional biopolymers from marine crustaceans. *Mar Biotechnol* 8(3):203–226
84. Laftah WA, Hashim S, Ibrahim AN (2011) Polymer hydrogels: a review. *Polym Plast Technol* 50(14):1475–1486

85. Lagerwall JPF, Schutz C, Salajkova M, Noh J, Hyun Park J, Scalia G, Bergstrom L (2014) Cellulose nanocrystal-based materials: from liquid crystal self-assembly and glass formation to multifunctional thin films. *NPG Asia Mater* 6:E80
86. Lam E, Male KB, Chong JH, Leung ACW, Luong JHT (2012) Applications of functionalized and nanoparticle-modified nanocrystalline cellulose. *Trend Biotechnol* 30(5):283–290
87. LeCorre D, Bras J, Dufresne A (2010) Starch nanoparticles: a review. *Biomacromolecules* 11(5):1139–1153
88. LeCorre D, Bras J, Dufresne A (2011) Influence of botanic origin and amylose content on the morphology of starch nanocrystals. *J Nanopart Res* 13(12):7193–7208
89. LeCorre D, Vahanian E, Dufresne A, Bras J (2011) Enzymatic pretreatment for preparing starch nanocrystals. *Biomacromolecules* 13(1):132–137
90. LeCorre D, Bras J, Dufresne A (2012) Influence of native starch's properties on starch nanocrystals thermal properties. *Carbohydr Polym* 87(1):658–666
91. Lee KY, Mooney DJ (2001) Hydrogels for tissue engineering. *Chem Rev* 101(7):1869–1880
92. Li C, Li Y, Sun P, Yang C (2014) Starch nanocrystals as particle stabilisers of oil-in-water emulsions. *J Sci Food Agr* 94(9):1802–1807
93. Li C, Sun P, Yang C (2012) Emulsion stabilized by starch nanocrystals. *Starch Stärke* 64(6):497–502
94. Li J, Revol JF, Naranjo E, Marchessault RH (1996) Effect of electrostatic interaction on phase separation behaviour of chitin crystallite suspensions. *Int J Biol Macromol* 18(3):177–187
95. Li Y, Yang C, Khan M, Liu S, Hedrick JL, Yang Y-Y, Ee P-LR (2012) Nanostructured PEG-based hydrogels with tunable physical properties for gene delivery to human mesenchymal stem cells. *Biomaterials* 33(27):6533–6541
96. Lin N, Huang J, Chang PR, Anderson DP, Yu JH (2011) Preparation, modification, and application of starch nanocrystals in nanomaterials. a review. *J Nanomater*
97. Lin M-F, Thakur VK, Tan EJ, Lee PS (2011) Dopant induced hollow BaTiO<sub>3</sub> nanostructures for application in high performance capacitors. *J Mater Chem* 21:16500–16504
98. Lin M-F, Thakur VK, Tan EJ, Lee PS (2011) Surface functionalization of BaTiO<sub>3</sub> nanoparticles and improved electrical properties of BaTiO<sub>3</sub>/polyvinylidene fluoride composite. *RSC Adv* 1:576–578
99. Lin N, Huang J, Chang PR, Feng L, Yu J (2011) Effect of polysaccharide nanocrystals on structure, properties, and drug release kinetics of alginate-based microspheres. *Colloid Surf B* 85(2):270–279
100. Ling SJ, Li CX, Adamcik J, Wang SH, Shao ZZ, Chen X, Mezzenga R (2014) Directed growth of silk nanofibrils on graphene and their hybrid nanocomposites. *Acs Macro Lett* 3(2):146–152
101. Liu D, Zhang Y, Sun X, Chang PR (2014) Recent advances in bio-sourced polymeric carbohydrate/nanotube composites. *J Appl Polym Sci* 131(12)
102. Lu P, Hsieh Y-L (2012) Cellulose isolation and core-shell nanostructures of cellulose nanocrystals from chardonnay grape skins. *Carbohydr Polym* 87(4):2546–2553
103. Lu Y, Weng L, Zhang L (2004) Morphology and properties of soy protein isolate thermoplastics reinforced with chitin whiskers. *Biomacromolecules* 5(3):1046–1051
104. Ly B, Thielemans W, Dufresne A, Chaussy D, Belgacem MN (2008) Functionalization of cellulose fiber and their incorporation in renewable polymeric matrices. *Compos Sci Technol* 68:3193–3201
