Progress in Polymer Science xxx (xxxx) xxx

Contents lists available at ScienceDirect

Progress in Polymer Science

journal homepage: www.elsevier.com/locate/ppolysci

Development, processing and applications of bio-sourced cellulose nanocrystal composites

Céline Calvino[a,1], Nicholas Macke[a,1], Ryo Kato[a,1], Stuart J. Rowan[a,b,c,*]

[a] Pritzker School of Molecular Engineering, University of Chicago, Chicago, IL 60637, United States
[b] Department of Chemistry, University of Chicago, Chicago, IL 60637, United States
[c] Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, IL 60439, United States

ARTICLE INFO

Article history:
Available online xxx

Keywords:
Cellulose nanocrystals
Sustainability
Composites
Biopolymer
Poly(lactic acid)
Polysaccharides

ABSTRACT

Plastic pollution concerns have catalyzed research into green materials with the specific goal of accessing new bio-derived and bio-degradable polymers with improved property profiles. One way to achieve these new materials is through the incorporation of nanofillers into bio-based polymer matrices. Cellulose nanocrystals (CNCs), which are extracted from biomass, have been investigated as one route to bio-based composites with enhanced performance. The combination of the excellent reinforcement capabilities of these bio-derived, nanosized particles along with relatively low production cost and biodegradability makes cellulose-based nanocomposites an attractive and promising approach to the next generation of green materials. Discussed herein is an overview of the use of CNCs to access reinforced bio-based nanocomposites, with particular focus on bio-available polyester and polysaccharide matrices. The characteristic changes provided by the incorporation of the nanofillers into the bio-based materials and their advantages and drawbacks are discussed. Specifically, the different parameters influencing mechanical reinforcement and barrier properties, such as the nature of processing, use of additives or CNC surface modifications are reviewed. Finally, the benefits of using CNC fillers in a number of potential future application areas, including polymer compatibilization, water purification, biomedical and electronics are outlined.

Contents

Abbreviations: AR, aspect ratio; ATBC, acetyl tri-*n*-butyl citrate; BNA, beycostat A B09 surfactant; CAB, cellulose acetate butyrate; CL, caprolactone; CNC, cellulose nanocrystal; CNF, cellulose nanofiber; CTE, coefficient of thermal expansion; DLA, D-lactic acid; DMA, dynamic mechanical analysis; DMAc, *N,N*-Dimethylacetamide; DMF, dimethylformamide; HDT, heat distortion temperature; MCC, micro-crystalline cellulose; MFC, microfibrillated cellulose; MWCNT, multi-walled carbon nanotubes; OLED, organic light emitting diode; PBAT, poly(butylene adipate terephthalate); PBS, poly(butylene succinate); PCL, polycaprolactone; PDLA, poly(D-lactic acid); PE, polyethylene; PEG, poly(ethylene glycol); PEO, poly(ethylene oxide); PHA, polyhydroxyalkanoate; PHB, poly(3-hydroxybutyrate); PLA, poly(lactic acid); PLLA, poly(L-lactic acid); PP, polypropylene; PS, polystyrene; SAXS, small-angle x-ray scattering; SEM, scanning electron microscopy; TEMPO, (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl; Tg, glass transition temperature; Tm, melting temperature; WAXS, wide-angle x-ray scattering; WVP, water vapor permeability.

* Corresponding author at: Pritzker School of Molecular Engineering, University of Chicago, Chicago, IL 60637, United States.
E-mail address: stuartrowan@uchicago.edu (S.J. Rowan).

[1] These authors contributed equally

https://doi.org/10.1016/j.progpolymsci.2020.101221
0079-6700/

Please cite this article as: C. Calvino, N. Macke, R. Kato et al., Development, processing and applications of bio-sourced cellulose nanocrystal composites, Prog Polym Sci, https://doi.org/10.1016/j.progpolymsci.2020.101221

1. Introduction

Ever since the existence of macromolecules was proposed 100 years ago by Hermann Staudinger, polymeric materials have played an ever-growing role in our daily life on account of their outstanding properties, which include robustness, light weight, versatility, facile processing and low cost [1]. As a consequence, there has been a meteoric rise in production of commodity plastics since the Second World War, and worldwide plastic production surpassed 340 million metric tons in 2017 (Fig. 1) [2–4]. When these materials were developed, major efforts were focused on increasing their useable lifetime and preventing degradation; however, with mass consumption of plastics, the end-of-life of these materials has become a growing concern. It is currently estimated that less than 10 % of all plastics produced are recycled, around 10 % are incinerated, with the remaining 80 % accumulating in landfills or littered into terrestrial and aquatic environments [5]. The majority of plastics produced today are petroleum-based, such as polyethylene (PE), polypropylene (PP) and polystyrene (PS), and can take hundreds of years to degrade. Furthermore, approximately ten tons of these plastics are discarded into the ocean every minute [6]. As such, unless significant changes occur, the plastic accumulation in our marine environment will continue to grow over the coming years, to the point that it has been predicted that the amount of plastic in the ocean will outweigh fish by 2050 [7]. The increase of non-biodegradable plastics in the environment is an ongoing global concern; for example, the 2019 Group of Twenty (G20) meeting on the global environment for sustainable growth proposed a framework for action to reduce marine plastic litter [8].

Considering the continued rise in plastic consumption and impending depletion of fossil fuel reserves, next generation plastic technologies need to keep the environment in mind and take necessary actions to harmonize with it. Towards this goal, the development of "sustainable" polymeric materials has attracted much attention in recent years [9–13]. By definition, these materials should be produced from non-damaging, renewable feedstocks (a "green birth") and be able to be easily recycled (a "green rebirth") or quickly degraded into non-harmful components under mild environmental conditions (a "green death") [14,15]. While such considerations are a good starting point for defining sustainability, it is important to recognize that one must also consider the wide range of factors that can play a part in the total emissions generated by a material over its entire life cycle, from initial planting to final degradation. For example, the use of pesticides during biomass growth and the energy needed to isolate the monomer/polymer from the feedstock are two factors that are not commonly considered and can push the total negative environmental impacts of bio-based materials beyond those of their fossil fuel counterparts [16]. As such, while not the focus of this review, it is important to note that any "sustainable" material system aiming for commercialization will need a full life cycle assessment to determine whether or not it is truly "more sustainable" than the existing solutions.

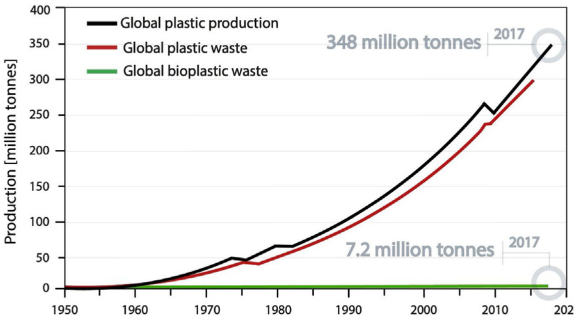


Fig. 1. Graph showing the increase in global plastic production (black), global plastic waste (red) and bio-derived plastic production (green) from 1950 to 2017 [17,18]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

Additionally, while many bio-degradable polymers have been developed and commercialized as "environmentally friendly" plastics, most of these plastics are not currently sourced from renewable feedstocks. For example, polycaprolactone (PCL), poly(butylene adipate terephthalate) (PBAT) and poly(butylene succinate) (PBS) are biodegradable, but predominately use fossil fuel-based chemicals to access their monomers on a commercial scale [19]. Some small-scale operations produce a minor portion of these monomers from biomass fermentation [20], but while this is a step in the right direction, it is not yet at a scale to make the polymers' life cycle sustainable. Increasing the percentage of these polyesters that are obtained from biomass-derived monomers is an active area of research [21] and if this can be achieved on a commercial scale, such polymers represent a significant advancement over their non-biodegradable alternatives. However, these polymers do not span the property matrix profiles that are available from the wide range of commercially available petroleum-based plastics.

Today there are two major classes of fully bio-based polymers that are commercially-viable, alkyl polyesters (predominantly poly(lactic acid) (PLA) [22] but also polyhydroxyalkonates (PHA)) [23] and carbohydrate-based [24] plastics. Unfortunately, these materials have relatively low thermal, physical and/or mechanical performance relative to their petroleum-based counterparts, which limits their use in many applications [25]. Indeed, the production percentage of bio-degradable and/or bio-based polymers was below 3 % of the total plastics market in 2017 [26]. While growing public concerns about the environment will continue to push the development and commercialization of sustainable polymers, improved material properties at a competitive cost will be a controlling factor in driving the growth of these "eco-friendly" plastics.

Among the different strategies used to improve the mechanical properties of sustainable polymers, the addition of nanofillers, such as graphene, titanium dioxide, calcium carbonate, silica, etc., appears to be a promising approach [27–30]. By controlling geometric dimensions, polymer-nanofiller interactions and particle dispersion, the incorporation of a small amount of nanofillers (usu-

Please cite this article as: C. Calvino, N. Macke, R. Kato et al., Development, processing and applications of bio-sourced cellulose nanocrystal composites, Prog Polym Sci, https://doi.org/10.1016/j.progpolymsci.2020.101221

ally less than 10 wt. %) has been shown to dramatically change the bulk material properties, such as improving strength, thermal resistance and gas permittivity [19,31]. However, the integration of non-bio-based or non-bio-degradable fillers into sustainable polymers diametrically opposes the material's sustainability and complicates recycling or composting processes. Thus, a focus on the development of sustainable bio-based nanofillers with renewable and degradable characteristics is of importance to achieve nanocomposite materials with sustainable lifecycles.

Among the various bio-based nanofiller materials, cellulose holds a key position as an abundant raw organic material that can be obtained from virtually inexhaustible biomass feedstocks, capable of meeting the increasing demand for green and bio-based products [32]. The use of cellulose as a material has been known since the beginning of civilization, from clothes and paper to its use in construction materials, yet over the past few decades there has been renewed interest in cellulose as a nanomaterial [33]. A variety of nanoparticles can be extracted from cellulose owing to its hierarchical structure and semi-crystalline nature (Fig. 2). Nanocelluloses are generally categorized by their size, aspect ratio and crystallinity, most often being divided into cellulose nanofibers (CNFs), which have relatively low degrees of crystallinity (ca. 60–80 %) and dimensions of nanometers in width and microns in length, and cellulose nanocrystals (CNCs) which are more crystalline (ca. > 85 %) but with aspect ratios generally less than 100. While CNFs have been employed as natural fillers for many polymer matrices including bio-based polymers, there have been a number of recent reviews that have summarized this work [34–37] and the interested reader is directed to these reviews for more information.

The focus of this review is on the other category of nanocellulose, namely cellulose nanocrystals and in particular on the use of CNCs to reinforce commercially-viable 100 % bio-based plastics. CNCs are isolated by extraction of the crystalline domains from the bio-sourced cellulosic material usually by a combination of mechanical and chemical processes [42]. Commonly, to obtain CNCs from the biomass cellulose, acid hydrolysis is carried out to degrade the amorphous connecting regions between crystals (Fig. 2). Broadly, CNCs are needle or rod-like nanoparticles that can be produced from diverse starting bio-sources (Table 1), such as wood, plants (bamboo, straw and grass, e.g. Miscanthus x. giganteus [43,44]) and select living organisms (e.g. bacteria, algae and sea tunicates). For clarity, a consistent naming scheme will be used throughout this review when discussing CNCs and their composites (Table 1). CNCs will be described by "*bio-source*-CNC-*functionality*", so a tunicate CNC with sulfate half esters on its surface will be described as *t*-CNC-SO_3^-.

