Chapter 8

Surface Modification of Biobased Polysaccharide Nanoparticles via Grafting

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1 Introduction

Since the work of H. Staudinger in 1922 [1], no one can question the added value of macromolecular science on new manufacturing objects. In the same way, in the last few decades, nanocomposites have become an essential sector of polymer science. Indeed, particles 80,000 thinner than a human hair can be a very interesting alternative for achieving not only mechanical properties but also optical, thermal, gas barrier, and flame retardancy properties of polymers. In the earlier stages, it was mainly the so-called "hard" nanomaterials such as carbon or clays that have been used across

Green Micro- and Nanocomposites
Edited by Sabu Thomas, Abitha V. K., and Hanna J. Maria

ISBN 000-000-0000-00-0 (Hardcover), 000-000-0000-00-0 (eBook)
www.jennystanford.com

many different applications with more or less success [2]. In another stream of activities, always driven by health and environmental concerns, biodegradable crystalline nanoparticles from renewable resources have attracted significant interest from the scientific community. In this framework, carbohydrate-based (polysaccharide) nanofillers have gained increased interest as part of an effort to avoid nanotoxicity and overcome environmental concerns [3].

The family of polysaccharides is characterized by a common morphology composed of alternating crystalline and amorphous zones. These last are highly susceptible to hydrolysis under defined conditions, with their removal leaving the crystalline regions intact in the form of remarkable nanoparticles – polysaccharide nanocrystals [4]. Whether from an environmental point of view or for specific applications, polysaccharide nanocrystals offer multiple promising opportunities [4], in particular, in drug delivery systems [5], nanoencapsulation [6], or as reinforcing agents in polymer matrices [7–12]. With regard to the potential of these natural, available, and low-cost raw materials, the thinking around new application fields will contribute to a greener and more sustainable technology development. Thorough bibliographic studies mainly point to cellulose nanocrystals, as they are characterized by high structural stability under chemical modification in comparison with chitin or starch nanocrystals. However, chitin nanowhiskers and starch nanoplatelets also deserve full attention for promoting specific applications based on their unique properties. Nowadays, industrial opportunities for natural polysaccharide nanocrystals are under development around the world. As an example, industrial production of nanocelluloses is promoted by an increasing number of countries supporting their valorization. Here, the construction of multiton capacity manufacturing facilities in North America, Japan, and Europe can be cited [4, 13–16].

Despite all benefits, the applicability of the polysaccharide nanoparticles faces significant difficulties resulting from their inherent hydrophilicity – the basis for incompatibility and bad dispersibility within most polymer matrixes (hydrophobic in character). In order to avoid these limitations, after appropriate conversion and extraction technologies, and suitable modification, polysaccharide nanocrystals might find a place in numerous biobased products. Initially, the development of polysaccharide-

reinforced nanocomposites was mainly restricted to hydrophilic media as these nanocharges possess inherent hydrophilicity and aggregate in hydrophobic media. However, their surface modification (mostly chemical) overcomes this limitation and has been largely applied in broadening the number of suitable polymeric matrices with processing from organic dispersions or melts instead of aqueous suspensions. In this light, promising developments in the design process of nanocelluloses allow to focus on research on all polysaccharide nanocrystals, including chitin and starch, with particular attention on their surface modification for better compatibilization with biobased materials.

Amongst all methods, surface grafting of polymer chains is a promising and attractive new process by which polysaccharide nanoparticles are transformed into apolar hybrid nanoparticles. The procedure is readily intriguing as fully biobased composites can be processed by classical methods such as extrusion, compression or injection molding, or thermoforming [17].

A lot of interesting and progressive work has been performed in this respect, thus paving the road for the forthcoming chapter that spans the surface modification of biobased polysaccharide nanoparticles via grafting.

8.2 Surface Grafting

In terms of chemistry, grafting is an often-used modification method through which polymers are introduced to a surface [18]. It allows for modulation of surface properties in terms of hydrophilicity/hydrophobicity, dimension stability, resistance to heat, abrasion and/or chemicals, biological activity or electrical properties, and functionality [18]. Depending on how polymers are introduced, three major types of grafting can be defined: 1) grafting from, 2) grafting onto, and 3) grafting through (Fig. 8.1). However, grafting can also be performed via a non-covalent approach – the so-called supramolecular grafting (Fig. 8.1d). This new and yet not much explored trend uses softer conditions and prevents surface integrity and functionality. The following parts discuss the different grafting approaches in terms of requirements and applicability to solid surfaces.

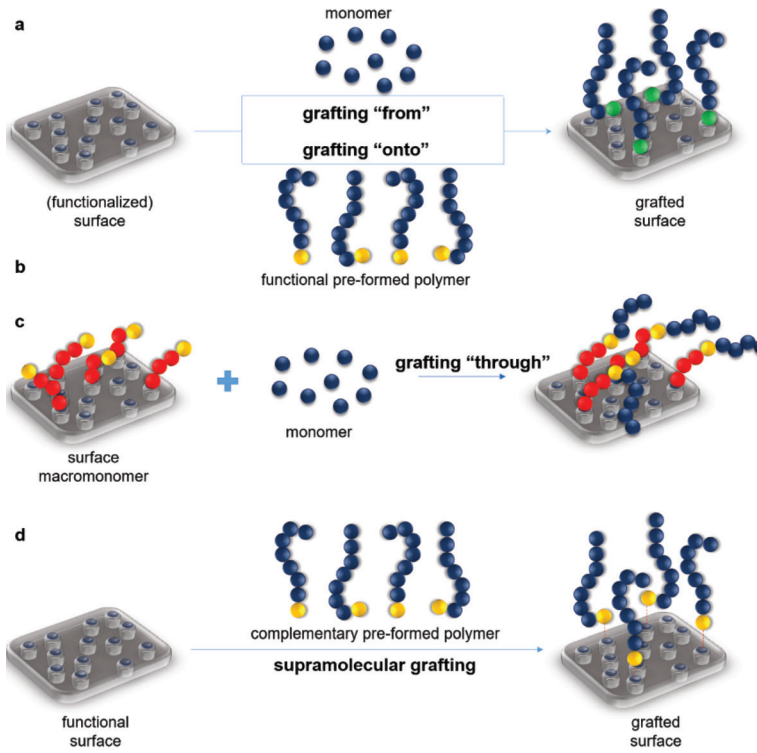


Figure 8.1 Schematic representation of the grafting methods used for introducing polymer chains to a surface.

8.2.1 Grafting from

The *grafting from* approach includes the *in situ* building up of a polymer layer by surface-initiated polymerization of monomer units (Fig. 8.1a). For this, an appropriate initiator (initiating sites) is first introduced on the surface to be grafted via external field (plasma, UV irradiation, ozone treatment) or reactive species introduction (chemical modification) [19]. Intriguingly, in some cases, the initiating sites are naturally available on the surface via the presence of reactive groups (e.g., OH-groups on cellulose substrates). A very attractive peculiarity here is the fact that the initiating sites are usually easy to access by the monomer molecules forming the chain ends of the covalently attached growing polymers. Thus high

grafting densities are achieved making this method very attractive from a scientific point of view [19].

Multiple polymerization methods such as surface-initiated free radical polymerization (SI-FRP), controlled radical polymerization (SI-CRP), and ring-opening polymerization (SI-ROP) have been elaborated in grafting *from* [20]. Like conventional FRP, the SI-FRP is a versatile chain-growth polymerization applicable to a large range of monomers, thus providing an unlimited number of (co)polymers [21]. The tolerance of this method to water or other impurities and functionalities (e.g., OH, OR, NH_2, NR_2, etc.), together with the mild and versatile (solution, emulsion, bulk, etc.) reaction conditions, makes the SI-FRP highly attractive. The method comprises all reaction steps of the conventional FRP (Fig. 8.2) and allows for obtaining a high grafting density due to the ease of contact between SI sites and monomers [18, 22, 23].

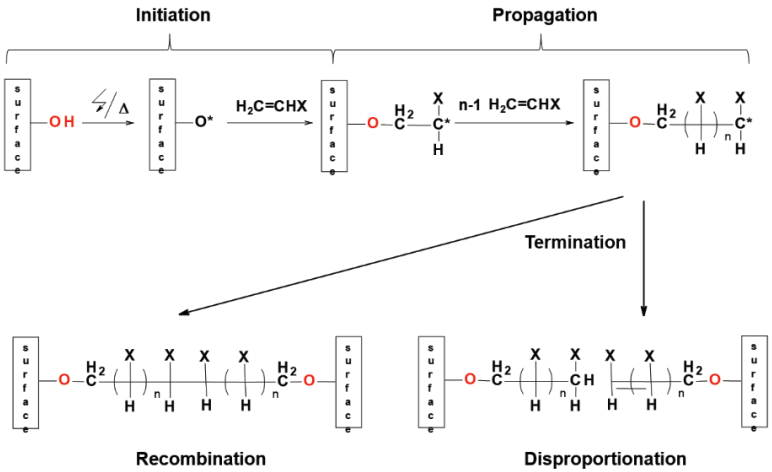


Figure 8.2 Schematic representation of the general FRP *grafting from* mechanism.

However, difficulties in the correct control or prediction of grafting density and resulting polymer chain length and architecture are often found. Moreover, the formation of free, unbound homopolymers is unavoidable. Therefore, other research groups introduced the SI-CRP techniques to the *grafting from* method [20].

Amongst all, the surface-initiated CRPs, nitroxide-mediated polymerization (NMP) [24], atom transfer radical polymerization (ATRP) [25–27], photoinduced Cu-mediated reversible-deactivation radical polymerization (RDRP) [22], and reversible addition–fragmentation chain transfer polymerization (RAFT) [28] received greatest attention [18]. Their principles (Fig. 8.3) are exhaustively discussed elsewhere [18, 20, 29] and therefore will only be recalled here. The NMP belongs to the family of stable RPs and involves a stable nitroxide radical (X^*) [30]. Here, the active propagating species (P_n^*) react with X^*, deactivate, and reversibly form dormant species (P_n–X). Once P_n^* reforms, it re-propagates by adding another monomer (M) or terminates the chain growth by recombination (Fig. 8.3A). NMP is usually performed under relatively high (> 100 °C) temperatures and is applicable to acrylate-type monomers. However, its application in methacrylates/methacrylamides requires specially designed stable radicals.

In a reversed way, ATRP starts with an alkyl halide (P_n-X) that undergoes a reversible redox process catalyzed by a transition metal complex (activator, Me^z-Y/ligand, where Y may differ from the ligand or be a counter ion) and forms the P_n^* and a metal halide complex ($X\cdots Me^{z+1}$–Y/L) [31]. The P_n^* reacts with a monomer and propagates or abstracts a halide atom from $X\cdots Me^{z+1}$–Y/L and reforms dormant species. The alkyl halide species is then reactivated by the activator and propagate further (Fig. 8.3B). ATRP is easily applicable to most of the vinyl and acrylic monomers over a wide temperature range and is known to be tolerant (to a certain extent) to oxygen and other inhibitors. Nevertheless, the reaction uses unconventional initiation systems that may suffer from poor solubility in the polymerization media. Additionally, the transition metal residues color and induce certain toxicity to the obtained polymers.

RAFT is the polymerization method of choice when grafting of vinyl and acrylic monomers is desired [18]. This polymerization is similar to the conventional RPs when performed in presence of a chain transfer agent (‘‘RAFT agent’’ – a thiocarbonyl thio compound). It results in polymers of narrow dispersities and of controlled chain lengths (Fig. 8.3C). The problem that one can relate to the coloration of the resulting product by the thiocarbonyl thiol end-group is easily solved by reduction, thermolysis, aminolysis, exposure to ultraviolet radiation, and treatment with peroxides or sodium hypochlorite.

Thus, it seems the RAFT process is the method of choice for grafting from cellulose.

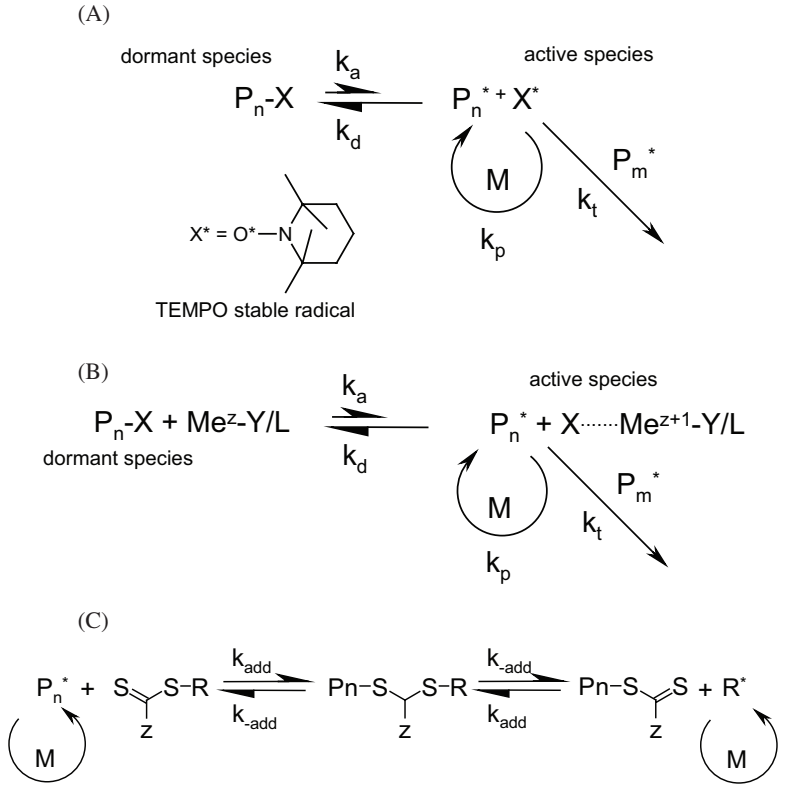


Figure 8.3 Schematic representation of the accepted mechanisms for NMP (A, [30]), ATRP (B, [31]), and RAFT (C, [18]).