105. Magdy EE (2011) *Biotechnology of biopolymers*. Intech, Rijeka, Croatia
106. Majeed K, Jawaid M, Hassan A, Abu Bakar A, Khalil H, Salema AA, Inuwa I (2013) Potential materials for food packaging from nanoclay/natural fibres filled hybrid composites. *Mater Des* 46:391–410
107. Malafaya PB, Elvira C, Gallardo A, San Roman J, Reis RL (2001) Porous starch-based drug delivery systems processed by a microwave route. *J Biomater Sci Polym Ed* 12(11):1227–1241
108. Mano E (1989) *Introdução à polímeros*. Edgar Blucher, São Paulo



109. Mariano M, El Kissi N, Dufresne A (2014) Cellulose nanocrystals and related nanocomposites: review of some properties and challenges. *J Polym Sci B Polym Phys* 52 (12):791–806
110. Mckee JR, Appel EA, Seitsonen J, Kontturi E, Scherman OA, Ikkala O (2014) Healable, stable and stiff hydrogels: Combining conflicting properties using dynamic and selective three-component recognition with reinforcing cellulose nanorods. *Adv Funct Mater* 24 (18):2706–2713
111. Mckee JR, Hietala S, Seitsonen J, Laine J, Kontturi E, Ikkala O (2014) Thermoresponsive nanocellulose hydrogels with tunable mechanical properties. *ACS Macro Lett* 3(3):266–270
112. MéLé P, Angellier-Coussy HLN, Molina-Boisseau S, Dufresne A (2011) Reinforcing mechanisms of starch nanocrystals in a nonvulcanized natural rubber matrix. *Biomacromolecules* 12(5):1487–1493
113. Miguel SP, Ribeiro MP, Brancal H, Coutinho P, Correia IJ (2014) Thermoresponsive chitosan–agarose hydrogel for skin regeneration. *Carbohydr Polym* 111:366–373
114. Mincea M, Negrulescu A, Ostafe V (2012) Preparation, modification, and applications of chitin nanowhiskers: a review. *Rev Adv Mater Sci* 30(3):225–242
115. Morais JPS, Rosa MDF, De Souza Filho MDSM, Nascimento LD, Do Nascimento DM, Cassales AR (2013) Extraction and characterization of nanocellulose structures from raw cotton linter. *Carbohydr Polym* 91(1):229–235
116. Mueller S, Weder C, Foster EJ (2014) Isolation of cellulose nanocrystals from pseudostems of banana plants. *RSC Adv* 4(2):907–915
117. Murphy P, Mitchell JR, Starch (2000) *Handbook of Hydrocolloids*. Woodhead Publishing, UK
118. Muzzarelli RAA (2011) Biomedical exploitation of chitin and chitosan via mechano-chemical disassembly, electrospinning, dissolution in imidazolium ionic liquids, and supercritical drying. *Mar Drug* 9(9):1510–1533
119. Naffakh M, Diez-Pascual AM, Marco C, Ellis GJ, Gomez-Fatou MA (2013) Opportunities and challenges in the use of inorganic fullerene-like nanoparticles to produce advanced polymer nanocomposites. *Prog Polym Sci* 38(8):1163–1231
120. Narjary B, Aggarwal P (2014) Evaluation of soil physical quality under amendments and hydrogel applications in a soybean–wheat cropping system. *Commun Soil Sci Plan* 45 (9):1167–1180
121. Nishiyama Y, Langan P, Chanzy H (2002) Crystal structure and hydrogen-bonding system in cellulose I beta from synchrotron x-ray and neutron fiber diffraction. *J Amer Chem Soc* 124 (31):9074–9082
122. Nishiyama Y, Sugiyama J, Chanzy H, Langan P (2003) Crystal structure and hydrogen bonding system in cellulose I(alpha), from synchrotron x-ray and neutron fiber diffraction. *J Amer Chem Soc* 125(47):14300–14306
123. Nizam El-Din HM (2012) Surface coating on cotton fabrics of new multilayer formulations based on superabsorbent hydrogels synthesized by gamma radiation designed for diapers. *J Appl Polym Sci* 125(S2):E180–E186