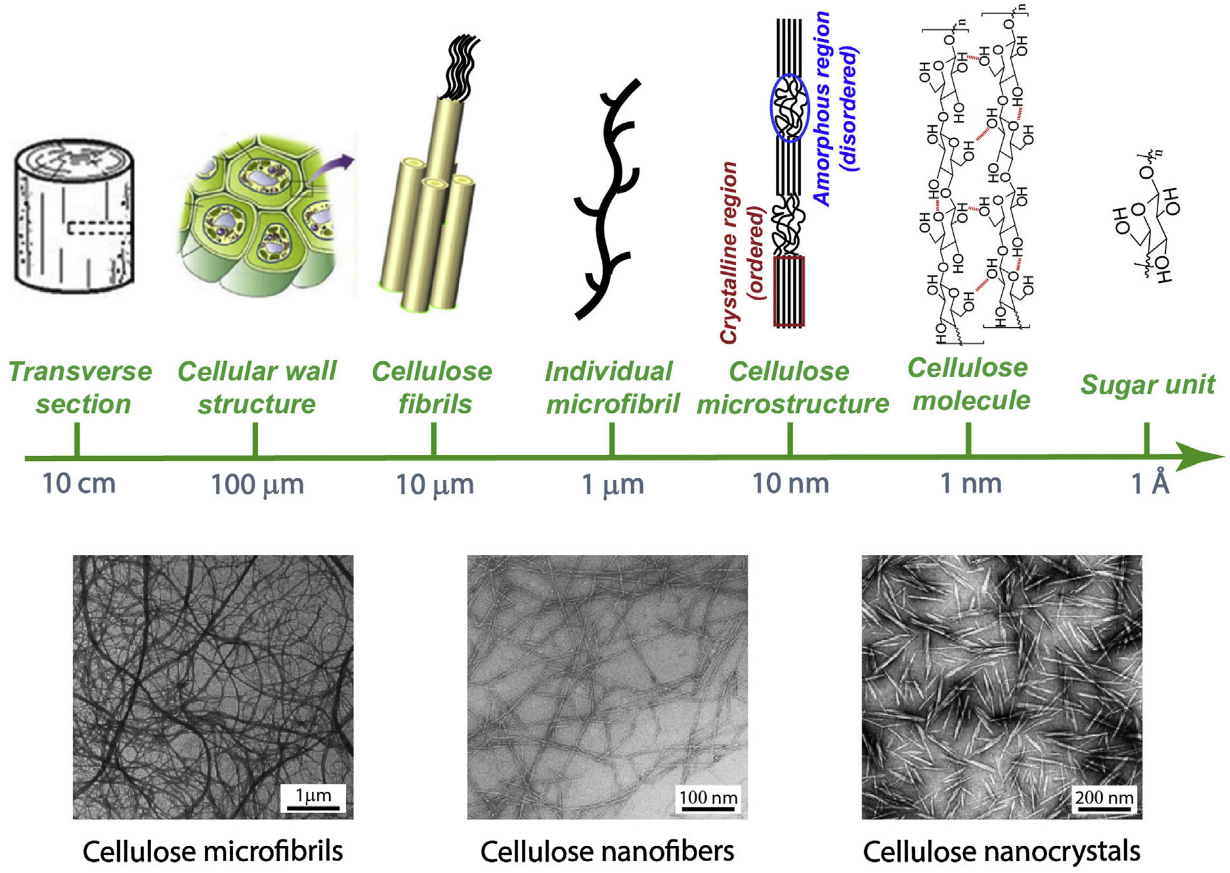
As shown in Table 1, the length, diameter and aspect ratio of CNCs vary between 100–3000 nm, 3–50 nm and 5–200 respectively, depending on the biological source and isolation protocol [60]. Removal of the non-crystalline cellulose results in CNCs having a high degree of crystallinity, generally around 85 % or greater [61]. Depending on the bio-source and the isolation protocol, CNCs can have a tensile modulus as high as 140 GPa, a density of about 1.5 g cm^{-3} and a specific modulus around 90 GPa g^{-1} cm^3 [62]. This combination of size and strength gives the CNCs outstanding reinforcing potential and renders them competitive with other commercially available nanofillers, such as silica [63], carbon nanofibers [64] and nanoclays [65], as a strong candidate for nanocomposite applications. In fact, wood-based CNCs have already begun production on a plant scale and are commercially available [66].

The relatively high aspect ratio (AR) of CNCs when compared to spherical particles is an advantage for reinforcing polymers matrices as it defines the CNC loading required to form a percolating network throughout a material (higher AR means lower filling fractions are required for percolation) [67]. A dramatic increase in mechanical stiffness is observed when percolation is achieved, making it an important consideration for the material's final properties. Despite these promising characteristics, there are still significant challenges to the use of CNCs in composite materials. In particular, the existence of hydroxyl groups on the surface of CNCs makes them hydrophilic in nature with a strong propensity for interparticle hydrogen bonding, causing agglomeration in polymer matrices, which significantly limits their reinforcement capability. However, it is important to note that most CNCs that are commercially available and reported in the literature are negatively charged, which enhances their dispersion in water and polar organic solvents. The surface negative charges are usually obtained during the CNC isolation procedure. As mentioned above CNCs are submitted to an acid treatment in order to remove the non-crystalline cellulose. If that acid treatment is sulfuric acid, then the surface of the CNCs will contain charged sulfate half-esters (CNC-SO_3^-). Another common negatively charged CNC is carboxylate CNCs (CNC-CO_2^-), usually prepared via a TEMPO/bleach oxidation process from uncharged CNCs (obtained through the use of HCl during the isolation process). The dispersibility of these charged CNCs in aqueous and polar solvents renders solvent casting a powerful strategy to optimize their dispersion in polymer matrices, and for this reason solvent casting is currently the most employed approach to prepare CNC nanocomposites [68]. In fact, CNC-based nanocomposites can be traced back to the pioneering work of Cavaillé, Chanzy and coworkers in the mid-1990's [69–72]. In these studies, they showed that sulfate functionalized CNCs obtained from either wheat straw or tunicin could be dispersed in an aqueous latex (of a styrene and butyl acrylate copolymer) solution and that a nanocomposite could be obtained by solution casting. The resulting film exhibited significant improvements in the mechanical strength of the material. Key to the success of this approach is both the latex and CNCs are dispersible in water, resulting in homogenous dispersions.

It is important to note that the surface hydroxyl groups of CNCs can be functionalized using various synthetic strategies making the CNCs more dispersible in hydrophobic solvents and polymers, however, one must remember that functionalization will also impact the reinforcement capability of the CNCs by altering the interactions of the nanofillers with themselves and the matrix [73].

CNCs by their bio-derived nature are already present in our ecosystems, albeit usually embedded in a composite structure with other components, such as lignin, amorphous cellulose and hemicelluloses. Nonetheless an important aspect that needs to be studied is their potential impact on human and environmental health. While, a complete story is not yet known and much more work remains to be done in this area to better understand their effects, this aspect of CNC research is starting to become more active For example, Vartiainen and coworkers looked into *w*-CNF toxicity and found that no significant negative effects were observed in mouse and human cell viability tests [74]. An ecotoxicity test (*V. fischeri*) showed no effects of the *w*-CNFs below 300 mg/L and EC50 (effective concentration) values could not be obtained up to 2500 mg/L, meaning that the materials are safe unless concentrations are higher than those expected in worst-case environmental scenarios. More relevant to this review, the ecotoxicity of *w*-CNC-SO_3^- has been investigated by Kovacs and coworkers in nine different aquatic species, with most species not being significantly affected. A greater than 25 % reduction in the reproduction in one species (the fathead minnow) was observed only at high concentrations of the *w*-CNC-SO_3^- (> 290 mg/L) [75]. Preliminary studies into human/mammalian health have shown little-to-no oral toxicity, no dermal toxicity and generally low cytotoxicity at low concentrations. However, perhaps the biggest concern with any nanomaterial is its pulmonary toxicity [76]. Using a 3D *in vitro* triple cell coculture model of the human epithelial airway barrier, Rothen-Rutishauser and Weder observed that *c*-CNC-SO_3^-, when

Please cite this article as: C. Calvino, N. Macke, R. Kato et al., Development, processing and applications of bio-sourced cellulose nanocrystal composites, Prog Polym Sci, https://doi.org/10.1016/j.progpolymsci.2020.101221



Cellulose microfibrils Cellulose nanofibers Cellulose nanocrystals

Fig. 2. Hierarchical structure of cellulose and transmission electron micrographs of cellulose microfibrils, nanofibers and nanocrystals [38–41]. Copyrights 1997, 2007, 2008. 2014, respectively. Adopted with permission from John Wiley & Sons Inc, the American Chemical Society, the Royal Society of Chemistry and Elsevier Science Ltd, respectively.

Table 1
List of common sources used to access CNCs, CNC nomenclature used in this article along with their corresponding approximate length, width and aspect ratio.

Bio-source	Abbreviation	Length	Width	Aspect Ratio	Reference
Wood	*w*-CNC	100–200	3–5	20–60	[45,46]
Cotton (and Filter Paper)	*c*-CNC	100–300	5–15	10–40	[47,48]
Ramie Fiber	*rf*-CNC	50–250	5–10	5–40	[40,49]
Tunicate	*t*-CNC	500–3000	10–30	10–200	[50,51]
Bamboo	*bamboo*-CNC	50–400	5–20	15–20	[52,53]
Bacteria	*b*-CNC	100–1000	5–50	5–200	[54,55]
Phormium tenax	*ph*-CNC	100–200	5–15	10–20	[56,57]
flax	*f*-CNC	100–500	10–30	10–50	[58,59]

delivered as an aqueous suspension, do elicit dose-dependent cytotoxicity and (pro-)inflammatory response, but at a level that is significantly lower than multiwalled carbon nanotubes or crocidolite asbestos fibers [77]. However, other studies by Shvedova and coworkers on *w*-CNC-SO_3^- have shown that different and more adverse pulmonary outcomes can occur depending on whether the CNCs are in a suspension or are a freeze-dried powder [78].

Part of the challenge here is that there is not enough data at the moment to fully understand the effects of CNCs. Further complications arise as not all CNCs are created equal. For example, size and shape of the CNCs, as well as the nature of the functional groups on the CNCs will undoubtedly play a role in any ecological or biological effects. In addition, CNCs can be isolated using a range of protocols involving the use of different chemicals and different levels of purification, therefore leading to the fact that the different CNCs used in these studies may well have different levels of (toxic) contaminants. As such, there is certainly a need for more research in this area, the results of which will play an important role in the future of sustainable CNC composites.

2. CNC-reinforced bioderived polymers

2.1. *Polysaccharide-based composites*

Polysaccharides such as cellulose, starch, chitin, chitosan, alginates and various naturally occurring gums have attracted great interest as a source of sustainable polymers on account of their abundant supply, low cost, renewability, biodegradability and ease of chemical modification [79]. In addition, some polysaccharides and their derivatives also have good solubility in water, which readily disperses negatively charged CNCs, thus allowing for relatively facile access to composite materials.

2.1.1. *Chitosan and alginate-based composites with negatively charged CNCs*

Chitosan, derived from chitin the second most abundant natural polysaccharide after cellulose, is a natural linear polysaccharide consisting of (1→4)-2-amino-2-deoxy-β-D-glucan and is soluble in acidic water (Fig. 3). Chitosan has been investigated for use in

Please cite this article as: C. Calvino, N. Macke, R. Kato et al., Development, processing and applications of bio-sourced cellulose nanocrystal composites, Prog Polym Sci, https://doi.org/10.1016/j.progpolymsci.2020.101221

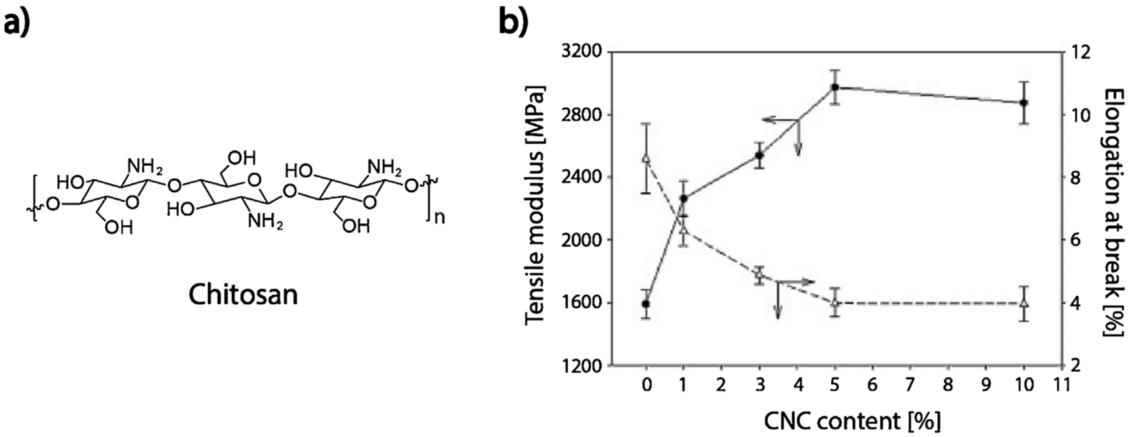


Fig. 3. **a**) Molecular structure of chitosan. **b**) Graphic showing the tensile modulus and the elongation at break of chitosan composites loaded with different *w*-CNC-SO_3^- content [83]. Copyright 2012. Adopted with permission from Elsevier Science Ltd.

a variety of different applications including biomedical, packaging and as a thickening agent [80–82].