However, these methods are not applicable in the case of cyclic monomers (lactones and lactides), where ROP is commonly used. This well-established technique relies upon alcohol (in general) initiation, which makes it suitable in cellulose or cellulose derivatives grafting from [32]. Depending on the monomer, initiator, and catalyst used, ROP operates through different mechanisms. For example, in the case of tin(II) 2-ethylhexanoate ($Sn(Oct)_2$) catalyzed ROP of monomers such as ε-caprolactone (ε-CL), lactide (LA), and p-dioxanone, the most commonly accepted mechanism is the "coordination-insertion" mechanism in which $Sn(Oct)_2$ converts to tin alkoxide (the actual initiator) by reaction with alcohols or other

protic compounds/impurities. The fine-tuning of the alcohol-to-monomer ratio allows better control over the molecular weight of the final polymer [32].

Nevertheless, none of the methods discussed here allows for overcoming the formation of non-grafted polymer chains or knowing their molecular characteristics. As a result, grafting onto is usually applied.

8.2.2 Grafting onto

In grafting onto (Fig. 8.1b), usually end-functionalized preformed polymer chains of known molecular characteristics (chemical structure, molecular weight, dispersity, morphology, etc.) are covalently attached to a (modified)hydroxyl groups of a substrate. Additionally, the grafting might be performed via the deactivation of living polymer chain ends by the surface functional groups, thus allowing attaching commercial polymers with a well-characterized structure, which makes the process very attractive for industrial applications [33]. For the method to be successful, it is necessary to apply efficient coupling chemistry such as 1) reactions between a living polymer chain end-group and a suitable group on the surface to be grafted [34, 35], 2) copper(I) catalyzed Huisgen 1,3-dipolar cycloaddition [36–38], 3) esterification and amidation [39–43], 4) isocyanate chemistry [17, 44, 45], and 5) nucleophilic substitution [46, 47] (Fig. 8.4).

However, steric hindrance can prevent reaching the available reactive sites at the surface, thus unfavorably reducing the surface grafting density via the grafting onto the method. A method aiming on combining grafting onto and grafting from to overcome their inconvenience is the grafting through.

8.2.3 Grafting Through

The grafting through process (Fig. 8.1c) involves (co)polymerization of macromonomer(s) [18, 30]. For its purposes, the surface to be grafted is firstly functionalized with a polymerizable group (a vinyl group) able to participate in polymerization as a macro-monomer (Fig. 8.5) [49]. As a particularity of the method, there is no relation between the amount of nanoparticles and initiator concentration.

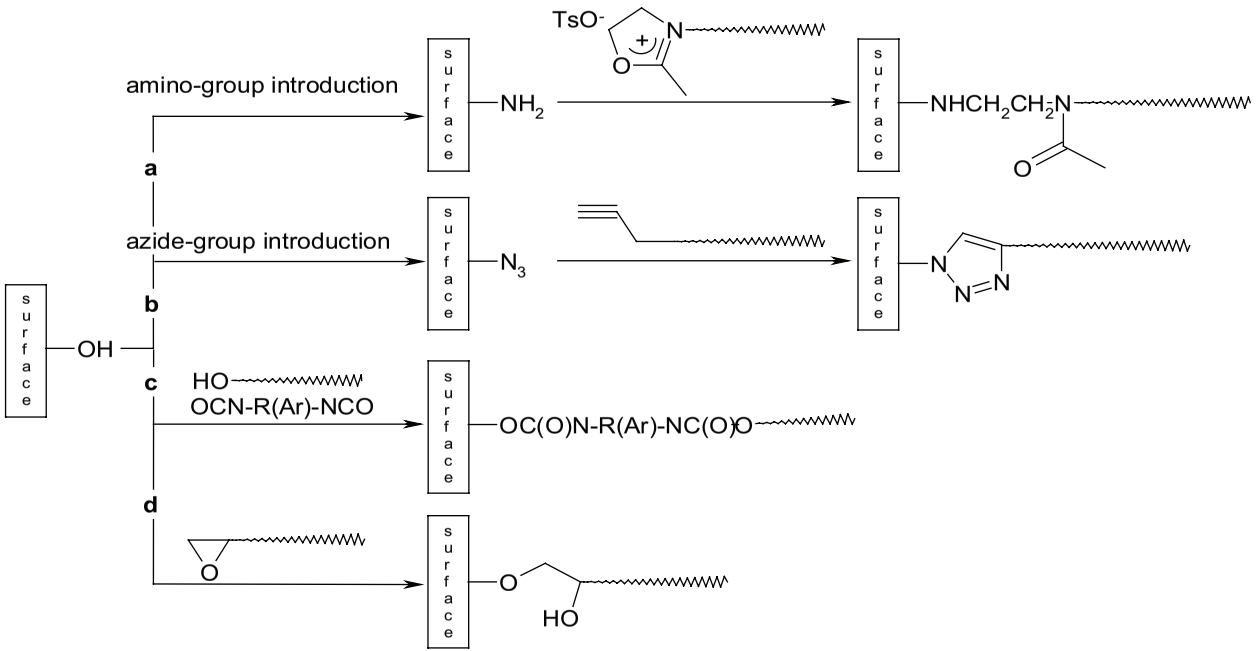


Figure 8.4 Grafting *onto* nanosurfaces: a – reactions between a living polymer chain end-group and a suitable group [35], b – copper(I) catalyzed Huisgen 1,3-dipolar cycloaddition [48], c – isocyanate chemistry [38], and d – nucleophilic substitution [46].

The grafting through technique overcomes the growth of long chains and promotes this of shorter chains. This is achieved by reversing the monomer concentration gradient in the grafting-from, where the monomer concentration is lowest at the substrate and highest in the surrounding solution.

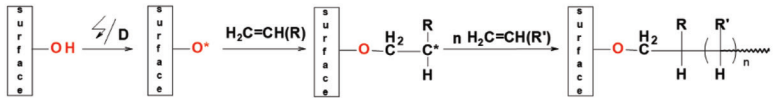


Figure 8.5 Grafting through CNC macromonomers.

However, the grafting through is yet scarcely applied due to the following reasons:

(1) Limited availability of polysaccharide macromonomers
(2) The possible interreference of the surface chemical modification for introducing suitable functionalities with polysaccharide nanocrystal (PSNC) integrity, crystallinity, and other surface properties [18]
(3) Possibility to cross-link the system via recombination of growing chains with two or more propagating sites on macromonomers [50]

Thus, further research must be done for taking advantage of the grafting through approach, or, alternatively, supramolecular grafting can be used.

8.2.4 Supramolecular Grafting

Supramolecular chemistry is non-covalent chemistry employing hydrogen bonding, metal coordination, hydrophobic forces, van der Waals forces, pi-pi interactions, and electrostatic effects in molecular self-assembly, folding, and recognition, host-guest chemistry, mechanically interlocked molecular architectures, and dynamic chemistry [51]. For several years, the method has been an alternative of choice for the surface modification of nanoparticles mainly because it involves milder and nondestructive conditions for surface functionalization/modification/grafting and thereby preserves structure, properties, and straightforwardness of nanoparticles [52]. When supramolecular chemistry is used for surface grafting, the so-called supramolecular grafting, preformed polymer chains of known

molecular characteristics and having special functionalities along their backbones react with the available functional groups of the surface to be modified in a mild and complementary nondestructive manner (Figs 8.1d and 8.6). Thus, the problems related to grafting from technique are avoided. Besides, the possibility to design and incorporate suitable functionalities along the preformed polymer chains overcomes the need for surface functional group modification.

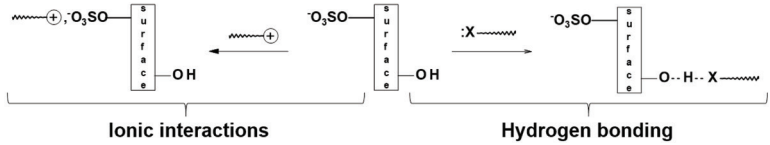


Figure 8.6 Chemistry of some supramolecular interactions.

Multiple examples of the application of these grafting techniques to polysaccharide nanoparticles (cellulose, starch, and chitin) will be given below, but prior to this, the next section discusses the particular base for their applicability.

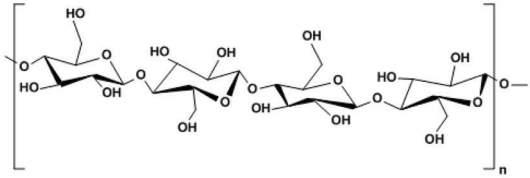
8.3 Polysaccharide Nanoparticles

8.3.1 Raw Material

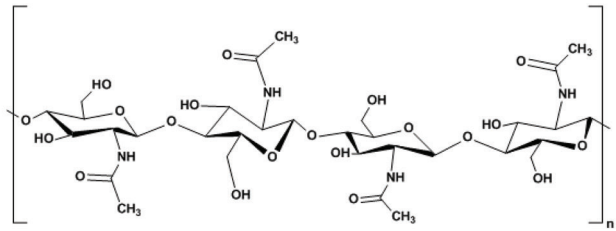
Polysaccharides nanocrystals can be "extracted" from raw materials such as cellulose and chitin (the most abundant polymers on Earth) or from starch (the major energy reserve of higher plants) and offer molecular and biological advantages for their use in the preparation of nanocomposites.

Cellulose is extracted from the cell walls of plants, from algae, tunicates, and bacteria [53, 54]. The exoskeleton of crustaceans, shellfish, and insects is the principal source of chitin [55] and starch can be found in seeds such as wheat, corn, or rice or in tubers such as potatoes [7, 56–58]. The chemistry of these polysaccharides varies from linear β–(1→4)-linked D-glucose residues (cellulose, Fig. 8.7A) to linear N-acetyl-D-glucosamine units linked through β–(1→4)-glycosidic linkage (chitin, Fig. 8.7B); or a mixture of amylose, a linear or slightly branched (1→4)-α-D-glucan, and amylopectin, a highly branched macromolecule consisting of (1→4)-α-D-glucan

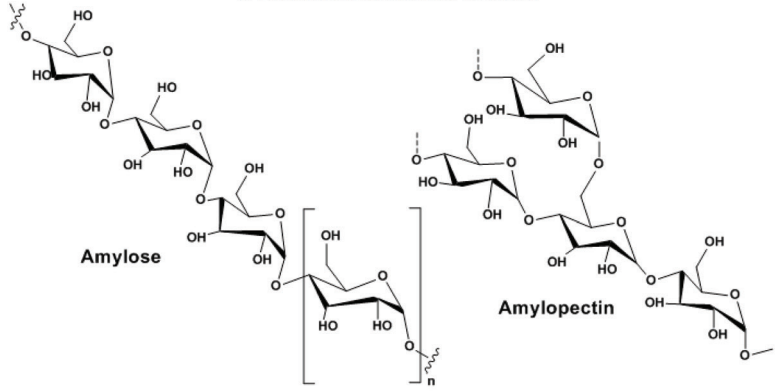
short chains linked through α-(1→6) linkages (starch, Fig. 8.7C). These carbohydrates are widely used in food (starch), clothing (cotton), communication (paper), packaging (paper and board), and construction (wood) and have always been a fundamental part of both industrial and academic R&D [59]. Furthermore, due to the depletion of fossil resources, climate changes, and toxicity impacts, polysaccharides remain pivotal options for the future of biobased materials. Currently, interest in polysaccharides has shifted toward nanoscale materials.



A : Chemical structures of cellulose



B : Chemical structures of chitin



C : Chemical structures of starch

Figure 8.7 Chemical structures of polysaccharides.

However, the greatest obstacles to their expansion are (i) the low thermal stability of polysaccharide nanocrystals to consider melt processing and (ii) poor compatibility with a number of polymer matrices. In this framework, surface modification of polysaccharide nanocrystals appears to be a powerful strategy to meet these challenges.

8.3.2 Preparation

8.3.2.1 Nanocellulose

Over the past several decades, there has been extensive research in nanocellulose. Nickerson and Habrle first reported an efficient procedure to prepare nanocellulose from cotton linters [60]. In 2011, the Technical Association of the Pulp and Paper Industry (TAPPI) confronted with numerous studies about cellulose nanocrystals and considered it appropriate to bring together experts to release a harmonized nomenclature about nanocellulose materials [61]. Based on their recommendations, several reviews and books described the methods for extracting different cellulose nano-objects, such as cellulose nanofibrils (CNFs) and cellulose nanocrystals (CNCs) [4, 12, 13, 54, 62–65] from plants (e.g., cotton [66], hemp [67], wood [68]), marine animals (e.g., tunicates [69]), algae (e.g., *Valonia* [70]*),* bacteria (e.g., *Acetobacter xylinum* [71]), and even amoeba (*Dictyostelium discoideum* [72]) to fabricate a wide range of functional materials such as reinforcing filler [54] as well as photonic crystal [73], barrier film [74], shape-polymer polymers [75], light-healable [76], drug-delivery [77] and mechanically adaptive nanocomposites [78]. There is a significant difference to be understood between CNF and CNC, although one is coming from the other. CNFs are bulky products of nanocellulose production with a large surface area and aspect ratio: diameters ranging from 20 to 60 nm and lengths of several microns. They are usually the finest result of the mechanical treatment stage, without any acid contact. While the terms microfibril, nanofibril, nanofiber, and elementary fibrils are usually used as synonyms for CNFs, they must be avoided in describing CNC – the finest product of acid hydrolysis of CNF amorphous regions. In contrast to CNFs, CNCs are rodlike particles of low aspect ratio and an elastic modulus of about 140 GPa [13, 79].