124. Northcote DH (1972) Chemistry of the plant cell wall. *Annu Rev Plant Physiol* 23(1):113–132
125. Oates CG (1997) Towards an understanding of starch granule structure and hydrolysis. *Trend Food Sci Technol* 8(11):375–382
126. Okamoto M, John B (2013) Synthetic biopolymer nanocomposites for tissue engineering scaffolds. *Prog Polym Sci* 38(10–11):1487–1503
127. Oksman K, Etang JA, Mathew AP, Jonoobi M (2011) Cellulose nanowhiskers separated from a bio-residue from wood bioethanol production. *Biomass Bioenergy* 35(1):146–152
128. Omidian H, Rocca JG, Park K (2005) Advances in superporous hydrogels. *J Control Release* 102(1):3–12
129. Osorio-Madrado A, Eder M, Rueggeberg M, Pandey JK, Harrington MJ, Nishiyama Y, Putaux J-L, Rochas C, Burgert I (2012) Reorientation of cellulose nanowhiskers in agarose hydrogels under tensile loading. *Biomacromolecules* 13(3):850–856

130. Paillet M, Dufresne A (2001) Chitin whisker reinforced thermoplastic nanocomposites. *Macromolecules* 34(19):6527–6530
131. Park S, Baker JO, Himmel ME, Parilla PA, Johnson DK (2010) Cellulose crystallinity index: measurement techniques and their impact on interpreting cellulase performance. *Biotechnol Biofuel* 3
132. Peng BL, Dhar N, Liu HL, Tam KC (2011) Chemistry and application of nanocrystalline cellulose and its derivatives: a nanotechnology perspective. *Can J Chem Eng* 9999:1–16
133. Peppas NA, Bures P, Leobandung W, Ichikawa H (2000) Hydrogels in pharmaceutical formulations. *Eur J Pharm Biopharm* 50(1):27–46
134. Pereira AGB, Muniz EC, Hsieh Y-L (2014) Chitosan-sheath and chitin-core nanowhiskers. *Carbohydr Polym* 107:158–166
135. Perez S, Samain D (2010) Structure and engineering of celluloses. *Adv Carbohydr Chem Biochem* 64(64):25–116
136. Phua YJ, Lau NS, Sudesh K, Chow WS, Ishak ZAM (2012) Biodegradability studies of poly (butylene succinate)/organo-montmorillonite nanocomposites under controlled compost soil conditions: Effects of clay loading and compatibiliser. *Polym Degrad Stabil* 97(8):1345–1354
137. Pillai CKS, Paul W, Sharma CP (2009) Chitin and chitosan polymers: Chemistry, solubility and fiber formation. *Prog Polym Sci* 34(7):641–678
138. Raabe D, Sachs C, Romano P (2005) The crustacean exoskeleton as an example of a structurally and mechanically graded biological nanocomposite material. *Acta Mater* 53 (15):4281–4292
139. Rahman MM, Afrin S, Haque P, Islam MM, Islam MS, Gafur MA (2014) Preparation and characterization of jute cellulose crystals-reinforced poly(l-lactic acid) biocomposite for biomedical applications. *Int J Chem Eng* 7
140. Rajisha KR, Maria HJ, Pothan LA, Ahmad Z, Thomas S (2014) Preparation and characterization of potato starch nanocrystal reinforced natural rubber nanocomposites. *Int J Biol Macromol* 67:147–153
141. Reddy MM, Vivekanandhan S, Misra M, Bhatia SK, Mohanty AK (2013) Biobased plastics and bionanocomposites: current status and future opportunities. *Prog Polym Sci* 38(10–11):1653–1689
142. Rehman N, De Miranda M, Rosa SL, Pimentel D, Nachtigall SB, Bica CD (2014) Cellulose and nanocellulose from maize straw: an insight on the crystal properties. *J Polym Environ* 22 (2):252–259
143. Revedin A, Aranguren B, Becattini R, Longo L, Marconi E, Lippi MM, Skakun N, Sinitsyn A, Spiridonova E, Svoboda J (2010) Thirty thousand-year-old evidence of plant food processing. *P Natl Acad Sci USA* 107(44):18815–18819
144. Revol JF, Marchessault RH (1993) In vitro chiral nematic ordering of chitin crystallites. *Int J Biol Macromol* 15(6):329–335