Chitosan/*w*-CNC-SO_3^- composite films have been prepared by simple aqueous mixing of a suspension of *w*-CNC-SO_3^- with a 1 % w/v chitosan acidic solution followed by solvent casting. The resulting composites show roughly 80 % higher tensile modulus (ca. 3 vs. 1.6 GPa) and a 50 % reduction in elongation at break (4.0 vs. 8.6 %) with the inclusion of 5 wt. % *w*-CNC-SO_3^- when compared to the neat chitosan films [83]. The increase in the mechanical strength was ascribed to the formation of strong ionic bonding interactions between the negatively charged *w*-CNC-SO_3^- and positively charged amine groups on chitosan. In addition, the same filler content loading has been shown to lower the water vapor permeability (2.4 vs. 3.3 g·mm/m^2/day/kPa) by 25 %, consistent with increased crystallinity induced by the incorporation of the CNCs. In fact, there are numerous reports that show mechanical property improvements in chitosan-based materials when CNCs are incorporated [84,85], specifically for applications in drug delivery [86], gas barrier [87] and filtration materials [88].

Alginate is another water-soluble polysaccharide (this time in basic solutions) from which CNC composites have been prepared and studied. For example, alginate/*w*-CNC-SO_3^- composite films prepared by solvent casting from an aqueous mixture of sodium alginate and *w*-CNC-SO_3^- showed improved tensile strength relative to neat alginate. The tensile strength increased with *w*-CNC-SO_3^- content up to the addition of 5 wt. % (tensile strength of ca. 80 MPa vs ca. 55 MPa for neat alginate) [89]. The presence of carboxylate moieties on the alginate means that alginate gels can be formed through the addition of Ca^{2+} ions on account of the formation of carboxylate-Ca^{2+}-carboxylate salt bridges (Fig. 4**a**) [90]. A number of reports in the literature investigate alginate/CNC hydrogels and aerogels crosslinked with Ca^{2+} ions [91–93]. As an example, alginate/CNC-based aerogels have been prepared by adding an aqueous Ca^{2+} solution to a lyophilized mixture of alginate and *c*-CNC-COOH (10 wt. % CNCs) [94]. The resulting ionically crosslinked gels were then lyophilized to yield the aerogel (Fig. 4**b**). Mechanical properties of both the alginate/Ca^{2+} and alginate/*c*-CNC-COOH/Ca^{2+} aerogels showed that the addition of CNCs enhanced the compressive strength by ca. 190 % at 70 % compressive strain (compressive strength of ca. 130 kPa vs ca. 45 kPa for alginate/Ca^{2+} aerogel), and that carboxylic acid CNCs had a higher reinforcement effect relative to sulfated CNCs (ca. 100 kPa).

The incorporation of CNCs is not only a benefit for mechanical reinforcement but they can also be used to alter other properties of the material. For example, Tam et al. reported the use of CNC-containing alginate aerogel beads for the adsorption of the cationic dye methylene blue [95]. Alginate/*w*-CNC-SO^{3-}/Ca^{2+} (1 wt. % CNCs) hydrogel beads were prepared by dropping the aqueous mixture of alginate and *w*-CNC-SO^{3-} into Ca^{2+} solution followed by freeze drying to obtain the aerogel material. The adsorption of methylene blue, conducted by stirring the aerogel beads in methylene blue aqueous solutions, showed that the dye removal increased from 20 % to 60 % by adding CNCs into the aerogel, presumably (at least in part) by the increase in negative charges in the composite system.

2.1.2. *Cellulose-based composites with negatively charged CNCs*

As mentioned before, cellulose is the most bio-available polysaccharide and historically, numerous cellulose derivatives have been produced and sold on a commercial scale. In particular, cellulose esters and cellulose ethers, produced by chemical modification of cellulose, have found use in a wide variety of applications [96]. For example, cellulose acetate butyrate (CAB) is one of the most commonly used cellulose esters in the coatings industry on account of its enhanced solubility relative to cellulose, its chemical resistance and the fact that it is compatible with other polymers [97]. Furthermore, there is a certain amount of property tunability in these materials by altering the ratio of butyrate to acetate moieties on the cellulose backbone. Although the addition of CNC fillers may be expected to improve some of the properties of CAB, its general insolubility in water or polar solvents makes it difficult to prepare homogeneous CAB/CNC composite films.

As will been seen throughout this review, the insolubility of a polymer matrix in water or polar solvents is a recurring challenge in accessing many CNC composites. One way to tackle this difficulty is to use a solvent-exchange method. This approach involves the dispersion of the CNCs in water followed by the addition of an organic solvent that both dissolves the polymer and is miscible with water. The mixture is then centrifuged, the supernatant removed, more organic solvent is added to the remaining gel and the system agitated. This process can be repeated resulting in CNC-organic solvent dispersions that have limited temporal stability (Fig. 5). To access the nanocomposites, a solution of the polymer in the organic solvent is added to the organic solvent-suspended CNCs and the films are obtained by solution casting.

As an example, Oksman et al. reported CAB/*w*-CNC-SO_3^- composite films prepared via a solvent-exchange procedure (from water to acetone, a good solvent for CAB) followed by solution casting [98]. The CAB composite film with 10 wt. % *w*-CNC-SO_3^- showed 30 times higher storage modulus (ca. 85 MPa) than that of pure CAB (ca. 3 MPa) at 155 °C, above the glass transition temperature (136 °C).

Please cite this article as: C. Calvino, N. Macke, R. Kato et al., Development, processing and applications of bio-sourced cellulose nanocrystal composites, Prog Polym Sci, https://doi.org/10.1016/j.progpolymsci.2020.101221

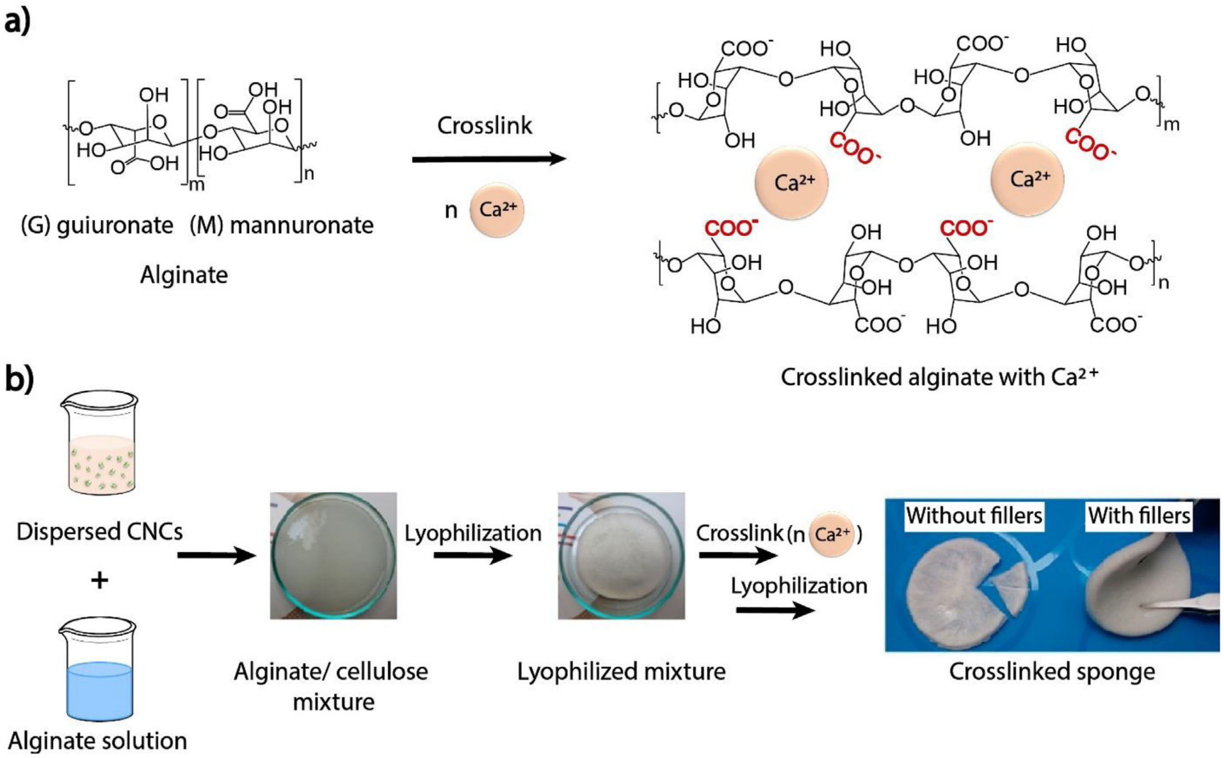


Fig. 4. **a**) Molecular structure of alginate composed of guiuronate and mannuronate units and the proposed resulting crosslink structure upon addition of calcium cations. **b**) Scheme depicting the preparation of a crosslinked alginate sponge. Reproduced and adapted from references [90] Copyright 2018. Reproduced with permission from MDPI AG, and [94], Copyright 2012. Reproduced with permission from the American Chemical Society.

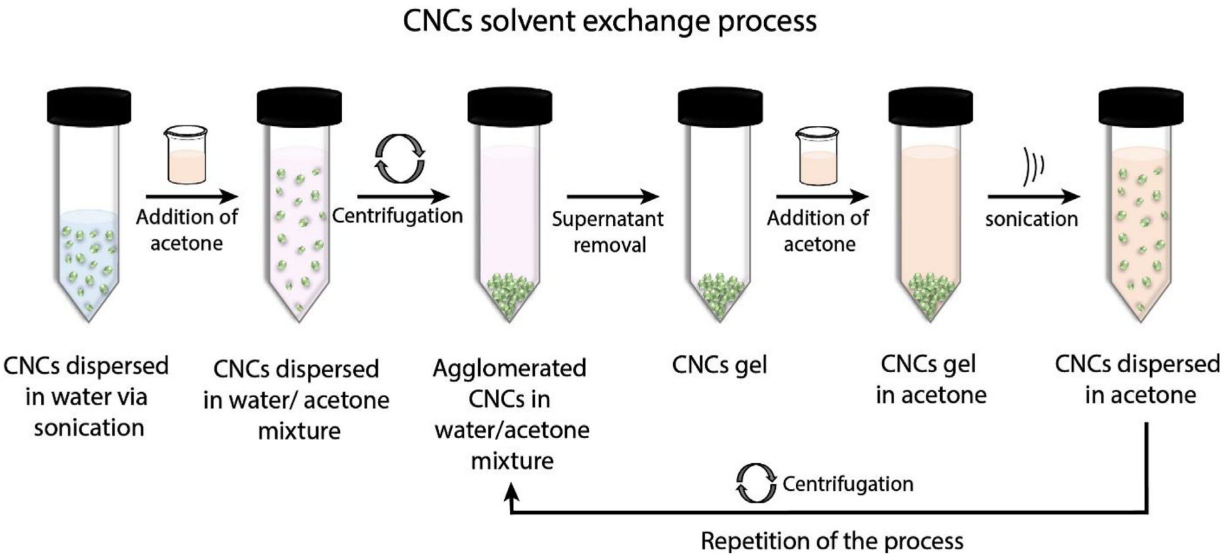


Fig. 5. Scheme depicting a standard CNC solvent exchange process from aqueous solution to a water miscible solvent such as acetone.