As the methods for nanocellulose production are well described in numerous studies, reviews, and chapters, they will not be discussed here. However, Fig. 8.8 summarizes cellulose fiber treatments for extracting both CNFs and CNCs, and some additional explanations are given below.

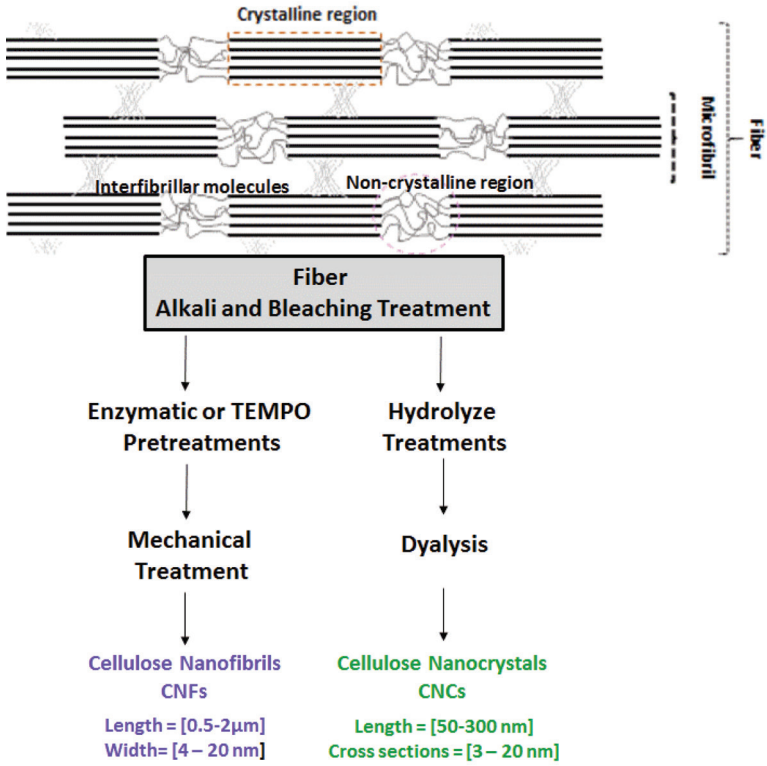


Figure 8.8 Schematic representation of the extraction procedures for both CNFs and CNCs from cellulose.

With respect to cellulose nanofibrils (CNFs), scaling-up production and reduction of energy consumption forced researchers to set up a global procedure including chemical or enzymatic pretreatments before a mechanical treatment and high-pressure homogenization process [13, 53, 54, 80–82]. Regarding the procedure to extract cellulose nanocrystal (CNCs), ideally the amorphous regions are hydrolyzed and the remaining crystals will be nanometer size [13]. Actually, the shape of CNCs is strongly dependent on acid hydrolysis

conditions. Composed of β–(1→4)-linked D-glucose units, linear polymer chains are arranged in highly crystalline cellulose I (native cellulose). The typical methodology for CNC extraction involves strong-acid hydrolysis under well controlled conditions (temperature, stirring, and time) of purified cellulose. Depending on the source and parameters of the hydrolyze, the author's product ranges from 50 to 300 nm in length and cross sections of 3–20 nm [4, 12, 13, 53, 62]. A comparative and thorough reading of the literature makes it possible to show that the structure, properties, and behavior of the CNCs are strongly dependent on their source and the extraction method [4, 13, 62]. Additionally, the production (as integrated forest biorefinery [80]) changed scale, forcing the users to adequately characterize nanofillers prior to any use. The real question, nowadays, is whether production scale, starting material, or purification affects nanocellulose behavior. A recent publication by Reid et al. [16] proposes an interesting benchmarking of CNCs from laboratory to industrial production. Overall, sulfuric acid extracted CNCs compare well with CNCs produced at the laboratory scale with the final product being highly crystalline, high aspect ratio "nano-only" CNCs. However, differences in sulfate half ester content, colloidal stability, crystallinity, and morphology are clearly observable. It is established that the community needs to have industrially produced nanocelluloses to continue to develop nanocellulose research. These results must just us to lead to set up proper characterization to forecast nanocellulose behaviors [16].

8.3.2.2 Nanochitin

The fully acetylated version of chitin is insoluble in water and in most organic solvents due to the strong hydrogen bonding between the acetyl group. In this light, chitin is challenging to work, and it is difficult to maintain the chitin nanofiber structure during processing. Chitin exists in three polymorphs α, β and γ that differ in orientation and packing of the chitin molecular chains. The most abundant is the α-chitin (*from* crab and shrimp shells). There, the polymer chains align in an antiparallel arrangement that favors strong intermolecular hydrogen bonds. In contrast, the β-chitin (*from* squid pens) polymer chains pack in parallel, what weaker intermolecular interactions. The γ-chitin structure is a mixture of the α- and β-forms [55]. A very recent publication investigating

engineering strategies for chitin nanofibers (ChNF) allows to review all previously developed syntheses by both "top-down" and "bottom-up" routes [83]. So far, the top-down approach, consisting of breaking the native chitin microfibril to individual building blocks of interest, has been preferred in order to prevent the difficulties of dissolution at the molecular level. In this approach, pure chitin is first isolated upon demineralization and deproteinization using acid and alkali treatment. Then, the resulting mass is strongly mechanically disintegrated to chitin nanofiber dispersion with range diameters of 10–20 nm [83–87]. Wu et al. proposed an easier route to successfully extract ChNF from crab α-chitin by a milder high-pressure homogenization process under acidic conditions [88]. The synergistic effect between high-pressure homogenization and cationization of chitin was also found to disintegrate effectively the large chitin fibers to give nanofibers of an average diameter of 20 nm [88]. Other 'top-down' approaches are mediated oxidation with strong acid hydrolysis, intensive mechanical disintegration, and 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO), which led to ChNF with an average width of 8 nm [83, 89] or a chemical-etching-free approach to disintegrate chitin using calcium ions and solvent exchange [90]. In parallel, the bottom-up approach involves dissolving chitin fibers before reassembling into chitin nanofibers. Some microfibers have been prepared using electrospinning after dissolution into 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) with an average diameter of 160 nm. A pretreatment with ionic liquids allows dissolving chitin before electrospinning for making thinner microfibers (i.e., average diameter between 30 and 80 μm). Zhang and Rolandi proposed a different route of self-assembling chitin nanofibers from squid pen β-chitin previously dissolved into HFIP or LiCl/*N*,*N*-dimethylacetamide (DMAC) with electrospinning free step [83]. Promising chitin nanofibers with a diameter of 3 nm have been obtained.

The procedures for obtaining chitin nanocrystals (ChNCs) are obviously very similar to the one for CNCs [91] and will not be a subject of this review.

8.3.2.3 Nanostarch

Introduced by Le Corre et al. [7], Lin et al. [4, 57], or, more recently, Kim et al. [92, 93], the main method to obtain starch nanocrystals

relies again on the disruption of the amorphous and paracrystalline domains of semicrystalline starch granules via acid hydrolysis. The optimization of the process is studied by varying diverse parameters including the acid used or the botanic origin of the native starch [94, 95]. However, the first studies of Le Corre et al. [7], Lin et al. [57], or, more recently, Kim et al. [93] are the basis of a global review on the preparation of starch nanocrystals with lengths ranging 20–150 nm with possible crystallinity preservation. In parallel, starch nanoparticles were prepared from gelatinized starch using numerous physical treatments including extrusion [96], high-pressure homogenization and emulsification [56, 97], ionic liquid medium [98–100], solvent displacement method [58, 93, 101], or ultrasonication [102] with promising results for industrial applications [93].

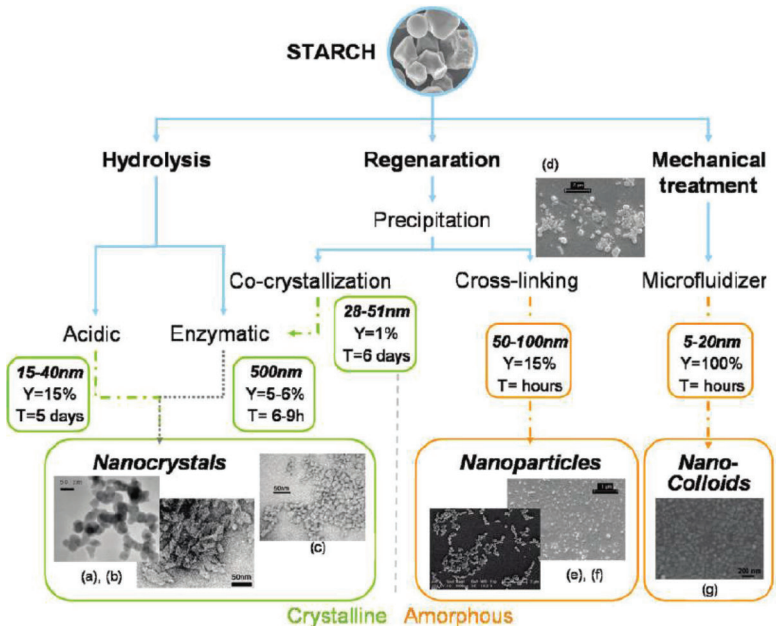


Figure 8.9 Different ways of producing crystalline and amorphous starch nanoparticles: hydrolysis leads to nanocrystals, whereas regeneration and mechanical treatment lead to both amorphous and crystalline particles in the final batch. Adapted with permissions from Ref. [7]. Copyright 2019 American Chemical Society.

For example, Song et al. investigated the mechanism of starch nanoparticle formation during extrusion. They show that an appropriate use of a cross-linker at 75°C facilitates the reduction of particle size to around 160 nm [96]. However, as expected, mechanical damages are caused by the longtime of melt blending under high shear. On the other side, with the high-pressure homogenization technique, Liu et al. developed an alternative sustainable approach to reducing the size of SNPs. This method uses a microfluidizer to manipulate the continuous flow of liquid through microchannels [93]. Based on specific experimental parameters (starch slurry, passes, high pressure), the decrease of starch granules particle size from a few micrometers to a few nanometers. However, experimental conditions must be optimized for better preservation of the crystalline structure and improving the recovery yield [97]. The nanoprecipitation process is also a promising anti-solvent method to extract SNPs. This method consists of the deposition of polymers using a semipolar solvent miscible with water from a hydrophobic solution [92]. Here, the successive addition of a diluted starch solution to a non-solvent leads to the precipitation of nanostarch [58]. In this respect, the nanoprecipitation method, initially reported by Qin et al., allows to obtain differential structural and morphological properties of SNPs using several native starches with various amylose content and different types of crystalline structures. Authors conclude that the obtained SNPs display a typical V-crystalline structure (i.e., nanoplatelet-like) with particle sizes ranging from 20 to 225 nm depending on native starch granules.

8.3.3 Physicochemical Properties

Physicochemical properties of polysaccharides nanocrystals have been outlined clearly by Lin et al. [4]. In the framework of this chapter, Table 8.1 proposes a comparative presentation of the main differences between cellulose, chitin, and starch nanoparticles. In general, the morphology and geometrical dimensions of polysaccharide nanocrystals are related to the starch origins and extracting method. More specifically, common cellulose nanocrystals with rodlike morphology derived from cotton, flax, ramie, sisal, and so on are characterized by a length range of 100–700 nm and diameter 5–30 nm, while animal tunicate presents a considerable

aspect ratio of about 100 and bacterial cellulose gives L and D of 100 to several mm and from 5 to 50 nm, respectively [91]. Dimensions of chitin nanowhiskers extracted from shrimp shell, crab shell, or squid pen were found to be close to those reported for cotton whiskers, while for Riftia tubes ChNC, the average L was around 2.2 mm and the aspect ratio was 120 [4]. As for the platelet-like starch nanocrystals, they are generally derived from crops, such as pea, potato, corn, and waxy maize L is between 20 and 100 nm, W - around 25–30 nm, and T - 6–8 nm [4].

Table 8.1 Physical characteristics of polysaccharide nanocrystals

NC	Morphology	Stiffness, GPa	Crystallinity, %	T_m, °C	OH content, mol/g
CNC	Rodlike [54] Spherical [103]	120–170 [104]	54–88 [63]	200–300 [105]	0.0038 [4]
ChNC	Rodlike [106] Whiskers [107]	150 [108]	>80 [109]		
SNP	Platelet-like [110]		40–50 [4]	250 [4]	0.0025 [4]

The small dimensions cause some difficulties in manipulating individual nanocrystals, and direct measurement of their stiffness is not easy. However, some data are reported from theoretical calculations, XRD analyses, or Raman spectra, well summarized in Table 8.1 and in a recent review [4].

For what is to the degree of crystallinity, theoretically, it should be total, but the often-incomplete removal of the amorphous phase results in lower values. The classical values reported in the literature are within the range 54–88% [63] for CNCs, >80% for ChNCs [109], and 45–50% for SNPs [57] depending on the sources.