145. Rey C, Combes C, Drouet C, Glimcher MJ (2009) Bone mineral: update on chemical composition and structure. *Osteoporosis Inter* 20(6):1013–1021
146. Rinaudo M (2006) Chitin and chitosan: properties and applications. *Prog Polym Sci* 31 (7):603–632
147. Rittmeyer EN, Allison A, Gründler MC, Thompson DK, Austin CC (2012) Ecological guild evolution and the discovery of the world's smallest vertebrate. *PLoS One* 7(1):E29797
148. Rodrigues FHA, Spagnol C, Pereira AGB, Martins AF, Fajardo AR, Rubira AF, Muniz EC (2014) Superabsorbent hydrogel composites with a focus on hydrogels containing nanofibers or nanowhiskers of cellulose and chitin. *J Appl Polym Sci* 131(2):1323–1329
149. Rowell RM (2005) Handbook of wood chemistry and wood composites. CRC Press, Taylor and Francis, Boca Raton
150. Rudall KM, Kench W (1973) Chitin system. *Biol Rev Camb Philos Soc* 48(4):597–605
151. Sagheer FAA, Al-Sughayer MA, Muslim S, Elsabee MZ (2009) Extraction and characterization of chitin and chitosan from marine sources in arabian gulf. *Carbohydr Polym* 77(2):410–419

152. Samir M, Alloin F, Dufresne A (2005) Review of recent research into cellulosic whiskers, their properties and their application in nanocomposite field. *Biomacromolecules* 6(2): 612–626
153. Singha AS, Thakur VK (2008) Effect of fibre loading on urea-formaldehyde matrix based green composites. *Iran Polym J* 17(11):861–873
154. Singha AS, Thakur VK (2010) Mechanical, morphological, and thermal characterization of compression-molded polymer biocomposites. *Int J Polym Anal Ch* 15(2):87–91
155. Singha AS, Thakur VK (2010) Synthesis, characterization, and study of pine needles reinforced polymer matrix based composites. *J Rein Plast Comp* 29(5):700–709
156. Sionkowska A (2011) Current research on the blends of natural and synthetic polymers as new biomaterials: review. *Prog Polym Sci* 36(9):1254–1276
157. Siqueira G, Bras J, Dufresne A (2008) Cellulose whiskers versus microfibrils: influence of the nature of the nanoparticle and its surface functionalization on the thermal and mechanical properties of nanocomposites. *Biomacromolecules* 10(2):425–432
158. Siqueira G, Bras J, Dufresne A (2010) Cellulosic bionanocomposites: a review of preparation, properties and applications. *Polymers* 2(4):728–765
159. Slavutsky AM, Bertuzzi MA (2014) Water barrier properties of starch films reinforced with cellulose nanocrystals obtained from sugarcane bagasse. *Carbohydr Polym* 110:53–61
160. Spagnol C, Rodrigues FHA, Neto AGVC, Pereira AGB, Fajardo AR, Radovanovic E, Rubira AF, Muniz EC (2012) Nanocomposites based on poly(acrylamide-co-acrylate) and cellulose nanowhiskers. *Eur Polym J* 48(3):454–463
161. Spagnol C, Rodrigues FA, Pereira AB, Fajardo A, Rubira A, Muniz E (2012) Superabsorbent hydrogel nanocomposites based on starch-g-poly(sodium acrylate) matrix filled with cellulose nanowhiskers. *Cellulose* 19(4):1225–1237
162. Spagnol C, Rodrigues FHA, Pereira AGB, Fajardo AR, Rubira AF, Muniz EC (2012) Superabsorbent hydrogel composite made of cellulose nanofibrils and chitosan-graft-poly (acrylic acid). *Carbohydr Polym* 87(3):2038–2045
163. Swift G (1994) Water-soluble polymers. *Polym Degrad Stabil* 45(2):215–231
164. Taylor NG (2008) Cellulose biosynthesis and deposition in higher plants. *New Phytol* 178 (2):239–252
165. Thakur VK, Yan J, Lin M-F et al (2012) Novel polymer nanocomposites from bioinspired green aqueous functionalization of BNNTs. *Polym Chem* 3:962–969