2.1.3. Starch-based composites with negatively charged CNCs and plasticizer

Starch is another commercially available biopolymer that can be obtained from a number of renewable plant sources, such as corn, potatoes, peas, rice, etc [99,100]. Starch is comprised of two polysaccharides, amylose (20–25 wt. %) and amylopectin (75–80 wt. %), which are the linear and branched polymers of α-glucose respectively (Fig. 6**a**). In its natural form, the two components combine to form a semi-crystalline, hydrogen-bonded network, resulting in an insoluble material that is difficult to reprocess. Solution processing of the natural material is difficult as starch is insoluble in cold water and undergoes gelatinization in hot water, while melt processing is not possible as thermal decomposition starts to occur before T_m. Dried starch is brittle and mechanically weak, making it uninteresting as a replacement for any plastic [101]. While water is known to plasticize starch, the resulting material has poor properties that includes high water vapor permeability and low tensile strength [102]. In addition, starch is hygroscopic, so its water content is often difficult to control. Nonetheless starch is cheap and has generated considerable attention as a biodegradable granular filler in commodity plastics; however, such starch-based fillers generally have low reinforcing capability [103].

Please cite this article as: C. Calvino, N. Macke, R. Kato et al., Development, processing and applications of bio-sourced cellulose nanocrystal composites, Prog Polym Sci, https://doi.org/10.1016/j.progpolymsci.2020.101221

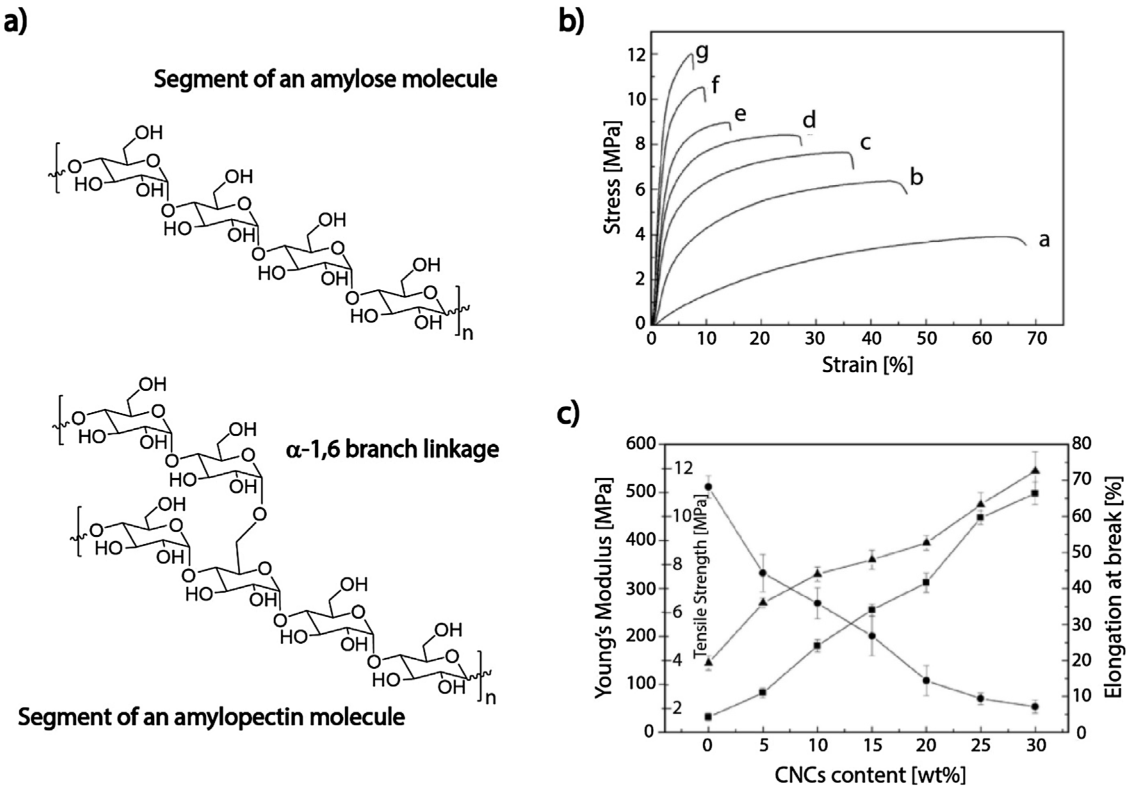


Fig. 6. **a)** Molecular structure of the two polymer present in starch, the linear form; amylose and the branched form; amylopectin. **b)** Strain-stress curves of starch/glycerol (ca. 35 wt. % of starch)/*f*-CNC-SO_3^- nanocomposite film with 0 wt. % (a), 5 wt. % (b), 10 wt. % (c), 15 wt. % (d), 20 wt. % (e), 25 wt. % (f) and 30 wt. % (g) of *f*-CNC-SO_3^-. **c)** The mechanical properties of tensile strength (▲), Young's modulus (■) and elongation at break (●), of the same nanocomposite film. The composite film was kept at 43 % relative humidity. [108], Copyright 2008. Adopted with permission from Express Polymer Letters.

Plasticizers other than water (such as polyols, urea, formamide, etc.) can be used to access more mechanically flexible and melt processable starch-based materials [104]. As such, these plasticized starches are able to be manufactured using traditional methods employed for synthetic plastics giving access to cheap and renewable bio-degradable materials that can be used in short-lived applications, such as packaging [105]. Unfortunately, the use of a plasticizer to improve processability comes at the cost of mechanical strength and usually does not improve water sensitivity issues. Thus, the use of a renewable filler such as CNCs as a reinforcing agent is one strategy to cope with the poor mechanical performance of plasticized starch while maintaining eco-friendly characteristics. Various reports have demonstrated a high compatibility between starch and CNC fillers, presumably as a consequence of the strong hydrogen bonding interactions between the two polysaccharide structures [106,107].

Glycerol is a commonly used plasticizer to access thermoplastic starch [109,110], although it has to be remembered that water also plays a role in such materials [111]. Interestingly, the addition of glycerol to starch yields a phase separated material (a glycerol rich and amylopectin rich phase) as highlighted by the presence of two glass transitions (ca. -50 and 40 °C) [111]. Fig. 6**b** and **c** show the effect that the incorporation of *f*-CNC-SO_3^- has on the mechanical properties of starch/glycerol (ca. 35 wt. % of starch) composites [108]. Such CNC composites can be accessed by mixing starch granules, glycerol and *f*-CNC-SO_3- in water before gelatinizing via heat treatment. Drying of the gels results in composite films which exhibit properties commonly observed in CNC reinforced materials; increases in the tensile strengths (from 4 to 12 MPa) and Young's moduli (ca. 30–500 MPa) along with decreases in the elongations at break (ca. 70 to 10 %) with varying CNC content from 0 to 30 wt. %, respectively. In comparison to multi-walled carbon nanotubes (MWCNT), a less sustainable filler that is also often used to reinforce polymers, the starch/CNC system performs just as well, if not better. While exact comparisons are difficult to make on account of variances in source materials and processing methods, the starch/glycerol/MWCNT materials showed around 40 % increase in Young's modulus, compared to nearly 250 % increase with *f*-CNC-SO_3^- at the same 5 % loading [112]. An advantage the CNCs have over MWCNTs from a mechanical reinforcement perspective is they are water dispersible and as such are generally easier to process from aqueous solutions to yield composites with a more homogenous nanofiller dispersion.

The starch/*f*-CNC-SO_3^- composites also exhibited two glass transitions (T_gs) (similar to the unreinforced matrix) with both transitions shifting to slightly higher temperatures with higher CNC content. Wide-angle x-ray scattering (WAXS) measurements showed the appearance of a new amylopectin crystal peak in the starch/glycerol/*t*-CNC-SO_3^- composite materials, implying that the CNCs also act as a nucleating agent. It was suggested that the glycerol (and water) rich phase would localize near the CNC surfaces [50,113] potentially leading to a two-fold effect: (1) the local plasticization of amylopectin chains near the CNCs, aiding in transcrystallization, and (2) antiplasticization of the amylopectin phase, reducing the overall material ductility.

The use of sorbitol in place of glycerol as a plasticizer for starch yields materials that only exhibit one T_g, which has been ascribed to a decrease in mobility of the sorbitol. Starch/sorbitol (ca. 30 wt. % of starch) composite films containing *t*-CNC-SO_3^- have been prepared by solvent casting. Interestingly, these materials do not exhibit transcrystallization of amylopectin nor show a significant antiplasticizing effect, suggesting that sorbitol does not accumulate near the CNCs [114]. Compared to pure plasticized starch/sorbitol films, a starch/sorbitol/*t*-CNC-SO_3^- (ca. 25 wt. %) composite film

Please cite this article as: C. Calvino, N. Macke, R. Kato et al., Development, processing and applications of bio-sourced cellulose nanocrystal composites, Prog Polym Sci, https://doi.org/10.1016/j.progpolymsci.2020.101221

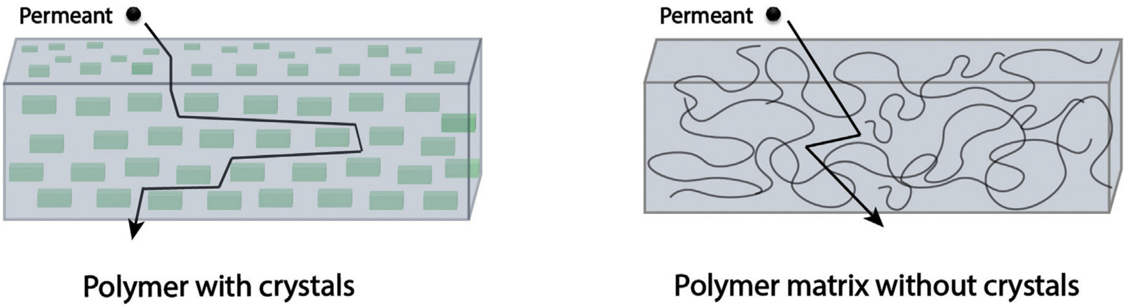


Fig. 7. The presence of non-permeable crystals (e.g. CNCs) in the polymer matrix (left) increases the permeant tortuosity/path length thus reducing permeability of water vapor and oxygen relative to an amorphous polymer matrix (right) [131]. Copyright 2004. Reproduced with permission from Elsevier Science Ltd.

showed an increase in tensile strength from ca. 5 MPa to 40 MPa and Young's modulus from ca. 50 MPa to 750 MPa (measured at 43 % relative humidity), while elongation at break of films with and without CNCs were low (below 10 %) [115]. Overall the starch/sorbitol/*t*-CNC-SO_3^- materials showed better mechanical reinforcement than the starch/glycerol/*t*-CNC-SO_3^- composites. It was suggested that the absence of sorbitol accumulation near the CNCs allows more effective stress transfer between CNCs and the starch matrix, leading to composites that exhibit a more significant increase in the modulus and tensile strength relative to pure glycerol-plasticized materials.

2.2. Poly(lactic acid)-based composites

Poly(lactic acid) (PLA) (most commonly the L-lactide enantiomer, PLLA) is currently one of the most commercially relevant bio-based polymers on account of its easy, and relatively cheap, access on a large scale as well as its overall eco-friendly properties such as bio-degradability, renewability, non-toxicity and compostability [116–118]. PLA can be prepared via ring opening polymerization of lactide monomers, which can be obtained via distillation from corn, sugar cane and other fermentation crops, giving access to large scale production at competitive costs relative to petroleum-based polymers [119]. Additionally, unlike other bio-sourced polymers, PLA can be melt-processed by extrusion, thermoforming, or injection molding to be shaped into fibers, films, or other functional forms [120].

While PLA has the potential to be a promising replacement for some commodity petroleum-based plastics, as with other bio-based polymers, it is limited in its mechanical and thermal properties. For example, its heat distortion temperature (HDT, the temperature at which the polymer deforms under a specific load) is low (55 °C) which, along with its brittleness (strain at break ~2.5 %) and poor impact resistance (impact strength ~2.6 kJ/m^2), limits its utilization in a range of applications [116]. Nonetheless, PLA has already been used in some commercial applications, including packaging material e.g. corn chip bags. However, the poor barrier properties of the neat material (oxygen transmission rate over 30 cm^3/m^2/day compared to most commercial materials with less than 15 cm^3/m^2/day) prevent application in air and water-tight systems [121,122]. Since plastic packaging was a $260bn market in 2013, it is clear why improving these properties could make a major impact in the industry [7].