8.3.4 Chemical Properties

From a chemical point of view, polysaccharide nanocrystals are a challenging platform possessing reactive surface hydroxyl (and amino) groups, which allow the modification using chemical reactions (Fig. 8.7). In the last decades, numerous expert studies focused this possibility usually to ensure nanocrystals applications as

strengthening agents in composite materials or specific properties for novel nanomaterials [4]. More precisely, in the case of rodlike cellulose nanocrystals with very uniform geometrical dimensions, around 0.0038 mol/g of active hydroxyl groups on the surface of nanocrystals is calculated [4]. Using the same calculations, the amount of surface available OH-groups in SNP was estimated to be ca. 0.0025 mol/g of the total amount [111].

Another significant point is the difference in the activity of the hydroxyl groups. The methylene OH group in the C6 position, for example, is known to be more active than the other two hydroxyl groups (C2 and C3). Besides, the chemical modification initially occurs at the surface of the nanocrystals, inducing a superficial chemical reaction [4]. Consequently, the reactive activities of the hydroxyl groups on the surface of polysaccharide nanocrystals can be quantified with the experiments as well as their different orders or gradient chemical modifications can be controlled.

Special attention should, however, be paid to reaction time, as with increasing it, surface modification can propagate to the inner part of the crystallites and induce their erosion and, subsequently, the loss of crystallinity [4]. Accordingly, an effort must be focused on the preservation of the structure, morphology, and crystalline properties of nanocrystals even though the degree of substitution or grafting efficiency is enhanced.

Attention is also needed to the amount of sulfur groups on the surface of the particles. Indeed, sulfuric acid is used as the hydrolyzing agent and hydrolysis treatment leads to the introduction of negatively charged sulfur groups ($OSO3^-/H^+$) able to favorize homogeneous dispersion while keeping thermal stability due to the stabilization electrostatic of nanocrystals in water. [4]. In the meantime, the decrease of potential surface hydroxyl groups, because of the incomplete replacement by the surface acid groups, reduces the reactivity for chemical modification. The same issues concern reactions with the amine functional groups available on the surface of chitin nanocrystals.

8.3.5 Surface Modification of Biobased Polysaccharide Nanoparticles via Grafting

All biobased polymer composites (biocomposites) where both the polymer and the (nano)particles (nanofillers) are of (biodegradable)

renewable materials have received a tremendous interest over the last decades. Amongst all biofillers, polysaccharide nanocrystals including cellulose, starch, and chitin show superior properties as reinforcing reagents for biocomposites due to their biocompatibility, nontoxicity, and relatively low cost [112]. Unfortunately, hydrophilic nanocrystals self-aggregate easily, which leads to a low degree of dispersion and low efficiency of reinforcement in nanocomposites. Additionally, the hydroxyl groups on the surface of nanocrystals are immiscible with hydrophobic polymers as polyesters. To overcome this drawback, modification of the crystal surface is most commonly used, between all methods, via grafting techniques (Fig. 8.1). The applicability of each grafting method to all three types of polysaccharide nanoparticles will be discussed below.

8.3.5.1 The nanocellulose: nanocrystals and nanofibers

As already discussed in the previous section, nanocellulose is one of the most abundant and promising renewable nanomaterials for multiple applications that combines low thermal expansion, excellent mechanical properties, and high surface area with versatile modification capacity [113]. According to the Technical Association of the Pulp and Paper Industry (TAPPI), there are three forms of nanocellulose: cellulose microfibrils, cellulose nanofibrils, and cellulose nanocrystals, mainly based on variations in dimensions and flexibility [114]. A lot of research has been concentrated on the surface modification of these nanocelluloses and more particularly of the cellulose nanocrystals via grafting reactions. Most of the published papers are thoroughly summarized in several exhaustive reviews and books and therefore will not be discussed in detail here [12, 20, 29, 115]. Here, some new trends, mostly in relation to *supramolecular grafting*, will be discussed.

Nanocrystalline cellulose supramolecular interactions are well known and described in a multitude of studies [116]. However, supramolecular grafting is a new, softer, and nondestructive trend that in most cases does not need modification of the existing functional groups [52]. In the case of nanocelluloses, this grafting method was pioneered by the studies of Zhao et al. [117] who reported covalent modification of the cellulose microfibrils functional groups with cyclodextrins (CD) followed by *supramolecular grafting* of

adamantine-capped poly(ε-caprolactone) (PCL) oligomers via the host-guest inclusion complexation in DMF dispersion (Fig. 8.10).

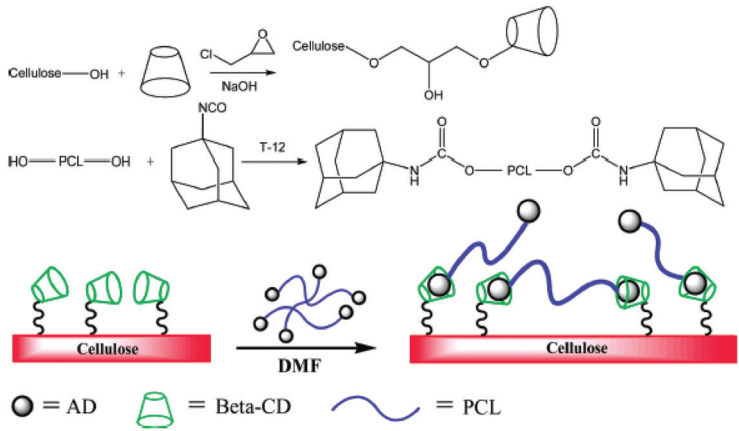


Figure 8.10 Synthesis pathway for the cellulose-CD and PCL-AD and the conceptual illustration for the assembly process of cellulose-CD with guest polymer PCL-AD (Reprinted with permission from [117]. Copyright 2017 American Chemical Society).

The successful assembly was confirmed by FTIR-ATR, XPS, and the increasing weight with CD concentration. Contact angle and TGA measurements reflected enhanced hydrophobicity and thermal stability of the cellulose fibers. Their morphological evaluations with SEM showed smooth surfaces exhibiting visible undulations along the axial direction, similarly to the pure cellulose before grafting [117]. Indeed, in this particular case, modification of cellulose functional groups prior to grafting was used but proved to be unnecessary by the following studies.

The supramolecular approach toward surface grafting of nanocelluloses was continued by the studies of Tatsumi et al. [118] in their attempts to synthesize novel composites comprising poly(2-hydroxyethyl methacrylate) (PHEMA) and cellulose nanocrystals (CNC) from CNC suspensions in aqueous 2-hydroxyethyl methacrylate (HEMA) monomer solution. The starting suspensions separated in isotropic upper and anisotropic bottom phases resulting after drying in transparent birefringent films of isotropic phase, embryonic non-separating mixture, and anisotropic phase, respectively. A fingerprint texture was found depending on the

phase formed and the corresponding presence/absence of liquid-crystalline organization (Fig. 8.11) [118].

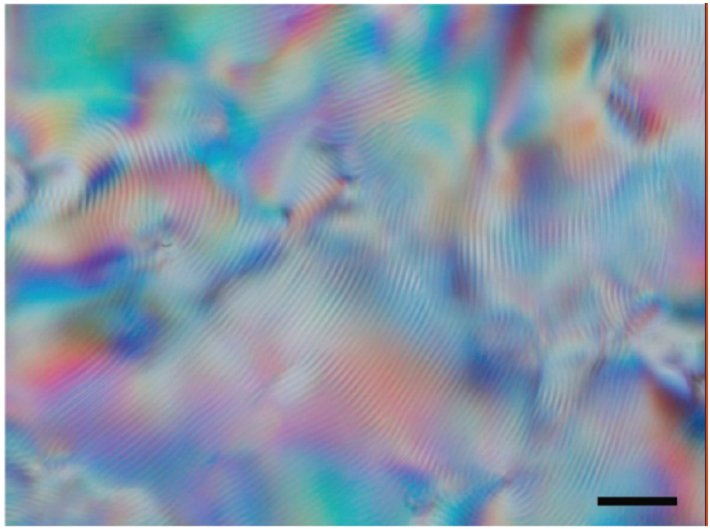


Figure 8.11 Polarized optical micrograph of the anisotropic phase of a 5.0 wt% CNC suspension in water/HEMA (0.46:1 in weight). The scale bar denotes 50 µm. (Reprinted with permission from [118]. Copyright 2017 American Chemical Society.)

The interest in such a stable cholesteric[1] liquid-crystalline phase was further exploited by several groups [36, 119–122] for the obtaining of cellulose-polymer iridescent[2] films. Ionic and nonfunctional polymers/monomers were used (Table 8.2).

The self-assembly of the CNCs into cholesteric phases is ascribed to their twisted (left-handed helicoidal) shape and anisotropic charge distribution [126] and the formation of ordered phases requires neutral, fully water-soluble polymers. Thus, the electrostatically driven self-assembly of the colloidal-scale CNCs will not be altered by changes in the CNC charge distribution or excessive CNC agglomeration [36, 120]. In a very interesting biomimicking approach, Malho et al. [123, 124] have designed cellulose binding proteins with a natural tendency toward multimer complex formation as an adhesive matrix for combinations with nanofibrillated cellulose. Their findings show

1 Chiral nematic

2 Changing color with illumination or observation angle

that the protein matrix affects the material mechanic properties mainly through interactions during plastic deformation and that the dynamic rearrangements lead to increased interactions between fibrils over higher length scales. Other studies, scarcely found in the literature, reveal that supramolecular grafting can also be used in the design of light-healable supramolecular nanocomposites, with significantly improved mechanical properties [47]. In this respect, Biyani et al. [125] developed nanocomposites based on a telechelic poly(ethylene-*co*-butylene) functionalized with ureidopyrimidone (UPy) and CNCs decorated with the same binding motif. Again, the nanocomposites show better mechanical properties. Moreover, when exposed to ultraviolet radiation, deliberately introduced defects are healed quickly and efficiently. This is because light-excited UPy motifs convert the absorbed energy into heat, thus causing temporary disengagement of the hydrogen-bonding motifs and concomitant reversible decrease of the supramolecular polymer molecular weight and viscosity. The results are valid even at a filler content of 20% w/w, that is, in compositions that exhibit high strength and stiffness.

Table 8.2 Nanocellulose use for (1) crustacean-like cholesteric iridescent films, (2) healable nanocomposites, and (3) adhesive matrices

Nanocellulose	Polymer/monomer	Application	Ref.
Microfibrils	PCL	1	[117]
	Protein	3	[123, 124]
Nanocrystals	PHEMA	1	[118]
	Poly(ethylene glycol)	1	[120]
	Anionic sodium poly(acrylate)	1	[120]
	Urea Formaldehyde	1	[121]
	Poly(vinyl alcohol)	1	[36, 119]
	Poly(oligoethylene glycol methacrylate-*co*-2-ureido-4-pyrimidone methacrylate)	1	[122]
	Telechelic poly(ethylene-*co*-butylene) functionalized with ureidopyrimidone (UPy)	2	[125]

Further studies are needed for a more precise understanding of the mechanisms behind this passionate supramolecular grafting of nanocellulose.

8.3.5.2 Starch nanoparticles

Insofar as SNPs are recovered and processed, nanocrystals are not only poorly dispersible in solvents generally used with polymers (due to reaggregation via strong hydrogen bonding), but also characterized by a very low thermal stability [7, 93, 128]. A negative SNP melting, specifically with water trace, has to be avoided during processing. In order to avoid it, the solvent casting method is often used to prepare SNPs/polymer composites. The interest in starch nanocrystals is related to their platelet-like structures suitable for possible improvement of barrier properties. However, to stimulate industrial-scale use, melt blend preparation has to be investigated [57]. For that, the surface modification of SNPs is required [128–131] to confer customized functions to expand the SNP applications. As CNCs and ChNCs, reactive hydroxyl groups are present on starch nanocrystals surfaces providing modifications by appropriate chemical reactions. However, the investigations of composite materials incorporating these particles are again relatively limited, that is, poly(styrene-*co*-butyl acrylate), natural rubber, pullulan, thermoplastic starch, polyvinyl alcohol, soy protein, or waterborne polyurethane [92] have been mixed up with SNPs. Four strategies have already been investigated in the literature [57]: (i) modification by chemical modification with small molecules, (ii) *grafting from* polymer chains with polymerization of a monomer (Fig. 8.1a), (iii) *grafting onto* polymer chains with coupling agents (Fig. 8.1b), and (iv) *supramolecular grafting* (Fig. 8.1d).

The feasibility of SNPs surface modification was first confirmed by Angellier et al. [95]. In this study, after sulfuric acid hydrolysis of native starch granules, SNPs obtained were superficially modified using two different reagents, that is, alkenyl succinic anhydride (ASA) and phenyl isocyanate (PI). After surface chemical treatment, the platelet-like geometric form of the PI-modified starch nanocrystals seemed preserved even though the size of the nano-objects was decreased (Fig. 8.12) [111]. The PI-modified starch nanocrystals dispersed well in methylene chloride solution, contrary to unmodified SNPs. Therefore, isocyanate functions modify the

polarity of nanostarch allowing to melt process composite materials using nonpolar polymers as matrices [111].