166. Thakur VK, Singha AS, Thakur MK (2012) Graft copolymerization of methyl acrylate onto cellulosic biofibers: synthesis, characterization and applications. *J Polym Environ* 20: 164–174
167. Thakur VK, Singha AS, Thakur MK (2012) Modification of Natural Biomass by Graft Copolymerization. *Int J Polym Anal Charact* 17:547–555
168. Thakur VK, Singha AS, Thakur MK (2012) Green composites from natural fibers: mechanical and chemical aging properties. *Int J Polym Anal Charact* 17:401–407
169. Thakur VK, Singha AS, Thakur MK (2012) In-air graft copolymerization of ethyl acrylate onto natural cellulosic polymers. *Int J Polym Anal Charact* 17:48–60
170. Thakur VK, Singha AS, Thakur MK (2012) Surface modification of natural polymers to impart low water absorbency. *Int J Polym Anal Charact* 17:133–143
171. Teixeira EDM, Bondancia TJ, Teodoro KBR, Corrêa AC, Marconcini JM, Mattoso LHC (2011) Sugarcane bagasse whiskers: extraction and characterizations. *Ind Crop Prod* 33 (1):63–66
172. Thakkar KN, Mhatre SS, Parik RY (2010) Biological synthesis of metallic nanoparticles. *Nanomed Nanotech Biol Med* 6:257–262
173. Thakur VK, Singha AS, Thakur MK (2013) Natural cellulosic polymers as potential reinforcement in composites: physicochemical and mechanical studies. *Adv Polym Technol* 32:E427–E435
174. Thakur VK, Singha AS, Thakur MK (2013) Fabrication and physico-chemical properties of high-performance pine needles/green polymer composites. *Int J Polym Mater Polym Biomater* 62:226–230

175. Thakur VK, Singha AS, Thakur MK (2013) Ecofriendly biocomposites from natural fibers: mechanical and weathering study. *Int J Polym Anal Charact* 18:64–72
176. Thakur VK, Thakur MK, Gupta RK (2013) Synthesis of lignocellulosic polymer with improved chemical resistance through free radical polymerization. *Int J Biol Macromol* 61:121–126
177. Thakur VK, Thakur MK, Gupta RK (2013) Development of functionalized cellulosic biopolymers by graft copolymerization. *Int J Biol Macromol* 62:44–51
178. Thakur VK, Singha AS, Mehta JK (2014) Renewable resource based green polymer composite: analysis and characterization. *Int J Anal Ch* 15(3):137–146
179. Thakur VK, Thakur MK, Gupta RK (2014) Graft copolymers of natural fibers for green composite. *Carbohydr Polym* 104(1):87–93
180. Thakur VK, Thakur MK, Reghavan P, Kessler MR (2014) Progress in green polymer from lignin of multifunctional application. *ACS Sustain Chem Eng* 2(5):1072–1092
181. Thakur VK, Thakur MK (2014) Recent advances in graft copolymerization and applications of chitosan: a review. *ACS Sustain Chem Eng* 2:2637–2652
182. Thakur VK, Thakur MK (2014) Recent trends in hydrogels based on psyllium polysaccharide: a review. *J Clean Prod* 82:1–15
183. Thakur VK, Thakur MK (2014) Processing and characterization of natural cellulose fibers/thermoset polymer composites. *Carbohydr Polym* 109:102–117
184. Tou ZQ, Koh TW, Chan CC (2014) Poly(Vinyl Alcohol) hydrogel based fiber interferometer sensor for heavy metal cations. *Sensor Actuat B Chem* 202:185–193
185. Uddin AJ, Fujie M, Sembo S, Gotoh Y (2012) Outstanding reinforcing effect of highly oriented chitin whiskers in PVA nanocomposites. *Carbohydr Polym* 87(1):799–805
186. Van De Velde K, Kiekens P (2002) Biopolymers: overview of several properties and consequences on their applications. *Polym Test* 21(4):433–442
187. Vincent JFV (2002) Arthropod cuticle: A natural composite shell system. *Compos Part A Appl S* 33(10):1311–1315