A range of strategies have been developed to overcome these issues and improve PLA's overall properties, such as copolymerization, stereocomplexation, polymer blending and addition of plasticizers and/or nanofillers [123–126]. While all of these approaches result in the enhancement of either thermomechanical or barrier properties of PLA, some of them require the addition of unsustainable components to the sustainable matrix, reducing the eco-friendly aspects of the material. The use of cellulose nanocrystals as a nanofiller, on the other hand has the potential to address the material drawbacks while maintaining the green nature of the material.

2.2.1. Poly(lactic acid)-based composites with negatively charged CNCs

As discussed above, solution processing is the most common way to access CNC composites. Unfortunately, PLA is not soluble in water and as such, direct mixing with aqueous CNC suspensions is not possible. The most common solvent used for solution processing PLA in the literature is chloroform, however, good dispersion of CNCs in this solvent is difficult. As discussed in Section 2.1.2, solvent exchange processes (Fig. 5) can be used to access dispersions of CNCs in organic solvents. As chloroform is not miscible with water, the aqueous dispersion of CNCs needs to be first solvent exchanged into a water miscible organic solvent (e.g. acetone) and then exchanged to chloroform. Lagaron et al. investigated if such a solvent exchange process aids the dispersion of CNCs in PLLA matrix [127]. To do this, chloroform dispersed *w*-CNC-SO_3^- were prepared either by the solvent exchange process or by adding in freeze-dried *w*-CNC-SO_3^- (from water) directly to chloroform followed by sonication. The two different chloroform CNCs suspensions were independently mixed with PLA in chloroform and cast to furnish nanocomposites loaded with 1, 2, 3 and 5 wt. % *w*-CNC-SO_3^-.

No matter how the CNCs were dispersed in the chloroform the modulus and tensile strength of the composites were reduced relative to neat PLLA suggesting inhomogeneous dispersion [127] and that solvent exchange into chloroform does not appear to be a viable route to homogenously dispersed CNCs in PLA. Nonetheless, the incorporation of CNCs by either route did result in an increase in the crystallinity of the PLLA (e.g. from ca. 9 % for neat PLLA to 15 % with 1 wt. % of freeze-dried *w*-CNC-SO_3^-) as well as to an increase in water and oxygen barrier properties (from 1.37 $\times$ 10^{-17} $m^3{\cdot}m/s{\cdot}m^2{\cdot}Pa$ of O_2 for neat PLLA down to 0.23 $\times$ 10^{-17} $m^3{\cdot}m/s{\cdot}m^2{\cdot}Pa$ with 1 wt. % of freeze-dried CNCs), suggesting that the CNCs act as a nucleating agent for PLLA [128].

These latter observations have been made in a number of studies and as such, the ability of CNCs to enhance the barrier properties is one of the advantages of the PLA/CNC composites. It has been shown that the degree of barrier improvement for PLA-based CNC nanocomposites depends on the surface modification of the CNCs and the processing methods [129,130]. In addition, it was also reported that the type of CNC polymorph (cellulose I vs. cellulose II) employed can play a role in barrier properties. Dhar et al. showed that the incorporation of 3 wt. % *bamboo*-CNC-SO_3^- (either in the cellulose I or cellulose II form) into PLLA by solvent exchange into chloroform (via acetone) and casting, resulted in films with different oxygen permeation properties; 14.0 cm^3/m^2/day for cellulose I CNC composites and 7.8 cm^3/m^2/day for cellulose II CNC composites [121]. A common hypothesis used to explain why CNCs improve

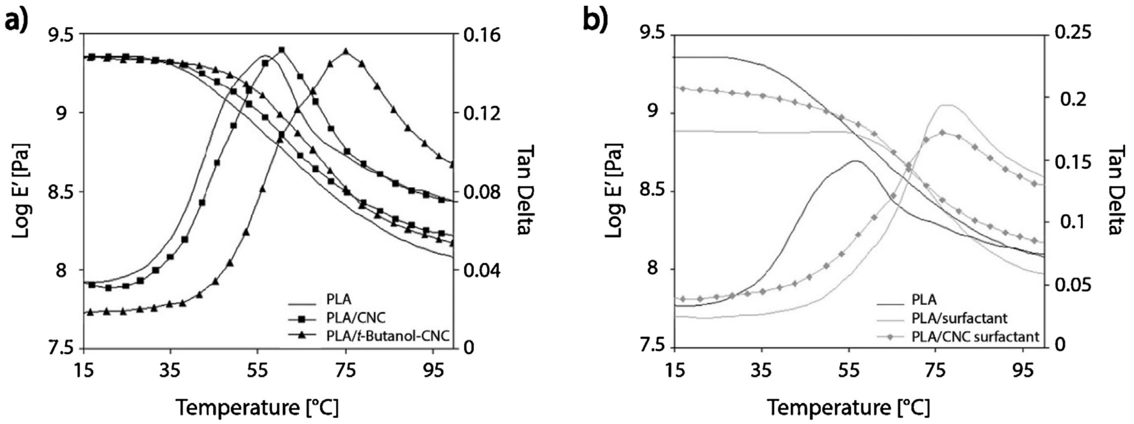


Fig. 8. Storage modulus and tan delta curves determined by DMA measurements of **a**) a comparison of neat PLA, PLA/CNC composite and PLA composite with tert-butanol CNCs. **b**) and BNA surfactant. Reproduced and adapted with permission from Ref. [138], Copyright 2007. Adopted with permission from Elsevier Science Ltd.

barrier properties is that the addition of these non-permeable crystals results in a more tortuous pathway for transport of gas or water molecules through the film, whereas the matrix without crystals does not hinder this transport (Fig. 7) [131]. In addition, the increased PLLA crystallinity induced by the nucleating effect of the CNCs reduces free volume between chains and creates more internal impermeable barriers that further limit the diffusion of small molecules [132]. It is worthy to note that improved barrier properties have been observed upon incorporating CNCs into other bio-based matrices such as alginate, polyhydroxybutyrate (PHB) and starch [133–137].

Petersson et al. investigated a slightly different protocol to access PLA/CNC composites. In this case the *w*-CNC-SO_3^- were solvent transferred from water to *t*-butanol and the *t*-butanol CNC dispersion was then freeze-dried. Those freeze-dried CNCs were then dispersed in chloroform by ultrasonication [138]. *t*-Butanol has a melting point of 23–25 °C, which was expected to accelerate the freezing of the suspension and thereby limit the aggregation of the CNCs during the freezing process. The mechanical properties of PLA/CNC composites prepared from chloroform suspensions of either *t*-butanol freeze-dried *w*-CNC-SO_3^- or water freeze-dried *w*-CNC-SO_3^- showed that there is indeed a better mechanical reinforcement when using the *t*-butanol freeze-dried *w*-CNC-SO_3^- (Fig. 8**a**). At 60 °C there is 64 % increase in storage modulus, *E'* for 5 wt. % *t*-butanol freeze-dried *w*-CNC-SO_3^- relative to a 23 % increase when using water freeze-dried *w*-CNC-SO_3^-. In addition, there is a shift to higher temperatures in the tan δ peak by 15 °C with the *t*-butanol freeze-dried *w*-CNC-SO_3^- films (compared to the films made with water freeze-dried *w*-CNC-SO_3^-), indicating a more pronounced effect on the segmental motion of PLA chains in these composites (Fig. 8**b**) which is consistent with a better dispersed nanofiller.

Petersson et al. also investigated the use of surfactants as an alternative to improve the dispersion of the CNCs in PLA. It was assumed that the surfactant would hinder the hydrogen bonding between the CNCs during the freeze-drying process and result in a better distribution within the matrix. The selected surfactant, Beycostat A B09 (BNA), a phosphoric ester of polyoxyethylene(9)nonylphenyl ether, had been employed earlier by Heux et al. as a coating for *c*-CNC-SO_3^- and *t*-CNC-SO_3^- to yield birefringent toluene suspensions [48]. The surfactant coated *w*-CNC-SO_3^- also showed birefringence when dispersed in chloroform (which was not observed with the *t*-butanol freeze-dried *w*-CNC-SO_3- discussed above), highlighting the benefit of the surfactant to improve the dispersion of the nanofillers. The composites where made by simple solution casting resulting in a transparent film upon melt pressing, consistent with good dispersion of the CNCs in the matrix. Comparison of dynamic mechanical analysis (DMA) curves of PLA/surfactant composites with the PLA/surfactant/*w*-CNC-SO_3^- composites showed that the CNC composite materials had an 83 % greater storage modulus at 20 °C. However, it is important to note that both materials show reduced modulus relative to neat PLA at this temperature. In fact, while there is a shift in tan δ of ca. + 20 °C for the surfactant containing materials relative to PLA, there is only a small increase in modulus for the PLA/*w*-CNC-SO_3^-/surfactant composites relative to PLA observed above 55 °C. Overall, while these CNCs may be well dispersed in the matrix, the mechanical studies are consistent with the surfactant coating on the CNCs preventing direct interactions between the PLA and the CNCs. As such, while it is important to obtain well dispersed CNCs in a matrix, this in and of itself is not enough to obtain good mechanical reinforcement. Ensuring good interfacial adhesion between the filler and matrix and/or good filler-filler interactions are also important considerations.

One application-focused benefit of surfactant addition is the blocking of hydrophilic groups on the CNC surfaces, which can reduce water uptake and transport. Reduced water vapor permeability (WVP) has been shown to prevent bacterial growth in packaging materials and the hydrophilic nature of negatively charged CNCs can be antithetical to this goal [139]. In one study, Fortunati and coworkers showed that the reduction in WVP caused by increased tortuosity and crystallinity in a PLA matrix was offset entirely by the hydrophilicity of *w*-CNC-SO_3^- at 1 wt. % loading [140]. Adding surfactant (Beycostat A B09) blocked the hydrophilic surface groups from associating with water molecules and decreased WVP by 34 % relative to the negatively charged *w*-CNC-SO_3^- composites at the same 1 wt. % loading.

Water uptake of PLA-based materials can have significant effects on their material properties. The degradation rate of PLA has been shown to be influenced by the relative humidity of the surrounding environment, with more humid environments causing PLA to degrade more quickly [141]. More rapid degradation of PLA/cellulose fiber composites has been observed with both macrocellulose (wood pulp and wood fibers) [142] as well as nanocellulose [143] composites, where the rate changes are attributed to the increased water uptake caused by the hydrophilic cellulose. To further back up this hypothesis, the use of surfactant-coated CNCs at a 1:1 surfactant to CNC weight ratio resulted in a reduced PLA degradation rate under composting conditions with 5 wt. % *w*-CNC-SO_3^-/surfactant in a PLA matrix [143]. While not extensively investigated in many matrices, it may be possible to somewhat tune the degradation rate of CNC sustainable composites through the hydrophilic or hydrophobic modification of the nanocrystal surface, broadening

Please cite this article as: C. Calvino, N. Macke, R. Kato et al., Development, processing and applications of bio-sourced cellulose nanocrystal composites, Prog Polym Sci, https://doi.org/10.1016/j.progpolymsci.2020.101221

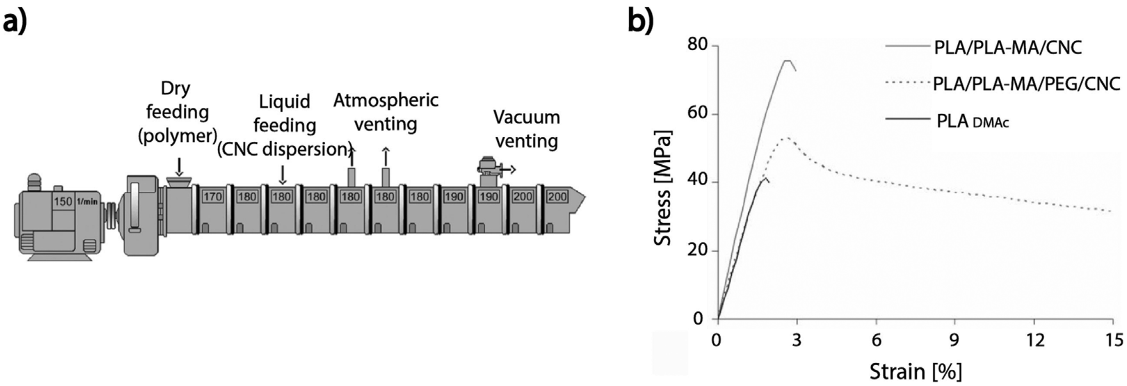


Fig. 9. **a**) Scheme showing the different compartments (feeding zone, venting zone and vacuum zone) of an extruder used to process CNC composites . **b**) The comparison of the measured tensile stress strain curves of PLA/PLA-MA/CNC, PLA/PLA-MA/PEG/CNC and PLA$_{\mathrm{DMAc}}$ [145]. Copyright 2006. Adopted with permission from Elsevier Science Ltd.

the application window for bio-based CNC composite packaging materials.