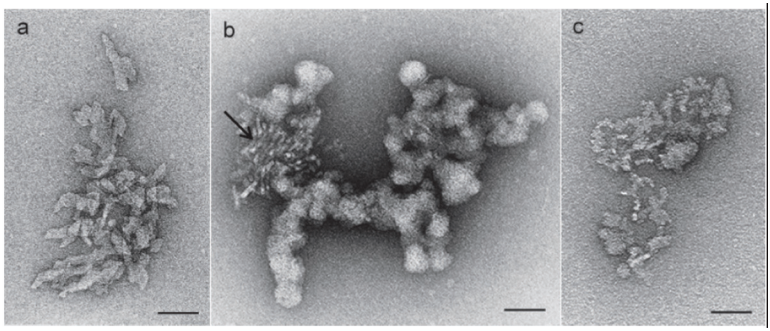


Figure 8.12 TEM micrographs of waxy maize starch nanocrystals (a) before and after chemical treatment with (b) alkenyl succinic anhydride (ASA) and (c) phenyl isocyanate (PI). Scale bar: 50 nm. Reprinted with permission from [111]. Copyright (2019) American Chemical Society.

The modification of SNPs with acetic anhydride also leads to promising results [57, 132]. With hydrophobic property and improved solubility in common organic solvents, the crystalline structure of acetylated starch nanocrystals was also changed from A-style to V-style. In addition, the platelet-like starch nanocrystals became sphere shaped after modification and the size increased from the original 20–40 nm to 63–271 nm. [57, 132]. However, surface chemical modification with small molecule attachment does not always provide miscibility between nanoparticles and polymers. In this regard, grafting methods are as usual exploited.

8.3.5.2.1 Grafting onto SNPs

Grafting onto SNPs was investigated with various preformed polymers using different coupling agents. The studies are exhaustively discussed by Lin *et al.* [57], concluding that SNPs surface modification needs mild conditions (temperature, pH) to preserve morphology integrity. Table 8.3 summarizes the conditions for the main *grafting onto* SNPs modifications including native starch source. In this case also, *grafting onto* suffers from drawbacks, that is, low reaction control and weak grafting, mainly to long-chain polymers. In a manner to overcome these drawbacks, the *grafting from* strategy was also investigated with SNPs.

Table 8.3 Surface modification of nanostarch via grafting

	Grafting technique			
Source	**Method**	**Variation**	**Modification**	**Reference**
Waxy Maize	Chemical reaction	–	PI	[111]
Corn	Chemical reaction	–	AA	[132]
Waxy Maize	Onto	2,4-TDI surface modification	PEGME	[131]
Waxy Maize	Onto	2,4-TDI surface modification	PTHF, PPGBE, PCL	[135]
Potato and Waxy Maize	Onto	Esterification	Aliphatic chloride	[136]
Pea	From	ROP	PCL	[133, 137]
Potato	From	ROP	PCL	[130]
Corn	From	FRP	PS	[134]
Waxy Maize	Supramolecular	ROP; ATRP	PDLA-*b*-PGMA	[138]

TDI: Toluene diisocyanate; **PI**: Phenyl isocyanate; **AA**: Acetic anhydride; **PEGME**: Poly(ethylene glycol) methyl ether; PPGBE: Poly(propylene glycol) monobutyl ether; **PTHF**: Poly(tetrahydrofuran); **PCL**: Poly(caprolactone); **PS**: Polystyrene; **PDLA-*co*-PGMA**: Poly(D-lactide)-*co*-poly(glycidyl methacrylate)

8.3.5.2.2 Grafting from SNPs

Both microwave-assisted and thermal ROP of caprolactone to PCL [129, 130, 133] have been studied, as well as the free radical polymerization (FRP) for polystyrene (PS) [134]. With *grafting from* strategy, a higher grafting density can be realized, and the properties of starch nanocrystals can be regulated through the selection and control of the grafting polymer chains length and type. The grafted SNPs were found to have improved compatibility with a PLA matrix. Grafting PCL polymer chains to starch nanocrystals using bulk polymerization was also successfully used [130] leading to crystalline structure and morphology of nanocrystals unaltered.

As an alternative to ROP, starch nanocrystals were modified by surface induced free radical polymerization of styrene. A starch

nanocrystal copolymer was prepared by graft copolymerization of starch nanocrystals with styrene [134]. After grafting the hydrophobic polystyrene chains, the modified starch nanocrystals became amphiphilic nanoparticles with SNP sizes increased from 50 nm nanoplatelet-like morphology to 80–100 nm spherical morphology. Table 8.3 summarizes the surface modification of nanostarch via grafting.

Some issues, however, are to be discussed in terms of morphology preservation during grafting and/or melt processing. In this respect, as a method proceeding in milder conditions, *supramolecular grafting* can be used.

8.3.5.2.3 Supramolecular grafting on SNPs

Fully biobased and biodegradable nanocomposites based on poly(L-lactide) (PLLA) and starch nanoplatelets (SNPs) were prepared by Benali et al. [138] using an original strategy involving supramolecular chemistry. To this end, poly(D-lactide)-*b*-poly(glycidyl methacrylate) (PDLA-*b*-PGMA) was first synthesized via the combination of ring-opening poly merization (ROP) and atom transfer radical polymerization (ATRP). NMR spectroscopy and SEC analysis confirmed an efficient control over the copolymer synthesis. The SNPs were then blended with the copolymer for producing a PDLA-*b*-PGMA/SNPs masterbatch. The solvent casting method was studied to improve the SNPs thermal resistance and their compatibility with the PLLA matrix. A masterbatch (PDLA-*b*-PGMA/SNPs) was obtained by solvent casting with specific attention to the solvent selection to preserve SNPs morphology. The copolymer-SNPs supramolecular interactions taking place with hydrogen bonding are highlighted using near-infrared (NIR) spectroscopy. Thereafter, the masterbatch was melt-blended with virgin PLLA and then a thin film of PLLA/PDLA-*b*-PGMA/SNPs nanocomposites was melt-processed by compression molding. The obtained nanocomposites films were by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Our findings allow us to conclude that supramolecular interactions, that is, stereocomplexation between the PLLA matrix and the PDLA block of the copolymer formed on one side and hydrogen bonding between SNPs and the PGMA block of the copolymer on the other side led to a synergetic effect with the

maintenance of SNPs nanoplatelets and their morphology during melt processing. Quartz crystal microbalance (QCM) highlighted a promising effect on PLLA barrier properties against water vapor.

8.3.5.3 Chitin nanoparticles

Chitin nanocrystals (extraction presented in Fig. 8.13 [139]) attract attention with their unique cationic structure [140]. Recently, they were used as reinforcing agents in different polymeric matrices, such as natural rubber [141] and polycaprolactone [142]. However, as with all other hydrophilic nanoparticles, nanochitin self-aggregates easily and is immiscible with hydrophobic polymer matrices. Several studies deal with surface modification of chitin nanoparticles to introduce small lipophilic molecules such as stearic acid chloride, alkenyl succinic anhydride, and phenyl isocyanate. They are summarized and well discussed in the review of Dufresne from 2010 [143] and will not be discussed here.

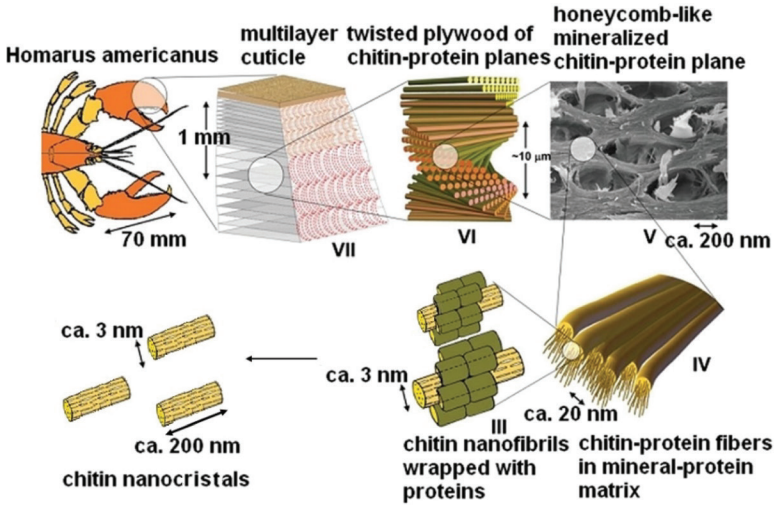


Figure 8.13 Schematic representation of chitin nanocrystals extraction. Adapted with permission from [139].

Besides, a number of scientific papers report on the surface modification of chitin nanoparticles via grafting of polymer chains (Table 8.4). *Grafting from* and *grafting onto* were successfully applied to surface modify chitin nanofibers and nanocrystals.

Table 8.4 Surface modification of nanochitin via grafting

		Grafting technique			
Nanochitin	**Source**	**Method**	**Variation**	**Polymer**	**Ref.**
Nanofibers	Crab shells	From	ROP	Poly(lactide-*co*-caprolactone)	[144]
	Unknown	From	FRP	Poly(acrylic acid)	[145]
Nanocrystals (whiskers)	Crab shells	From	ROP	Poly(caprolactone)	[142]
	Unknown	From	ROP	Poly(lactide)	[146, 147]
	Unknown	Onto	Esterification	Methoxy poly(ethylene glycol) acid	[148]
	Shrimp shells	Onto	Thionyl chloride activated esterification	Poly(hydroxybutyrate-*co*-hydroxyvalerate)	[149]

8.3.5.3.1 Grafting from nanochitin

Most of the related studies here take advantage of the fast and relatively easy *grafting from* technique (no steric hindrance and low viscosity of the reaction medium) for introducing hydrophilic and hydrophobic polymer chains. For example, Ifuku et al. [145] use the free-radical polymerization of acrylic acid (AA) with persulfate as an initiator in an aqueous medium to introduce poly(acrylic acid) (PAA) chains on the surface of chitin nanofibers (Fig. 8.14). Multiple analytical methods showed AA was grafted on the surface and in the amorphous part, thus preserving the original crystal structure of the chitin – preserved chitin nanofibers morphology after polymerization and with efficient dissociation and homogeneous dispersion due to electrostatic repulsion between the PAA-grafted nanofibers.

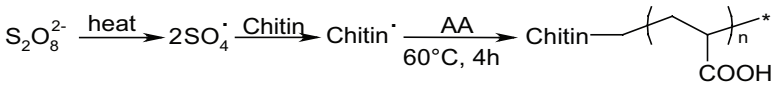


Figure 8.14 Free-radical graft polymerization of AA on chitin nanofibers.

Other groups tried ROP for polyester grafting on chitin nanofibers and whiskers [142, 144, 146, 147]. Thus, poly(lactide-

co-caprolactone) (P(LA-*co*-CL)), PCL, and PLA were successfully *introduced* in order to disperse nanochitin into a PLLA matrix [146, 147] or to directly form nanocomposites [142, 144]. In all cases, the initial structure of nanochitin was remarkably preserved and the tensile strength and elongation at break as well as the hydrophobicity of the nanocomposites were significantly improved.

However, the possible residues of non-grafted homopolymers as well as the undefined polymer chain characteristics still presented a disadvantage of the method. Therefore, the groups of Wang et al. [149] and Mol et al. [148] applied the *grafting onto* approach.

8.3.5.3.2 Grafting onto nanochitin

So far, there are only two studies dealing with the *grafting onto* nanochitin [148, 149], both using chitin whiskers as the starting material. The group of Wang et al. [149] obtained chemically modified chitin nanocrystals by grafting poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) (PHBV) onto chitin backbone via chlorination while preserving the amino group. Analyses revealed successful grafting and preserved whiskers structure but with a modified appearance. A large amount of white dots (suggested to be PHBV) surrounded the chitin and blurred the outlines of the nanocrystals, while the degree of aggregation seemed to be reduced [149]. As expected, contact angle measurement showed that improved hydrophobicity of chitin whiskers and also found to suppress PHBV crystallization.

In an attempt to enhance recyclability of acrylonitrile-butadiene-styrene (ABS) rubber, Mol et al. [148] derived chitin whiskers surface grafted with methoxy poly(ethylene glycol) (mPEG) of different molar masses. Indeed, nowadays recyclability of polymeric materials is a very important question and gathers growing attention from both universities and industry. The major problem with this reprocessing comes from the severe damage to the molecular architecture and microstructure of the polymer, which often results in poorer mechanical properties of the recycled material. A possible solution considers the incorporation of nanoparticles as reinforcing agents. In this case [148], the modified chitin whiskers were incorporated into reprocessed ABS (acrylonitrile–butadiene–styrene) to yield nanocomposites with 0.5% (mass/mass) whiskers. The results showed that high molar mass mPEG grafts increase the

strength, elongation at break, and stiffness of the reprocessed ABS over virgin, reprocessed ABS and reprocessed ABS/unmodified whiskers. This indicates that the use of surface-modified chitin whiskers can be valuable in improving the mechanical properties of recycled polymers and, consequently, enhancing their recyclability.

8.4 Conclusions

The current progress in surface modification of biobased polysaccharide nanoparticles, for example, nanocelluloses, starch, and chitin nanoparticles via grafting techniques, was carefully examined. Description about the different methods, for example, *grafting from*, *grafting onto*, *grafting through*, and *supramolecular grafting*, is provided in the first section. Further, the current state of the art in polysaccharide particle preparation and physical and chemical properties was renewed, including very recent trends and strategies. The final section thoroughly discussed the latest methods and achievements toward surface-modified nanocelluloses, nanochitin, and nanostarch particles via *grafting from*, *grafting onto* and most importantly *supramolecular grafting*. Thus, this chapter summarizes the most recent trends in the field of functional nanomaterials from bioderived polysaccharide nanoparticles.