188. Visakh PM, Thomas S, Oksman K, Mathew AP (2012) Crosslinked natural rubber nanocomposites reinforced with cellulose whiskers isolated from bamboo waste: processing and mechanical/thermal properties. *Compos Part-A Appl S* 43(4):735–741
189. Wang DX, Yu J, Zhang JM, He JS, Zhang J (2013) Transparent bionanocomposites with improved properties from poly(propylene carbonate) (PPC) and cellulose nanowhiskers (Cnws). *Compos Sci Technol* 85:83–89
190. Wang H, Zhu E, Yang J, Zhou P, Sun D, Tang W (2012) Bacterial cellulose nanofiber-supported polyaniline nanocomposites with flake-shaped morphology as supercapacitor electrodes. *J Phys Chem C* 116(24):13013–13019
191. Wang Q, Zhu L (2011) Polymer nanocomposites for electrical energy storage. *J Polym Sci Part B Polym Phys* 49(20):1421–1429
192. Watthanaphanit A, Supaphol P, Tamura H, Tokura S, Rujiravanit R (2008) Fabrication, structure, and properties of chitin whisker-reinforced alginate nanocomposite fibers. *J Appl Polym Sci* 110(2):890–899
193. Wongpanit P, Sanchavanakit N, Pavasant P, Bunaprasert T, Tabata Y, Rujiravanit R (2007) Preparation and characterization of chitin whisker-reinforced silk fibroin nanocomposite sponges. *Eur Polym J* 43(10):4123–4135
194. Wu Q, Meng Y, Wang S, Li Y, Fu S, Ma L, Harper D (2014) Rheological behavior of cellulose nanocrystal suspension: influence of concentration and aspect ratio. *J Appl Polym Sci* 131(15):898–912
195. Xu X, Liu F, Jiang L, Zhu JY, Haagensohn D, Wiesenborn DP (2013) Cellulose nanocrystals vs cellulose nanofibrils: a comparative study on their microstructures and effects as polymer reinforcing agents. *ACS Appl Mater Interface* 5(8):2999–3009
196. Yamamoto Y, Nishimura T, Saito T, Kato T (2010) CaCO<sub>3</sub>/Chitin-whisker hybrids: formation of CaCO<sub>3</sub> crystals in chitin-based liquid-crystalline Suspension. *Polym J* 42(7):583–586

197. Yang J, Han C-R, Duan J-F, Xu F, Sun R-C (2013) Mechanical and viscoelastic properties of cellulose nanocrystals reinforced poly(ethylene glycol) nanocomposite hydrogels. *ACS Appl Mater Interface* 5(8):3199–3207
198. Yang J, Zhao J-J, Xu F, Sun R-C (2013) Revealing strong nanocomposite hydrogels reinforced by cellulose nanocrystals: insight into morphologies and interactions. *ACS Appl Mater Interface* 5(24):12960–12967
199. Zanetti M, Lomakin S, Camino G (2000) Polymer layered silicate nanocomposites. *Macromol Mater Eng* 279(6):1–9
200. Zeng J-B, He Y-S, Li S-L, Wang Y-Z (2011) Chitin whiskers: an overview. *Biomacromolecules* 13(1):1–11
201. Zhang JF, Sun XZ (2004) Mechanical properties of poly(lactic acid)/starch composites compatibilized by maleic anhydride. *Biomacromolecules* 5(4):1446–1451
202. Zhang X, Huang J, Chang PR, Li J, Chen Y, Wang D, Yu J, Chen J (2010) Structure and properties of polysaccharide nanocrystal-doped supramolecular hydrogels based on cyclodextrin inclusion. *Polymer* 51(19):4398–4407
203. Zhao JQ, He X, Wang YR, Zhang W, Zhang XX, Zhang XD, Deng YL, Lu CH (2014) Reinforcement of all-cellulose nanocomposite films using native cellulose nanofibrils. *Carbohydr Polym* 104:143–150
204. Zhao R, Torley P, Halley PJ (2008) Emerging biodegradable materials: starch- and protein-based bio-nanocomposites. *J Mater Sci* 43(9):3058–3071
205. Zheng S, Shin JY, Song SY, Yu SJ, Suh H, Kim I (2014) Hexafunctional poly(propylene glycol) based hydrogels for the removal of heavy metal ions. *J Appl Polym Sci* 131(16):1987–1996

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