The future of packaging materials is trending toward more active materials which, for example, have antimicrobial characteristics built into the packaging, reducing the likelihood of bacterial build up over the lifetime of the product. Unmodified negatively charged CNCs have few to no antimicrobial properties, but the addition of other additives, such as silver nanoparticles, can impart these desired effects [140]. Unfortunately, the same hydrophobic surface modifications that have been used to reduce water uptake have also been shown to have negative effects on antibacterial nanoparticle migration and leeching. Fortunati and coworkers showed enhanced leeching in PLA films filled with *w*-CNC-SO$_3^-$ coated with an ethoxylated nonylphenol surfactant and silver nanoparticles [144], presumably on account of increased mobility in the hydrophobic surfactant layer. In some cases, as much as 10 times increase in the amount of nanoparticle leeching was observed relative to the neat PLA films or PLA loaded with unmodified *mcc*-CNC-SO$_3^-$.

Surfactants are not the only additives that have been investigated to access improved PLA/CNC composites. Oksman et al. studied the use of *N*,*N*-dimethylacetamide (DMAc) with LiCl for the preparation of CNC-based PLA nanocomposites [145]. It is important to note that DMAc/LiCl mixtures with high LiCl content dissolve cellulose and allow access to individual cellulose macromolecules [146,147]. However, DMAc containing a lower amount of LiCl (0.5 wt. %) can be utilized to separate individual *w*-CNC-SO$_3^-$ from microcrystalline cellulose (MCC) with ultrasonication and allow access to relatively concentrated *w*-CNC-SO$_3^-$ suspensions (10–17 wt. %). Oksman et al. investigated melt mixing of PLA with the concentrated DMAc/LiCl/*w*-CNC-SO$_3^-$ suspensions. The CNC suspensions (enough to obtain 5 wt. % CNCs in the final composite) were pumped directly into an extruder containing molten PLA at 170−200 °C. The extruder was equipped with several venting systems that allowed the removal of vapors upon heating (Fig. 9**a**) [145]. However, using this melt processing technique resulted in brown/degraded materials. To address this issue processing aids, such as polyethylene glycol (PEG1500) (15 wt. %) or maleated PLA (PLA-MA, 2.2 % maleic anhydride) (10 wt. %), were incorporated into the molten PLA to decrease the viscosity or act as a coupling agent, respectively.

Fig. 9**b** shows the stress-strain curves of three different compositions of the melt processed PLA using this technique. PLA$_{\mathrm{DMAc}}$ is the film formed by simply injecting a DMAc/LiCl solution (i.e. no CNCs) into molten PLA and shows stress at break and strain at break similar to neat PLA. Adding in the DMAc/LiCl/*w*-CNC-SO$_3^-$ suspension to a molten mixture of PLA and PLA-MA results in a film that exhibits almost double the tensile strength relative the PLA$_{\mathrm{DMAc}}$ (ca. 78 and 40 MPa, respectively) and an increase in Young's Modulus (3.9 vs. 2.9 MPa). These values compare well with PLA composites containing maleic anhydride-modified multi-walled carbon nanotubes (MA-MWCNT) [148]. The PLA/MA-MWCNT material showed a tensile strength of around 76 MPa at a similar 4 parts per hundred loading, showing that the CNC-based composites offer a competitive, renewable alternative to MWCNTs in this case.

Interestingly the addition of PEG (1500 g/mol) to the melt processed PLA/PLA-MA/PEG/*w*-CNC-SO$_3^-$ films yields a more ductile material that exhibits an eight times increase in the strain at break (up to 18 %) while also showing a slight increase maximum tensile strength relative to PLA$_{\mathrm{DMA}}$. No explanation was provided on why the PEG improved the ductility of this PLA/PLA-MA/PEG/*w*-CNC-SO$_3^-$ composite. However, similar effects have been previously observed in other PEG/CNC containing composites and has been attributed to the interactions between the low molar mass PEG and CNCs, reducing the CNC-CNC interactions and improving their dispersion in the matrix [149]. While the use of DMAc/LiCl/*w*-CNC-SO$_3^-$ does allow access to melt processable PLA/CNC composites, the DMAc/LiCl appears to result in the degradation of the *w*-CNC-SO$_3^-$ at high temperatures [145], as was suggested by the brown-colored composites obtained. As such, optimization in the compounding process would require the use of a feed medium which does not cause CNC (or PLA) degradation at the high temperatures required for processing. Additionally, this study highlights how the addition of a coupling/compatibilizing agent (in this case the PLA-MA) into the polymer melt can be used to prevent/inhibit the re-aggregation of the CNCs upon removal of the dispersing medium [150,151].

The use of plasticizers has been investigated as a way to access more flexible PLA/CNC composites. For example, the natural compound limonene has been shown to plasticize PLA (20 wt. % blended into PLA drops the T_g from 58 to 42 °C), lower its crystallinity and improve its barrier properties, which are important factors in packaging films. To access PLA/limonene/CNC composites, the PLA and limonene were melt blended (15–25 wt. % of the plasticizer at ca. 180 °C) prior the direct addition of 1 or 3 wt. % of *ph*-CNC-SO$_3^-$ (dried at 40 °C overnight) to the molten polymer [57,152]. The resulting films were transparent and exhibited a single T_g (DSC) at ca. 34 (1 wt. %) or 32 °C (3 wt. %). The DSC also revealed a decrease in the cold crystallization temperature (T_{cc}) of PLA in the composites consistent with the dispersed *ph*-CNC-SO$_3^-$ promoting the crystallization of the matrix in the plasticized PLA [153]. The PLA/limonene/*ph*-CNC-SO$_3^-$ composites revealed high values of elongation at break 288 % (1 wt. % CNC) and 272 % (3 wt. % CNC) primarily as a consequence of the plasticization effect of the limonene (PLA/limonene has an elongation of break ca. 250 %).

As such, adding *ph*-CNC-SO_3^- (up to 3 wt. %) to the PLA/limonene system appears to not have a significant effect on the mechanical properties.

The above discussion shows that it is possible to utilize different processing techniques and/or additives to enhance the dispersion of the CNCs in PLA. However, to date the amount of mechanical reinforcement in such composites appears not to have been optimized. The use of plasticizers/surfactants may enhance the mobility of PLA chains in the matrix, benefiting elongation at break, but they can also block CNC-CNC interactions along with filler-matrix interactions. As such, while the organization of such agents at the CNC surfaces may improve dispersion, it can also reduce the ability for stress transfer from the matrix to the filler, limiting mechanical reinforcement. Thus, a key challenge here is how does one effectively quantify the level of dispersion of the CNCs within the matrix. Does one method provide better dispersion than another? Given that the different processes discussed above add in a variety of different components it is hard to isolate the simple effect of the added component versus the effect of CNC dispersion on the material properties. Instead, one must rely on less objective evidence, like birefringence in solution and transparency of materials, but neither of these provide a quantifiable level of homogeneity. In the end what is important is how well does a given processing technique improve the properties of the composite but there is certainly an argument to be made for the development of more comprehensive methods for measuring the CNC filler dispersion.

2.2.2. *Poly(lactic acid)-based composites with polymer grafted CNCs*

Given the challenges of dispersing CNCs in PLA, primarily on account of the differences in polarity of the filler and matrix, covalent functionalization of the CNCs is an alternative strategy to adding additives to aid their dispersion in PLA. Most of the work in this area has focused on grafting polymers to the CNCs and investigating the resulting PLA composites. It has been demonstrated that the grafting of polymer chains to the CNC surface can not only improve the dispersion of the CNCs within the matrix but can also enhance the interfacial adhesion between the filler and matrix [154]. Grafting of polymers to the CNCs prevents aggregation of the nanocrystals through steric hindrance and the nature of the interactions between the grafted polymer and matrix can be used to facilitate dispersion within the matrix.

Polymer grafting to the CNCs can be achieved by either a "grafting-to", where a preformed polymer chain is reacted with functional groups on the CNC surface, or "grafting-from" method, where an initiating site on the surface is used to polymerize the monomer directly from the CNCs. For PLA specifically, the "grafting-from" approach has generally been employed in the preparation of the modified fillers, predominantly through the use of the surface –OH groups as initiating sites for ring opening polymerization (ROP) [155–158]. Not surprisingly, the most common polymer grafted from the CNCs in this context is PLA (Fig. 10**a**). This is most commonly achieved using tin(II)-based catalysts and through the variation of the monomer concentration, time and/or the addition of "free" OH groups, the molecular weight of the grafts can be somewhat controlled [159].

Generally, it is expected that grafted chains with higher molecular weight will penetrate deeper into a polymer matrix, assuming a constant matrix molecular weight and neutral or favorable interactions between the polymer graft and the matrix [160]. This should enhance the interfacial adhesion between the matrix and filler and result in better stress transfer from the matrix to the nanomaterial when load is applied. To the best of our knowledge detailed studies focusing on this aspect have yet to be carried out with CNC-based composites. However, Lönnberg et al. have shown that polycaprolactone (PCL) composites (matrix M_n ca. 80,000 g/mol) containing 10 wt. % PCL-grafted microfibrillated cellulose (MFC-*g*-PCL) exhibited better mechanical reinforcement with MFC-*g*-PCL that have longer grafts (Young's Modulus ca. 325 MPa for graft with M_n ca. 2200 g/mol and 290 MPa for graft with M_n ca. 700 g/mol). This compares to a Young's modulus of 190 MPa for the neat PCL and 260 MPa for the PCL reinforced with unmodified MFC [161]. However, this increase in stiffness does come at a cost of ductility, where the neat material had an elongation at break of roughly 900 % while all of the 10 wt. % composite materials fractured at less than 25 % strain.

Goffin et al. prepared *rf*-CNC-*g*-PLLA by carrying out the ROP of L-lactide in toluene-dispersed *rf*-CNC-SO_3^-, obtained via a solvent exchange process. The polymer-grafted *rf*-CNC-*g*-PLLA were shown to result in more stable chloroform suspensions after 3 days than the unmodified *rf*-CNC-SO_3^- or a blend of PLLA with *rf*-CNC-SO_3^-, thus highlighting the benefits of the polymer modification for compatibility with non-polar media [156]. Composites were prepared by melt blending *rf*-CNC-*g*-PLLA in PLLA with up to 8 wt. % filler, which resulted in nearly colorless materials with varying degrees of transparency depending on the CNC content (more CNCs resulted in hazier materials). Comparatively, materials prepared with *rf*-CNC-SO_3^- showed the expected thermal degradation upon melt processing at the same temperatures, 185–200 °C, suggesting that the polymer grafting aids the thermal stability of the CNCs. As seen in Section 2.1.3 with negatively charged CNCs, these functionalized CNCs are also capable of acting as nucleating agents in semi-crystalline matrices [162]. DSC analysis of the PLLA/*rf*-CNC-*g*-PLLA composites showed an increased in crystallinity and a decreased crystallization half-time (the time at which the extent of crystallization reaches 50 % completion) with the addition of *rf*-CNC-*g*-PLLA. At room temperature, no reinforcing effect is observed; however, reinforcement above T_g is seen and is primarily attributed to the increased PLLA crystallinity restricting the polymer chain mobility [163]. Interestingly, DMA showed a drop in the glass transition temperature at 8 wt.% loading, suggesting that the filler may also have a plasticizing effect on the matrix.