List of Abbreviations

AA	Acrylic acid
AcA	Acetic anhydride
AD	Adamantane
ASA	Alkenyl succinic anhydride
ATRP	Atom transfer radical polymerization
CD	Cyclodextrins
ChNCs	Chitin nanocrystals
ChNFs	Chitin nanofibers
CNCs	Cellulose nanocrystals
CNFs	Cellulose nanofibrils
DMAC	*N*,*N*-Dimethylacetamide
DMF	Dimethylformamide
DSC	Differential scanning calorimetry

FRP	Free radical polymerization
FTIR-ATR	Fourier-transform infrared attenuated total reflectance spectroscopy
HEMA	2-Hydroxyethyl methacrylate
HFIP	1,1,1,3,3,3-Hexafluoro-2-propanol
k_a	Activation constant
k_{add}	Addition constant
k_{-add}	Dissociation constant
k_d	Deactivation constant
LA	Lactide
LiCl	Lithium chloride
Me^z-Y/L	Transition metal complex (activator, where Y may be another differ from the ligand (L) or be a counter ion)
NIR	Near-infrared spectroscopy
NMP	Nitroxide-mediated polymerization
NMR	Nuclear magnetic resonance spectroscopy
NO*	Stable nitroxide radical
PAA	Poly(acrylic acid)
PCL	Poly(ε-caprolactone)
PDLA	Poly(D-lactide)
PDLA-*co*-PGMA	Poly(D-lactide)-*co*-poly(glycidyl methacrylate)
PEGME	Poly(ethylene glycol) methyl ether
PHEMA	Poly(2-hydroxyethyl methacrylate)
PI	Phenyl isocyanate
PLA	Polylactide
PLLA	Poly(L-lactide)
Pn*	Active propagating species
Pn-X	Dormant alkyl halide species
Pn–X	Dormant species
PPGBE	Poly(propylene glycol) monobutyl ether
PS	Polystyrene
PSNC	Polysaccharide nanocrystal
PTHF	Poly(tetrahydrofuran)
QCM	Quartz crystal microbalance
RAFT	Reversible addition–fragmentation chain transfer polymerization
RDRP	Reversible-deactivation radical polymerization
SEC	Size-exclusion chromatography

SEM	Scanning electron microscopy
SI	Surface initiated
SI-CRP	Surface-initiated controlled radical polymerization
SI-FRP	Surface-initiated free radical polymerization
SI-ROP	Surface-initiated ring-opening polymerization
$Sn(Oct)_2$	Tin(II) 2-ethylhexanoate
SNPs	Starch nanocrystals
TAPPI	The Technical Association of the Pulp and Paper Industry
TDI	Toluene diisocyanate
TEMPO	2,2,6,6-Tetramethylpiperidine-1-oxyl
TGA	Thermogravimetric analysis
UPy	Ureidopyrimidone
$X^{\cdots}Me^{z+1}$–Y/L	Metal halide complex
XPS	X-ray photoelectron spectroscopy
ε-CL	ε-Caprolactone

References

1. R. Mülhaupt, Hermann Staudinger and the origin of macromolecular chemistry, *Angew. Chemie Int. Ed*. 43 (2004) 1054–1063. doi:10.1002/anie.200330070.
2. S.K. Kumar, B.C. Benicewicz, R.A. Vaia, K.I. Winey, *50th Anniversary Perspective* : Are Polymer Nanocomposites Practical for Applications? *Macromolecules* (2017) acs.macromol.6b02330. doi:10.1021/acs.macromol.6b02330.
3. Y. Zheng, J. Monty, R.J. Linhardt, Polysaccharide-based nanocomposites and their applications, *Carbohydr. Res*. 405 (2015) 23–32. doi:10.1016/j.carres.2014.07.016.
4. N. Lin, J. Huang, A. Dufresne, Preparation, properties and applications of polysaccharide nanocrystals in advanced functional nanomaterials: A review, *Nanoscale* (2012).
5. N. Lin, G. Chen, J. Huang, A. Dufresne, P.R. Chang, Effects of polymer-grafted natural nanocrystals on the structure and mechanical properties of poly(lactic acid): A case of cellulose whisker-graft-polycaprolactone, *J. Appl. Polym. Sci*. 113 (2009) 3417–3425. doi:10.1002/app.30308.
6. M.V. Tzoumaki, T. Moschakis, V. Kiosseoglou, C.G. Biliaderis, Oil-in-water emulsions stabilized by chitin nanocrystal particles, *Food Hydrocoll*. 25 (2011) 1521–1529. doi:10.1016/j.foodhyd.2011.02.008.

7. D. Le Corre, J. Bras, A. Dufresne, Starch nanoparticles: A review, *Biomacromolecules* 11 (2010) 1139–53. doi:10.1021/bm901428y.
8. D. LeCorre, J. Bras, A. Dufresne, Influence of native starch's properties on starch nanocrystals thermal properties, *Carbohydr. Polym*. 87 (2012) 658–666. doi:10.1016/j.carbpol.2011.08.042.
9. S.J. Eichhorn, C.A. Baillie, N. Zafeiropoulos, L.Y. Mwaikambo, M.P. Ansell, A. Dufresne, et al., Review: Current international research into cellulosic fibres and composites, *J. Mater. Sci*. 36 (2001) 2107–2131. doi:10.1023/a:1017512029696.
10. P. Gatenholm, D. Klemm, Bacterial nanocellulose as a renewable material for biomedical applications, *MRS Bull*. 35 (2011) 208–213. doi:10.1557/mrs2010.653.
11. M. Valodkar, S. Thakore, Organically modified nanosized starch derivatives as excellent reinforcing agents for bionanocomposites, *Carbohydr. Polym*. 86 (2011) 1244–1251. doi:http://dx.doi.org/10.1016/j.carbpol.2011.06.020.
12. Y. Habibi, Key advances in the chemical modification of nanocelluloses, *Chem. Soc. Rev*. 43 (2014) 1519–1542. doi:10.1039/c3cs60204d.
13. M. Börjesson, G. Westman, Crystalline nanocellulose: preparation, modification, and properties, in: M. Poletto, H.L. Omaghi (Eds.), *Cellulose - Fundamental Aspects and Current Trends,* InTech, 2015: p. 282.
14. MarketResearch.com, The Global Market for Nanocellulose : Opportunity, Markets, Applications, Technologies and Companies, 2016.
15. H.P.S. Abdul Khalil, Y. Davoudpour, C.K. Saurabh, M.S. Hossain, A.S. Adnan, R. Dungani, et al., A review on nanocellulosic fibres as new material for sustainable packaging: Process and applications, *Renew. Sustain. Energy Rev*. 64 (2016) 823–836. doi:10.1016/j.rser.2016.06.072.
16. M.S. Reid, M. Villalobos, E.D. Cranston, Benchmarking cellulose nanocrystals : From the laboratory to industrial production, *Langmuir* 33 (2017) 1583–1598.
17. Y. Habibi, A. Dufresne, Highly filled bionanocomposites from functionalized polysaccharide nanocrystals, *Biomacromolecules* 9 (2008) 1974–1980. doi:10.1021/bm8001717.
18. D. Roy, M. Semsarilar, J.T. Guthrie, S. Perrier, Cellulose modification by polymer grafting: A review, *Chem. Soc. Rev*. 38 (2009) 2046–2064. http://dx.doi.org/10.1039/B808639G.

19. K. Schneider, Mechanical properties of polymers at surfaces and interfaces, *Polym. Surf. Interfaces* (2008) 139–160. doi:10.1007/978-3-540-73864-0.

20. H. Kang, R. Liu, Y. Huang, Graft modification of cellulose: Methods, properties and applications, *Polymer (United Kingdom*) 70 (2015) A1–A16. doi:10.1016/j.polymer.2015.05.041.

21. G. Moad, D.H. Solomon, The Chemistry of Radical Polymerization, Elsevier B.V., 2006.

22. F.L. Hatton, S.A. Kedzior, E.D. Cranston, A. Carlmark, Grafting-from cellulose nanocrystals via photoinduced Cu-mediated reversible-deactivation radical polymerization, *Carbohydr. Polym*. 157 (2016). doi:10.1016/j.carbpol.2016.10.064.

23. M.N. Gandini, Alessandro Belgacem, The surface and in-depth modification of cellulose fibers, *Adv. Polym. Sci.* 271 (2016) 169–206.

24. W.H. Daly, T.S. Evenson, S.T. Iacono, R. Walker Jones, Recent developments in cellulose grafting chemistry utilizing Barton ester intermediates and nitroxide mediation, *Macromol. Symp*. 174 (2001) 155–163. doi:10.1002/1521-3900(200109)174:1<155::AID-MASY155>3.0.CO;2-O.

25. J. Yi, Q. Xu, X. Zhang, H. Zhang, Chiral-nematic self-ordering of rodlike cellulose nanocrystals grafted with poly(styrene) in both thermotropic and lyotropic states, *Polymer (Guildf)* 49 (2008) 4406–4412. doi:10.1016/j.polymer.2008.08.008.

26. J. Yi, Q. Xu, X. Zhang, H. Zhang, Temperature-induced chiral nematic phase changes of suspensions of poly(N,N-dimethylaminoethyl methacrylate)-grafted cellulose nanocrystals, *Cellulose* 16 (2009) 989–997. doi:10.1007/s10570-009-9350-9.

27. G. Morandi, L. Heath, W. Thielemans, Cellulose nanocrystals grafted with polystyrene chains through surface-initiated atom transfer radical polymerization (SI-ATRP), *Langmuir* 25 (2009) 8280–8286. doi:10.1021/la900452a.

28. E. Zeinali, V. Haddadi-Asl, H. Roghani-Mamaqani, Nanocrystalline cellulose grafted random copolymers of N-isopropylacrylamide and acrylic acid synthesized by RAFT polymerization: Effect of different acrylic acid contents on LCST behavior, *RSC Adv*. 4 (2014) 31428–31442. doi:10.1039/C4RA05442C.

29. E. Malmstrom, A. Carlmark, Controlled grafting of cellulose fibres – An outlook beyond paper and cardboard, *Polym. Chem*. 3 (2012) 1702–1713. http://dx.doi.org/10.1039/C1PY00445J.

30. G. Odian, Principles of Polymerization, IVth, John Wiley & Sons, Hoboken, 2004.
31. K. Matyjaszewski, Handbook of radical polymerization, in: K. Matyjaszewski, T. P. Davis (Eds.), Handbook of Radical Polymerization, John Wiley & Sons, Hoboken, 2002: pp. 361–406.
32. C. Jérôme, P. Lecomte, Recent advances in the synthesis of aliphatic polyesters by ring-opening polymerization, *Adv. Drug Deliv. Rev*. 60 (2008) 1056–1076. doi:10.1016/j.addr.2008.02.008.
33. S. Hansson, V. Trouillet, T. Tischer, A.S. Goldmann, A. Carlmark, C. Barner-Kowollik, et al., Grafting efficiency of synthetic polymers onto biomaterials: A comparative study of grafting-from versus grafting-to, *Biomacromolecules*. 14 (2013) 64–74. doi:10.1021/bm3013132.
34. S. Yoshikawa, T. Takayama, N. Tsubokawa, Grafting reaction of living polymer cations with amino groups on chitosan powder, *J. Appl. Polym. Sci*. 68 (1998) 1883–1889. doi:10.1002/(SICI)1097-4628(19980613)68:11<1883::AID-APP21>3.0.CO;2-U.
35. N. Tsubokawa, T. Iida, T. Takayama, Modification of cellulose powder surface by grafting of polymers with controlled molecular weight and narrow molecular weight distribution, *J. Appl. Polym. Sci*. 75 (2000) 515–522. doi:10.1002/(sici)1097-4628(20000124)75:4<515::aid-app6>3.0.co;2-q.
36. H. Wang, J. He, M. Zhang, K.C. Tam, P. Ni, A new pathway towards polymer modified cellulose nanocrystals via a “grafting onto” process for drug delivery, *Polym. Chem*. 6 (2015) 4206–4209. doi:10.1039/c5py00466g.
37. J. Chen, N. Lin, J. Huang, A. Dufresne, Highly alkynyl-functionalization of cellulose nanocrystals and advanced nanocomposites thereof via click chemistry, *Polym. Chem*. 6 (2015) 4385–4395. doi:10.1039/C5PY00367A.
38. A. Benkaddour, K. Jradi, S. Robert, C. Daneault, Grafting of polycaprolactone on oxidized nanocelluloses by click chemistry, *Nanomaterials*. 3 (2013) 141–157. doi:10.3390/nano3010141.
39. A.P. Mangalam, J. Simonsen, A.S. Benight, Cellulose/DNA hybrid nanomaterials, Biomacromolecules (2009) 497–504. doi:10.1021/bm800925x.
40. N. Ljungberg, C. Bonini, F. Bortolussi, C. Boisson, L. Heux, J.Y. Cavaillé, New nanocomposite materials reinforced with cellulose whiskers in atactic polypropylene: Effect of surface and dispersion characteristics, *Biomacromolecules* 6 (2005) 2732–2739. doi:10.1021/bm050222v.
41. F. Azzam, L. Heux, B. Jean, J.-L. Putaux, Preparation by grafting onto,

characterization and properties of thermally responsive polymer-decorated cellulose nanocrystals, *Biomacromolecules* 11 (2010) 3652–3659.