Braun et al. have investigated the use of CNCs with a lower polymer grafting density [155,164]. This was achieved by acetylation of freeze-dried CNCs (*w*-CNC-Ac) resulting in blocking/protecting many of the possible –OH initiation sites. This procedure gave access to *w*-CNC-Ac with up to 60–70 % of the OH groups functionalized according FTIR (Fig. 10**b**). The group conducted grafting-from ROP reactions from freeze-dried *w*-CNC-Ac in either toluene solution or in the bulk monomer (L-lactide) to yield the polymer grafted acetylated CNCs (*w*-CNC-Ac:-*g*-PLLA). The acetylation and PLLA grafting were confirmed by the appearance of characteristic ester carbonyl peaks at 1736 cm^{-1} for the acetate and 1760 cm^{-1} for the polymer (Fig. 11**a**). PLA/*w*-CNC-Ac:-*g*-PLLA composites were prepared by mixing a PLA solution in chloroform with a chloroform suspension of *w*-CNC-Ac:-*g*-PLLA to create films with up to 25 wt. % *w*-CNC-Ac:-*g*-PLLA. After evaporation of the solvent, the resulting composites were compression molded and resulted in highly transparent materials, suggestive of a good dispersion of the modified fillers within the matrix (Fig. 11**b**). Composites prepared with the solution functionalized *w*-CNC-Ac:-*g*-PLLA had a substantially greater increase in the heat distortion temperature reaching 150 °C at a filler loading of 15 wt. % compared to 115 °C for the composite made with the bulk-functionalized *w*-CNC-Ac:-*g*-PLLA. This is compared to 70 °C for the neat PLA and 80 °C for the PLA/*w*-CNC-Ac composites (Fig. 11**c**). The difference between the two *w*-CNC-Ac:-*g*-PLLA nanocomposites highlights the importance in considering the polymer grafting methodology, which will impact the amount and molecular weight of the grafted polymer, factors that can play a significant role in the final properties of the composites.

As before, the crystallization half-time of the PLA composites with 5 wt. % *w*-CNC-Ac:-*g*-PLLA quenched at 110 °C from the melt

Please cite this article as: C. Calvino, N. Macke, R. Kato et al., Development, processing and applications of bio-sourced cellulose nanocrystal composites, Prog Polym Sci, https://doi.org/10.1016/j.progpolymsci.2020.101221

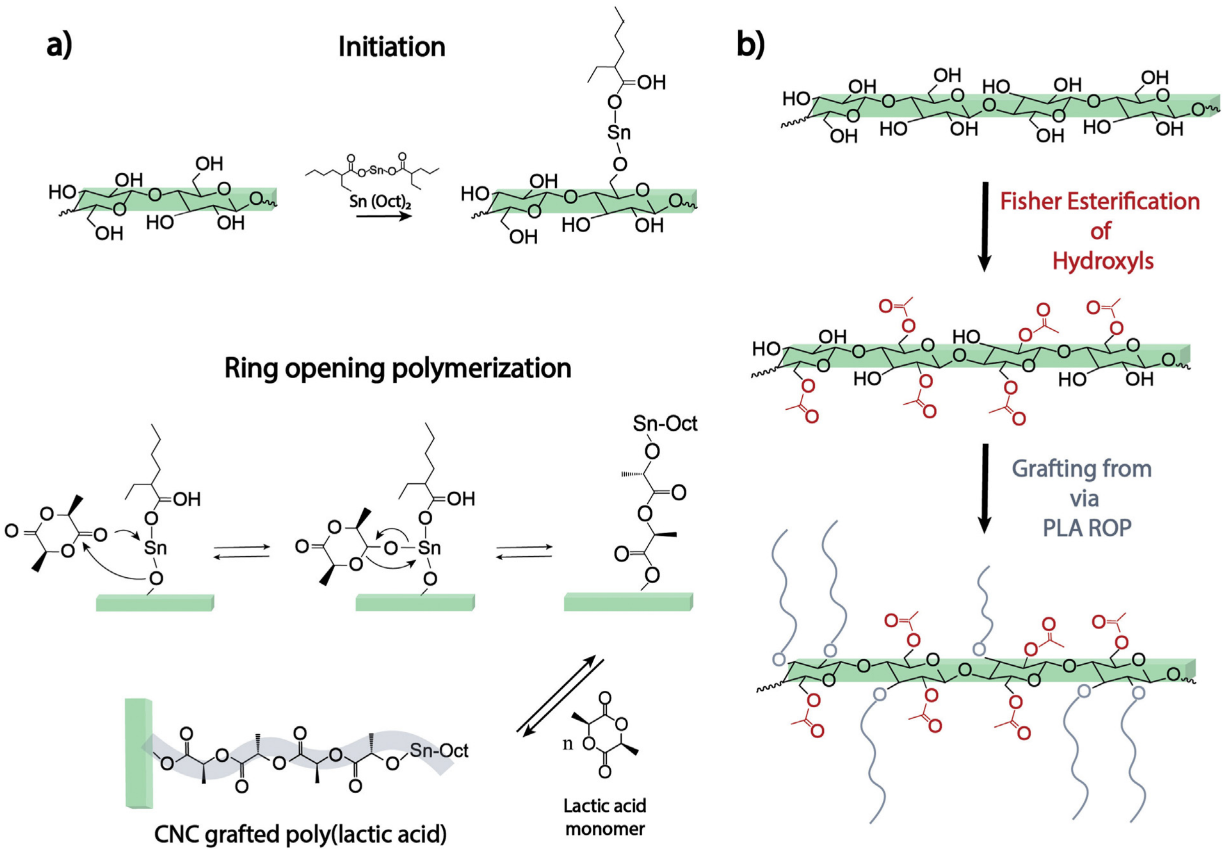


Fig. 10. **a)** Synthetic path of a ring opening polymerization of poly(lactic acid) initiated on the surface of the CNC and in presence of catalyst, the tin(II) 2-ethylhexanoate ($Sn(Oct)_2$). **b)** Scheme illustrating acetylation procedure to partially functionalize the surface of the CNCs [155]. Copyright 2012. Reproduced with permission from the American Chemical Society.

was 45 s compared to 90 s for neat PLA (Fig. 11**d**). A further reduction of the crystallization half-time down to 15 s was observed upon increasing the CNC loading to 15 and 20 wt. % (Fig. 11**d**). This is a useful result as one of the challenges of PLA from an industrial perspective is its slow crystallization time [165].

An aspect of PLA that we have not yet touched upon is its ability to form stereocomplexes [166]. PLLA has a melting point of 170–190 °C and a T_g of 50–65 °C, while racemic PLA is amorphous with a T_g ca. 50–60 °C. PDLA/PLLA blends form semi-crystalline stereocomplexes that have a melting point at 220–240 °C and a T_g ca. 65–70 °C, showing thermal improvements over the individual components [166]. Thus, conceptually one can envision grafting one stereoisomer (e.g. D-lactide) from the CNC and incorporate it in a matrix of the other (e.g. L-lactide) to obtain a material with enhanced properties. Zhang and coworkers employed this approach and obtained transparent PLLA/*c*-CNC-g-PDLA composite films by solvent casting from chloroform, which suggested that the modified filler had good dispersion within the matrix [167]. The composites also exhibited significant improvements in heat distortion resistance (40 % strain for the 10 wt. % composite after 10 min at 80 °C with a load of 50 g vs. 220 % for neat PLLA under the same conditions), but T_g shifted to lower temperatures as *c*-CNC-g-PDLA content increased from 0 to 10 wt. %.

Another key challenge for PLA is to develop ways to improve its toughness. While toughness improvements can be achieved by blending soft, ductile polymers, such as natural rubber or poly(butylene succinate) (PBS), into the matrix [168], an alternative approach has utilized PLA's stereocomplex characteristics [166]. Muiruri et al. grafted a random copolymer block of ε-caprolactone (CL) and D-lactide (DLA) on *w*-CNCs in toluene followed by a homo-D-lactide block to act as a compatibilizing block between the filler and the matrix [169]. The inclusion of CL into the grafted polymer was intended to act as a rubbery phase to absorb deformation energy and improve toughness of the composite material. The nanocomposites were prepared by solution casting a mixture of PLLA and 2.5 wt. % *w*-CNC-g-P(CLDLA-*b*-DLA) in chloroform and subsequently melt processing by injection molding. The stereocomplexation of the grafted D-lactide chains with the L-lactide matrix, enhanced filler–matrix interactions and inclusion of 2.5 % of the filler increased the toughness by 20 times, but decreased the tensile strength and modulus on account of plasticization. Scanning electron microscopy (SEM) and small-angle X-ray scattering (SAXS) measurements showed the major toughening mechanisms to be fibrillation and crazing during deformation of the nanocomposites. Such a biodegradable and tough CNC-filled PLA nanocomposites could open up new application avenues for PLA based materials [169].

2.3. Poly(3-hydroxybutyrate)-based composites with negatively charged CNCs

Poly(3-hydroxybutyrate) (PHB) is a thermoplastic polyester belonging to the family of polyhydroxyalkanoates which can be produced by bacteria or from sources, such as plants, sugar cane, etc [170]. As a result of its similar properties to petroleum-based polymers like PP (such as melting temperature ca. 180 °C and tensile strength ca. 30 MPa) combined with biodegradability and biocompatibility, PHB has been widely studied with a specific focus in biomedical [171,172] and food packaging applications [173]. However, material brittleness and a narrow processing window (low degradation temperature ca. 220 °C) still remain as challenges for broader implementation. One approach to overcome these issues is

Please cite this article as: C. Calvino, N. Macke, R. Kato et al., Development, processing and applications of bio-sourced cellulose nanocrystal composites, Prog Polym Sci, https://doi.org/10.1016/j.progpolymsci.2020.101221

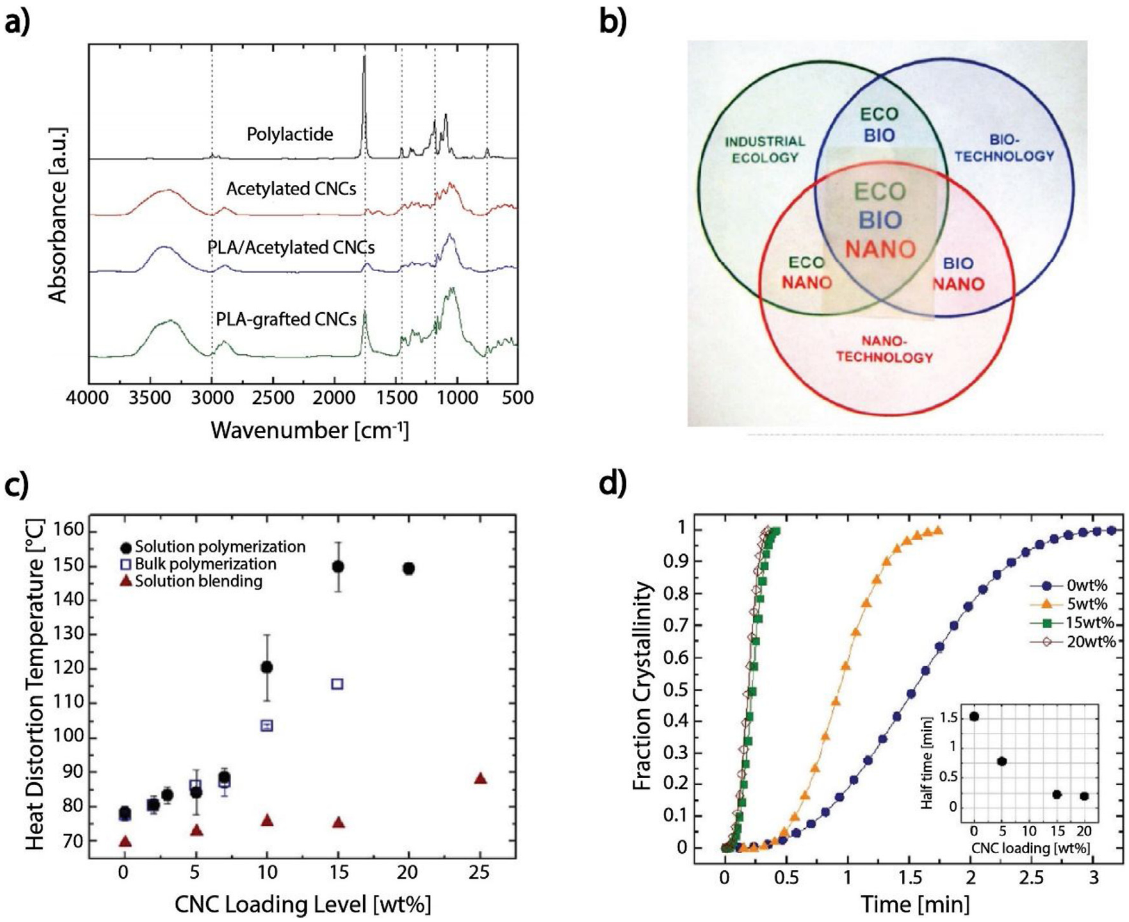


Fig. 11. **a**) Comparison of FTIR spectra of PLA (black), *w*-CNC-Ac (red), PLA/*w*-CNC-Ac (blue) and *w*-CNC-Ac:-*g*-PLLA (green). Dotted lines indicate PLA signals that do not overlap with peaks originating from the CNCs. **b)** Melt-pressed films of PLA/*w*-CNC-Ac:-*g*-PLLA nanocomposite with 10 wt% *w*-CNC-Ac:-*g*-PLLA loading. **c)** Comparison of the obtained heat distortion temperature for nanocomposites prepared by in situ polymerization in solution and in bulk compared with solution-blended nanocomposites, as a function of CNC weight loading. **d)** Comparison of the fraction of crystallinity over time for PLA composites with solution polymerized *w*-CNC-Ac:-*g*-PLLA when the materials are quenched from the melt to 110 °C. The crystallization half-time as a function of the content of CNC is plotted in the inset [155]. Copyright 2012. Adopted with permission from the American Chemical Society. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