42. S. Harrisson, G.L. Drisko, E. Malmström, A. Hult, K.L. Wooley, Hybrid rigid/soft and biologic/synthetic materials: Polymers grafted onto cellulose microcrystals, *Biomacromolecules* 12 (2011) 1214–1223. doi:10.1021/bm101506j.
43. J. Araki, M. Wada, S. Kuga, Steric stabilization of a cellulose microcrystal suspension by poly(ethylene glycol) grafting, *Cellulose* (2001) 21–27. doi:10.1021/la001070m.
44. A. Pei, J.M. Malho, J. Ruokolainen, Q. Zhou, L.A. Berglund, Strong nanocomposite reinforcement effects in polyurethane elastomer with low volume fraction of cellulose nanocrystals, *Macromolecules* 44 (2011) 4422–4427. doi:10.1021/ma200318k.
45. X. Cao, Y. Habibi, L. A. Lucia, One-pot polymerization, surface grafting, and processing of waterborne polyurethane-cellulose nanocrystal nanocomposites, *J. Mater. Chem*. 19 (2009) 7137–7145. doi:10.1039/b910517d.
46. E. Kloser, D.G. Gray, Surface grafting of cellulose nanocrystals with poly(ethylene oxide) in aqueous media, *Langmuir* 26 (2010) 13450–13456. doi:10.1021/la101795s.
47. Z. Li, X. Zhou, C. Pei, Synthesis and characterization of MPS-g-PLA copolymer and its application in surface modification of bacterial cellulose, *Int. J. Polym. Anal. Charact.* 15 (2010) 199–209. doi:10.1080/10236661003681222.
48. R. Mincheva, L. Jasmani, T. Josse, Y. Paint, J.M. Raquez, P. Gerbaux, et al., Binary mixed homopolymer brushes tethered to cellulose nanocrystals: A step towards compatibilized polyester blends, *Biomacromolecules* 17 (2016) 3048–3059. doi:10.1021/acs.biomac.6b00932.
49. V. K. Thakur, Cellulose-Based Graft Copolymers: Structure and Chemistry, Taylor & Francis Group, Washington, D.C., 2015. doi:https://doi.org/10.1201/b18390.
50. A. Bhattacharya, B.N. Misra, Grafting: A versatile means to modify polymers: Techniques, factors and applications, *Prog. Polym. Sci*. 29 (2004) 767–814. doi:10.1016/j.progpolymsci.2004.05.002.
51. G. V. Oshovsky, D.N. Reinhoudt, W. Verboom, Supramolecular chemistry in water, *Angew. Chemie Int. Ed*. 46 (2007) 2366–2393. doi:10.1002/anie.200602815.
52. R. Sengupta, S. Chakraborty, S. Bandyopadhyay, S. Dasgupta, R.

Mukhopadhyay, K. Auddy, et al., A short review on rubber/clay nanocomposites with emphasis on mechanical properties, *Polymer Engineering and Science.* 47 (2007) 21–25. doi:10.1002/pen.

53. C.J. Chirayil, L. Mathew, S. Thomas, Review of recent research in nano cellulose preparation from different lignocellulosic fibers, *Rev. Adv. Mater. Sci*. 37 (2014) 20–28.
54. I.A. Sacui, R.C. Nieuwendaal, D.J. Burnett, S.J. Stranick, M. Jorfi, C. Weder, et al., Comparison of the properties of cellulose nanocrystals and cellulose nanofibrils isolated from bacteria, tunicate, and wood processed using acid, enzymatic, mechanical, and oxidative methods, *ACS Appl. Mater. Interfaces* 6 (2014) 6127–6138. doi:10.1021/am500359f.
55. J. Kadokawa, Fabrication of nanostructured and microstructured chitin materials through gelation with suitable dispersion media, *RSC Adv*. 5 (2015) 12736–12746. doi:10.1039/C4RA15319G.
56. A.M. Shi, D. Li, L.J. Wang, B.Z. Li, B. Adhikari, Preparation of starch-based nanoparticles through high-pressure homogenization and miniemulsion cross-linking: Influence of various process parameters on particle size and stability, *Carbohydr. Polym*. (2011) 1604–1610. doi:10.1016/j.carbpol.2010.10.011.
57. N. Lin, J. Huang, P.R. Chang, D.P. Anderson, J. Yu, Preparation, modification, and application of starch nanocrystals in nanomaterials: a review, *J. Nanomater*. 2011 (2011) 20. doi:10.1155/2011/573687.
58. Y. Qin, C. Liu, S. Jiang, L. Xiong, Q. Sun, Characterization of starch nanoparticles prepared by nanoprecipitation: Influence of amylose content and starch type, *Ind. Crops Prod*. 87 (2016) 182–190. doi:10.1016/j.indcrop.2016.04.038.
59. J. Huang, P.R. Chang, A. Dufresne, Polysaccharide Nanocrystals: current status and prospects in material science in: J. Huang, P.R. Chang, A. Dufresne (Eds.), *Polysaccharide-Based Nanocrystals: Chemistry and Applications,* Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2015: pp. 1–14.
60. R.F. Nickerson, J.A. Habrle, Cellulose intercrystalline, *Ind. Engeenering Chem*. 39 (1947) 1507–1512.
61. Roadmap for the Development of International Standards for Nanocellulose, Arlington, Virginia, USA, 2011. Available at: https://www.tappinano.org/media/1468/2011-roadmapfornanocellulosestandards.pdf.

62. G. Siqueira, J. Bras, A. Dufresne, Cellulosic bionanocomposites: A review of preparation, properties and applications, *Polymers (Basel)* 2 (2010) 728–765. doi:10.3390/polym2040728.

63. R.J. Moon, A. Martini, J. Nairn, J. Simonsen, J. Youngblood, Cellulose nanomaterials review: Structure, properties and nanocomposites, *Chem. Soc. Rev*. 40 (2011) 3941–3994. doi:10.1039/c0cs00108b.

64. J. Huang, P.R. Chang, N. Lin, A. Dufresne, Polysaccharide-Based Nanocrystals: Chemistry and Applications, Chemical I, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2015.

65. Y. Habibi, L.A. Lucia, O.J. Rojas, Cellulose nanocrystals: Chemistry, self-assembly, and applications, Chem. Rev. (Washington, DC, United States) 110 (2010) 3479–3500. doi:10.1021/cr900339w.

66. S.M. Mukherjee, H.J. Woods, X-ray and electron microscope studies of the degradation of cellulose by sulfuric acid, *Biochim. Biophys. Acta*. 10 (1953) 499–511.

67. B. Wang, M. Sain, K. Oksman, Study of structural morphology of hemp fiber from the micro to the nanoscale, *Appl. Compos. Mater*. 14 (2007) 89–103.

68. J.N. Saddler, H.H. Brownell, L.P. Clermont, N. Levitin, Enzymatic hydrolysis of cellulose and various pretreated wood fractions, *Biotechnol. Bioeng*. 24 (1982) 1389–1402.

69. A.M.D. Lima, J.T. Wong, M. Paillet, R. Borsali, R. Pecora, Translational and rotational dynamics of rodlike cellulose whiskers, *Langmuir* 19 (2003) 24–29.

70. M.M. Lima, R. Borsali, Static and dynamic light scattering from polyelectrolyte microcrystal cellulose, *Langmuir* 18 (2002) 992–996.

71. P.L. Beltrame, E.D. Paglia, A. Seves, E. Pellizzoni, M. Romano, Structural features of native cellulose gels and films from their susceptibility to enzymatic attack, *J. Appl. Polym. Sci*. 44 (1992) 2095–2101.

72. H.R. Hohl, J. Jehli, Presence of cellulose microfibrils in proteinaceous slime track of *Dictyostelium discoideum*, *Archiv für Mikrobiologie,* 92 (1973) 179–187.

73. J.A. Kelly, A.M. Shukaliak, C.C.Y. Cheung, K.E. Shopsowitz, W.Y. Hamad, M.J. MacLachlan, Responsive photonic hydrogels based on nanocrystalline cellulose, *Angew. Chem. Int. Ed*. 52 (2013) 8912–8916.

74. H. Fukuzumi, T. Saito, T. Wata, Y. Kumamoto, A. Isogai, Transparent and high gas barrier films of cellulose nanofibers prepared by TEMPO-mediated oxidation, *Biomacromolecules* 10 (2009) 162–165.

75. J. Mendes, P.K. Annamalai, S.J. Eichhorn, R. Rusli, S.J. Rowan, E.J. Foster,

et al., Bioinspired mechanically adaptive polymer nanocomposites with water-activated shape-memory effect, *Macromolecules* 44 (2011) 6827–6835.

76. M.V. Biyani, E.J. Foster, C. Weder, Light-healable supramolecular nanocomposites based on modified cellulose nanocrystals, *ACS Macro Lett*. 2 (2013) 236–240.
77. K.A. Potter, M. Jorfi, K.T. Householder, E.J. Foster, C. Weder, J.R. Capadona, Curcumin-releasing mechanically adaptive intracortical implants improve the proximal neuronal density and blood-brain barrier stability, *Acta Biomater*. 10 (2014) 2209–2222.
78. J.R. Capadona, K. Shanmuganathan, D.J. Tyler, S.J. Rowan, C. Weder, Stimuli-responsive polymer nanocomposites inspired by the sea cucumber dermis, *Science* 319 (2008) 1370–1374.
79. Rojas, No Title, in: n.d.
80. [illegible] Bombeck, J. Hébert, A. Richel, Enzymatic hydrolysis to produce nanocellulose in an integrated forest biorefinery strategy. A review, *Biotechnol. Agron. Soc. Environ*. 20 (2016) 94–103.
81. Y. Mazlita, H. V Lee, S.B.A. Hamid, Preparation of cellulose nanocrystals bio-polymer from Agro-industrial wastes: Separation and characterization, *Polym. Polym. Compos*. 24 (2016) 719–728.
82. Y. Zhang, T. Nypelö, C. Salas, J. Arboleda, I.C. Hoeger, O.J. Rojas, Cellulose nanofibrils: From strong materials to bioactive surfaces, *J. Renew. Mater*. 1 (2013). doi:10.7569/JRM.2013.634115.
83. X. Zhang, M. Rolandi, Engineering strategies for chitin nanofibers, *J. Mater. Chem. B*. (2017) 1–23. doi:10.1039/C6TB03324E.
84. H. K. American Chemical Society. Books and Journals Division., S. P. Meyers, K. S. Lee, Journal of agricultural and food chemistry., [American Chemical Society, Books and Journals Division], n.d. http://cat.inist.fr/?aModele=afficheN&cpsidt=7207248 (accessed March 30, 2017).
85. A. Percot, C. Viton, A. Domard, Optimization of chitin extraction for shrimp shells, *Biomacromolecules* 4 (2003) 12–18.
86. J. Li, J. Revol, R.H. Marchessault, Effect of degree of deacetylation of chitin on the properties of chitin crystallites, *J. Appl. Polym. Sci*. 65 (1997) 373–380.
87. J.F. Revol, R.H. Marchessault, In vitro chiral nematic ordering of chitin crystallites, *Int. J. Biol. Macromol*. 15 (1993) 329–335.
88. J. Wu, K. Zhang, N. Girouard, J.C. Meredith, Facile route to produce chitin nano fibers as precursors for flexible and transparent gas barrier materials, *Biomacromolecules* 15 (2014) 4614–4620.

89. Y. Fan, T. Saito, A. Isogai, Preparation of chitin nanofibers from squid pen β-chitin by simple mechanical treatment under acid conditions, *Biomacromolecules* 9 (2008) 1919–1923.

90. D.X. Oh, Y. Cha, H.-L. Nguyen, Y. Je, Y. Jho, D. Hwang, et al., Chiral nematic self-assembly of minimally surface damaged chitin nanofibrils and its load bearing functions, *Sci. Rep*. 6 (2016) 23245.

91. A. Dufresne, Polysaccharide nanocrystal reinforced, *Can. J. Chem.* 494 (2008) 484–494. doi:10.1139/V07-152.

92. H.-Y. Kim, D.J. Park, J.-Y. Kim, S.-T. Lim, Preparation of crystalline starch nanoparticles using cold acid hydrolysis and ultrasonication, *Carbohydr. Polym*. 98 (2013) 295–301. doi:10.1016/j.carbpol.2013.05.085.

93. H.-Y. Kim, S.S. Park, S.-T. Lim, Preparation, characterization and utilization of starch nanoparticles, *Colloids Surf. B Biointerfaces* 126 (2015) 607–620. doi:10.1016/j.colsurfb.2014.11.011.

94. H.Y. Kim, J.H. Lee, J.Y. Kim, W.J. Lim, S.T. Lim, Characterization of nanoparticles prepared by acid hydrolysis of various starches, *Starch/ Staerke* 64 (2012) 367–373. doi:10.1002/star.201100105.

95. H. Angellier, L. Choisnard, S. Molina-Boisseau, P. Ozil, A. Dufresne, Optimization of the preparation of aqueous suspensions of waxy maize starch nanocrystals using a response surface methodology, *Biomacromolecules* 5 (2004) 1545–1551. doi:10.1021/bm049914u.

96. D. Song, Y.S. Thio, Y. Deng, Starch nanoparticle formation via reactive extrusion and related mechanism study, *Carbohydr. Polym*. 85 (2011) 208–214. doi:10.1016/j.carbpol.2011.02.016.

97. D. Liu, Q. Wu, H. Chen, P.R. Chang, Transitional properties of starch colloid with particle size reduction from micro- to nanometer, *J. Colloid Interface Sci*. 339 (2009) 117–124. doi:10.1016/j.jcis.2009.07.035.

98. W. Xie, Y. Zhang, Y. Liu, Homogenous carboxymethylation of starch using 1-butyl-3-methylimidazolium chloride ionic liquid medium as a solvent, *Carbohydr. Polym*. 85 (2011) 792–797. doi:10.1016/j.carbpol.2011.03.047.

99. K. Wilpiszewska, T. Spychaj, Ionic liquids: Media for starch dissolution, plasticization and modification, *Carbohydr. Polym*. 86 (2011) 424–428. doi:10.1016/j.carbpol.2011.06.001.

100. G. Zhou, Z. Luo, X. Fu, Preparation and characterization of starch nanoparticles in ionic liquid-in-oil microemulsions system, *Ind. Crops Prod*. 52 (2014) 105–110. doi:10.1016/j.indcrop.2013.10.019.

101. A. Hebeish, M.H. El-Rafie, M.A. EL-Sheikh, M.E. El-Naggar, Ultra-fine

characteristics of starch nanoparticles prepared using native starch with and without surfactant, *J. Inorg. Organomet. Polym. Mater*. 24 (2014) 515–524. doi:10.1007/s10904-013-0004-x.

102. S. Bel Haaj, A. Magnin, C. Pétrier, S. Boufi, Starch nanoparticles formation via high power ultrasonication, *Carbohydr. Polym*. 92 (2013) 1625–32. doi:10.1016/j.carbpol.2012.11.022.

103. N. Wang, E. Ding, R. Cheng, Langmuir 24 (2008) 5.

104. K. Tashiro, M. Kobayashi, Theoretical evaluation of three-dimensional elastic constants of native and regenerated celluloses: role of hydrogen bonds, *Polymer (Guildf)* 32 (1991) 1516–1526.

105. L. Petersson, K. Oksman, Biopolymer based nanocomposites: Comparing layered silicates and microcrystalline cellulose as nanoreinforcement, *Compos. Sci. Technol*. 66 (2006) 2187–2196.

106. J.D. Goodrich, W.T. Winter, Green composites prepared from cellulose nanoparticles, *ACS Symp. Ser*. 1017 (2009) 153–168.

107. M. Paillet, A. Dufresne, Macromolecules 34 (2001) 6527.

108. H. Sehaqui, N.E. Mushi, S. Morimune, M. Salajkova, T. Nishino, L.A. Berglund, Cellulose nanofiber orientation in nanopaper and nanocomposites by cold drawing, *ACS Appl. Mater. Interfaces* 4 (2012) 1043–1049.

109. M. Mincea, A. Negrulescu, V. Ostafe, Preparation, modification, and application of chitin nanowhiskers: a review, *Rev. Adv. Mater. Sci*. 30 (2012) 225–242.

110. H. Angellier-Coussy, J.L. Putaux, S. Molina-Boisseau, A. Dufresne, E. Bertoft, S. Perez, The molecular structure of waxy maize starch nanocrystals, *Carbohydr. Res*. 344 (2009) 1558–1566. doi:10.1016/j.carres.2009.04.002.

111. H. Angellier, S. Molina-Boisseau, M.N. Belgacem, A. Dufresne, Surface chemical modification of waxy maize starch nanocrystals, *Langmuir* 21 (2005) 2425–2433. doi:10.1021/la047530j.

112. H. Sashiwa, S.I. Aiba, Chemically modified chitin and chitosan as biomaterials, *Prog. Polym. Sci*. 29 (2004) 887–908. doi:10.1016/j.progpolymsci.2004.04.001.

113. D. Klemm, F. Kramer, S. Moritz, T. Lindström, M. Ankerfors, D. Gray, et al., Nanocelluloses: A new family of nature-based materials, . 50 (2011) 5438–5466. doi:10.1002/anie.201001273.

114. Roadmap for the Development of International Standards for Nanocellulose (2011). Available at: https://www.tappinano.org/media/1468/2011-roadmapfornanocellulosestandards.pdf.

115. N. Lin, A. Dufresne, Surface modification of polysaccharide nanocrystals, polysaccharide-based nanocrystals, *Chem. Appl*. (2015) 63–108. doi:10.1002/9783527689378.ch3.

116. C. Moreau, A. Villares, I. Capron, B. Cathala, Tuning supramolecular interactions of cellulose nanocrystals to design innovative functional materials, *Ind. Crops Prod*. 93 (2015) 96–107. doi:10.1016/j.indcrop.2016.02.028.

117. Q. Zhao, S. Wang, X. Cheng, R.C.M. Yam, D. Kong, R.K.Y. Li, Surface modification of cellulose fiber via supramolecular assembly of biodegradable polyesters by the aid of host-guest inclusion complexation, *Biomacromolecules* 11 (2010) 1364–1369.

118. M. Tatsumi, Y. Teramoto, Y. Nishio, Polymer composites reinforced by locking-in a liquid-crystalline assembly of cellulose nanocrystallites, *Biomacromolecules* 13 (2012) 1584–1591. doi:10.1021/bm300310f.

119. A.P. Tutor, (19) United States, 1 (2002) 0–2. doi:US 20100322867A1.

120. R. Bardet, N. Belgacem, J. Bras, Flexibility and color monitoring of cellulose nanocrystal iridescent solid films using anionic or neutral polymers, *ACS Appl. Mater. Interfaces* 7 (2015) 4010–4018. doi:10.1021/am506786t.

121. M. Giese, L.K. Blusch, M.K. Khan, W.Y. Hamad, M.J. Maclachlan, Responsive mesoporous photonic cellulose films by supramolecular cotemplating, *Angew. Chemie Int. Ed*. 53 (2014) 8880–8884. doi:10.1002/anie.201402214.

122. B. Zhu, R. Merindol, A.J. Benitez, B. Wang, A. Walther, Supramolecular engineering of hierarchically self-assembled, bioinspired, cholesteric nanocomposites formed by cellulose nanocrystals and polymers, *ACS Appl. Mater. Interfaces* 8 (2016) 11031–11040. doi:10.1021/acsami.6b00410.

123. J.M. Malho, S. Arola, P. Laaksonen, G.R. Szilvay, O. Ikkala, M.B. Linder, Modular architecture of protein binding units for designing properties of cellulose nanomaterials, *Angew. Chemie Int. Ed.* 54 (2015) 12025–12028. doi:10.1002/anie.201505980.

124. J.M. Malho, C. Ouellet-Plamondon, M. Rüggeberg, P. Laaksonen, O. Ikkala, I. Burgert, et al., Enhanced plastic deformations of nanofibrillated cellulose film by adsorbed moisture and protein-mediated interactions, *Biomacromolecules* 16 (2015) 311–318. doi:10.1021/bm501514w.

125. M. V Biyani, E.J. Foster, C. Weder, Light-healable supramolecular nanocomposites based on modified cellulose nanocrystals, *ACS Macro Lett.* 2 (2013) 236–240.

126. X. Mu, D.G. Gray, Formation of chiral nematic films from cellulose nanocrystal suspensions is a two-stage process, *Langmuir* 30 (2014) 9256–9260. doi:10.1021/la501741r.

127. J.R. McKee, J. Huokuna, L. Martikainen, M. Karesoja, A. Nykänen, E. Kontturi, et al., Molecular engineering of fracture energy dissipating sacrificial bonds into cellulose nanocrystal nanocomposites, *Angew. Chemie Int. Ed*. 53 (2014) 5049–5053. doi:10.1002/anie.201401072.

128. J.M. Raquez, A.-L. Goffin, E. Duquesne, Y. Habibi, A. Dufresne, P. Dubois, Novel nanocomposites reinforced with polysaccharide (Starch) nanocrystals: from interfacial ring-opening polymerization to melt-processing implementation, in: P.B. Smith, R.A. Gross (Eds.), *Biobased Monomers, Polymers, and Materials,* ACS Sympos, American Chemical Society, Washington, D.C., 2012: pp. 257–268. doi:10.102/bk-2012-1105.ch016.

129. J. Yu, F. Ai, A. Dufresne, S. Gao, J. Huang, P.R. Chang, Structure and mechanical properties of poly(lactic acid) filled with (starch nanocrystal)-graft-poly(ε-caprolactone), *Macromol. Mater. Eng*. 293 (2008) 763–770. doi:10.1002/mame.200800134.

130. H. Namazi, A. Dadkhah, Surface modification of starch nanocrystals through ring-opening polymerization of ε-caprolactone and investigation of their microstructures, *J. Appl. Polym. Sci*. 110 (2008) 2405–2412. doi:10.1002/app.

131. W. Thielemans, M.N. Belgacem, A. Dufresne, Starch nanocrystals with large chain surface modifications, *Langmuir* 22 (2006) 4804–4810. doi:10.1017/CBO9781107415324.004.

132. Y. Xu, W. Ding, J. Liu, Y. Li, J.F. Kennedy, Q. Gu, et al., Preparation and characterization of organic-soluble acetylated starch nanocrystals, *Carbohydr. Polym.* 80 (2010) 1078–1084. doi:10.1016/j.carbpol.2010.01.027.

133. P.R. Chang, F. Ai, Y. Chen, A. Dufresne, J. Huang, Effects of starch nanocrystal-graft-porycaprolactone on mechanical properties of waterborne polyurethane-based nanocomposites, *J. Appl. Polym. Sci.* 111 (2009) 619–627. doi:10.1002/app.29060.

134. Z. Yang, H. Peng, W. Wang, T. Liu, Crystallization behavior of poly(ε-caprolactone)/layered double hydroxide nanocomposites, *J. Appl. Polym. Sci.* 116 (2010) 2658–2667. doi:10.1002/app.

135. M. Labet, W. Thielemans, A. Dufresne, Polymer grafting onto starch nanocrystals, *Biomacromolecules* 8 (2007) 2916–27. doi:10.1021/

bm700468f.

136. H. Namazi, F. Fathi, A. Dadkhah, Hydrophobically modified starch using long-chain fatty acids for preparation of nanosized starch particles, *Sci. Iran.* 18 (2011) 439–445. doi:10.1016/j.scient.2011.05.006.

137. Y. Chen, F. Liu, X. Deng, D. Jia, Y. Luo, Structure and properties of comb-branched waterborne polyurethane/montmorillonite nanocomposites, *Huagong Xuebao/Journal of Chemical Industry and Engineering* (Chinese Ed. 59 (2008) 761–765.

138. S. Benali, F. Khelifa, D. Lerari, R. Mincheva, Y. Habibi, D. Lahem, et al., Supramolecular approach for an efficient processing of polylactide/starch nanocomposites, *ACS Omega* 3 (2018), 1069–1080.

139. A. Ilnicka, J.P. Lukaszewicz, Discussion remarks on the role of wood and chitin constituents during carbonization, *Front. Mater.* 2 (2015) 1–6. doi:10.3389/fmats.2015.00020.

140. J. Li, J. Revol, R. Marchessault, Effect of degree of deacetylation of chitin on the properties of chitin crystallites, J. Appl. Polym. (1997) 373–380. doi:10.1002/(SICI)1097-4628(19970711)65:2<373::AID-APP18>3.0.CO;2-0.

141. K.G. Nair, A. Dufresne, A. Gandini, M.N. Belgacem, Crab shell chitin whiskers reinforced natural rubber nanocomposites. 3. Effect of Chemical Modification of chitin whiskers, *Biomacromolecules* 4 (2003) 1835–1842. doi:10.1021/bm030058g.

142. C. Guo, L. Zhou, J. Lv, Effects of expandable graphite and modified ammonium polyphosphate on the flame-retardant and mechanical properties of wood flour-polypropylene composites, *Polym. Polym. Compos.* 21 (2013) 449–456. doi:10.1002/app.

143. A. Dufresne, Processing of polymer nanocomposites reinforced with polysaccharide nanocrystals, *Molecules* 15 (2010) 4111–4128. doi:10.3390/molecules15064111.

144. T. Setoguchi, K. Yamamoto, J.I. Kadokawa, Preparation of chitin nanofiber-graft-poly(l-lactide-co-ε-caprolactone) films by surface-initiated ring-opening graft copolymerization, *Polymer* (United Kingdom) 53 (2012) 4977–4982. doi:10.1016/j.polymer.2012.08.060.

145. S. Ifuku, M. Iwasaki, M. Morimoto, H. Saimoto, Graft polymerization of acrylic acid onto chitin nanofiber to improve dispersibility in basic water, *Carbohydr. Polym.* 90 (2012) 623–627. doi:10.1016/j.carbpol.2012.05.087.

146. H. Liu, W. Liu, B. Luo, W. Wen, M. Liu, X. Wang, et al., Electrospun composite nanofiber membrane of poly(l-lactide) and surface grafted chitin whiskers: Fabrication, mechanical properties and cytocompatibility, *Carbohydr. Polym.* 147 (2016) 216–225. doi:10.1016/j.carbpol.2016.03.096.

147. Z. Zou, C. Luo, B. Luo, W. Wen, M. Liu, C. Zhou, Synergistic reinforcing and toughening of poly(L-lactide) composites with surface-modified MgO and chitin whiskers, *Compos. Sci. Technol.* 133 (2016) 128–135. doi:10.1016/j.compscitech.2016.07.025.

148. A. De Sousa Mol, I. Martins, R.L. Oréfice, Surface-pegylated chitin whiskers as an effective additive to enhance the mechanical properties of recycled ABS, J. Appl. Polym. Sci. 132 (2015) 1–8. doi:10.1002/app.42463.

149. J. Wang, Z. Wang, J. Li, B. Wang, J. Liu, P. Chen, et al., Chitin nanocrystals grafted with poly(3-hydroxybutyrate-co-3-hydroxyvalerate) and their effects on thermal behavior of PHBV, *Carbohydr. Polym.* 87 (2012) 784–789. doi:10.1016/j.carbpol.2011.08.066.