the addition of plasticizers and fillers, such as CNCs, to tune the thermal and physical properties of PHB composites without altering the overall material biodegradability [174–176].

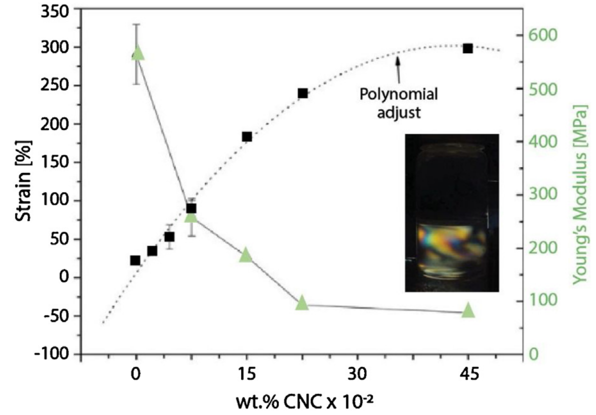


Fig. 12. The strain and Young's Modulus of PEG/PHB composite with low CNC content. (Inset: PEG/CNC dispersion at 1 wt. % concentration, observed between crossed polarizers) [177]. Copyright 2013. Adopted with permission from John Wiley & Sons Inc.

PHB is insoluble in water, making the processing of well dispersed PHB/CNC materials a challenge, similar to most other CNC composite systems. As such, solvent casting is most often done from organic solvents that can dissolve PHB, like DMF or chloroform [176]. Simple composites of PHB with CNCs have been investigated, but the expected increase in brittleness without improving thermal stability was observed, which is why the use of other additives is also necessary [176]. For example, Orefice et al. were able to achieve a birefringent dispersion of *w*-CNC-SO_3^- in a PHB matrix by using low molar mass PEG (200 Da) as a dispersing agent and plasticizer [177]. At first, *w*-CNC-SO_3^- were dispersed in PEG by evaporating the water from a PEG/*w*-CNC-SO_3^- solution (Fig. 12 inset), then the PEG/CNC blend was dissolved in a chloroform solution containing 5 w/v % PHB. Homogeneous PHB/PEG/*w*-CNC-SO_3^- (constant 15 wt.% PEG relative to PHB) composite films, as visualized under SEM, were obtained with varying CNC content by casting the mixture, evaporating off the solvent at room temperature followed by drying at 40 °C. These PHB/PEG/*w*-CNC-SO_3^- nanocomposite films exhibited a significant increase of the elongation at break (50 times greater than neat PHB and 25 times greater than PHB/PEG blends). While there was no significant loss of tensile strength (ca. 15–20 MPa), these composite materials did exhibit a substantial decrease in modulus (from > 600 to < 100 MPa from 0 wt. % to 0.45 wt. %) (Fig. 12). In addition to these mechanical changes, thermal stability was shown to be enhanced in the PHB/PEG/*w*-CNC-SO_3^- systems when compared to the PHB/PEG materials. The inclusion of CNCs was able to delay thermal degradation to be comparable to neat PHB, with degradation onset around 270 °C, which is around 40 °C better than the PHB/PEG system. All of these changes support the

Please cite this article as: C. Calvino, N. Macke, R. Kato et al., Development, processing and applications of bio-sourced cellulose nanocrystal composites, Prog Polym Sci, https://doi.org/10.1016/j.progpolymsci.2020.101221

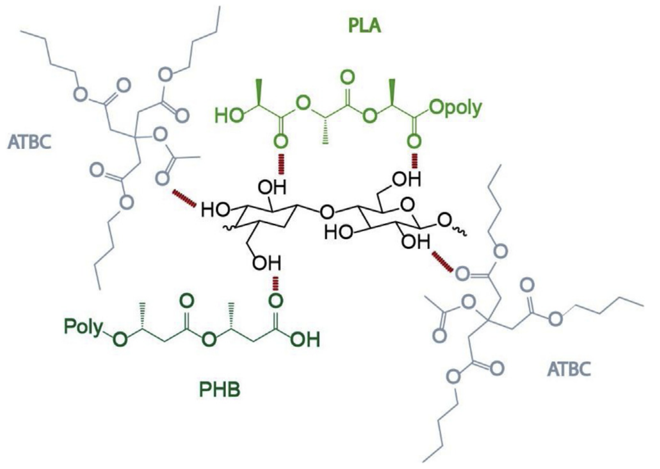


Fig. 13. The suggested molecular interaction on the CNCs with PLA, PHB and ATBC in the composite [179]. Copyright 2015. Adopted with permission from Elsevier Science Ltd.

ability of CNCs to enhance the processing and application window of PHB.

PHB and PLA can be blended together to expand their property profile resulting in improvements in both mechanical and barrier properties [178]. As such, CNC composites of these blended materials are also of interest [140]. Fortunati et al. melt mixed 5 wt. % *w*-CNC-SO_3^- or freeze-dried surfactant (STEPFAC 8170, nonylphenol phosphate ester) coated *w*-CNC-SO_3^- in 1:1 (w/w) with melt blended PLLA/PHB (75:25 wt. %) plasticized with 15 wt. % (relative to the PLLA/PHB blend) of acetyl tri-*n*-butyl citrate (ATBC) [179]. The ATBC was added to enhance the PLLA and PHB chain mobility and promote the dispersion of the CNCs within the matrix [180]. The transparency of the resulting materials suggested a good dispersion of the CNCs within the matrix for the composites made with either unmodified or surfactant-coated CNCs. However, transmission electron microscope images revealed some flakes within the PLLA/PHB/*w*-CNC-SO_3^- system, while the surfactant-modified CNCs did not show the formation of such agglomerates. SEM micrographs of the fractured cross-sections revealed rough surfaces and the formation of voids in the PLLA/PHB/ATBC materials, while the incorporation of either unmodified *w*-CNC-SO_3^- or surfactant-coated *w*-CNC-SO_3^- eliminated these voids. The authors suggest that the ATBC plasticizer resulted in a reduction of viscosity in the system, which facilitated processing and ultimately promoted the dispersion of CNCs in the polymer blend. However, the ATBC plasticizer does have side effects, as noticed in the barrier properties of the films. The PLLA/PHB/*w*-CNC-SO_3^- transmitted 13 cm^3/m^2/day of oxygen while the plasticized PLLA/PHB/ATBC/*w*-CNC-SO_3^- showed a rate of 23 cm^3/m^2/day (c.f. neat PLA ca. 30 cm^3/m^2/day). A T_g increase from 31 to ca. 45 °C with the incorporation of the CNCs into PLLA/PHB/ATBC suggests good filler matrix interactions (Fig. 13). In addition, two melting peaks are observed for the plasticized blends, one for PLLA (149 °C) and one for PHB (172 °C). However, there is only one melting peak at 147 °C in the PLLA/PHB/ATBC/*w*-CNC-SO_3^- composites, suggesting a drop of the overall crystallinity in this material, possibility as a result of the *w*-CNC-SO_3^- increasing compatibility between the PLA and PHB. The incorporation of the *w*-CNC-SO_3^- to PLLA/PHB/ATBC resulted in almost no changes to the Young's modulus but did significantly reduce the elongation at break (27 vs. 90 %). However, the incorporation of surfactant modified *w*-CNC-SO_3^- into the polymeric blends resulted in an increase in the elongation at break (147 %) allowing access to more ductile materials. These composite films showed a clear increase in degradation rate when CNCs and/or plasticizer were included in the blend, cutting degradation time in half for some samples. This is most likely attributable to the presence of more water within the matrix making hydrolysis more likely.

3. Other potential applications of sustainable cellulose nanocomposites

As covered in the previous sections, the ability for cellulose nanocrystals to positively impact properties of bio-based polymers has received significant attention in the past decade. While understanding the structure-property-processing relationships in these sustainable composites is an important goal, a parallel question to be addressed is where are the potential applications for such materials? The following section aims to highlight selected application areas in which CNCs, and their bio-based composites, may show promise that go beyond the mechanical reinforcement and packaging applications that have been touched upon in the prior sections.

3.1. *Compatibilization of immiscible polymers*

Most polymers are immiscible and as such, when they are blended together, the result is a macrophase separated material with poor physical properties. Compatibilization is the process of stabilizing the interface between the two immiscible polymers, thus creating a more homogenous material with improved properties. Compatibilizers include the use of surfactant-like molecules or block copolymers that are able to organize at the interface and lower the surface energy between the two phases. From a recycling perspective, the use of compatibilizers is attractive as it potentially offers a more facile route to processing of recycled polymers by reducing the need for costly separations [181]. Given that CNCs can be used to reinforce polymer matrices, if they can be used as a compatibilizer as opposed to say molecular/polymer based surfactants, then the resulting recycled blended material may show even more enhanced mechanical properties. This would create a potential opportunity for the upcycling of plastic waste, which is when the regenerated material has the same or more value than the virgin supply [182].

Habibi and coworkers reported an early example an immiscible polymer blends being compatibilized by *rf*-CNC-SO_3^- in a PLLA/PCL system [183]. The ternary composites of the PLLA/PCL blend along with either *rf*-CNC-SO_3^- or *rf*-CNC-*g*-PLLA-*b*-PCL showed a 2 or 3 order of magnitude increase in the storage modulus (over 1000 MPa) when compared to the binary PLLA/PCL system (ca. 5 MPa). The composites microstructure appeared much more homogenous compared to the blend without CNCs (Fig. 14). Similar compatibilization effects of CNCs have also been observed in less sustainable matrices, such as poly(vinyl alcohol)/PEO blends [184]. Such observations suggest that is may be possible to utilize CNC-based fillers to combine the previously mentioned mechanical, thermal and barrier property improvements with compatibilization expanding the capabilities of both virgin and recycled blends.

3.2. *Water filtration*

As discussed above, hydrophilic CNCs enhance the diffusion of water into polymer matrices, begging the question of whether these systems would be viable as membranes and filters for water purification. If the CNCs are also functionalized with a binding motif, then such systems could be tailored for selective filtration and toxin removal. Saito and Isogai were the first to show that TEMPO-oxidized *c*-CNC−COOH were capable of metal ion adsorption from aqueous solutions by association of the metal ions with the deprotonated carboxylate groups [185]. From that point, the field has expanded tremendously with work towards enhancing uptake of targeted ions, such as lead, through functionalization

Please cite this article as: C. Calvino, N. Macke, R. Kato et al., Development, processing and applications of bio-sourced cellulose nanocrystal composites, Prog Polym Sci, https://doi.org/10.1016/j.progpolymsci.2020.101221

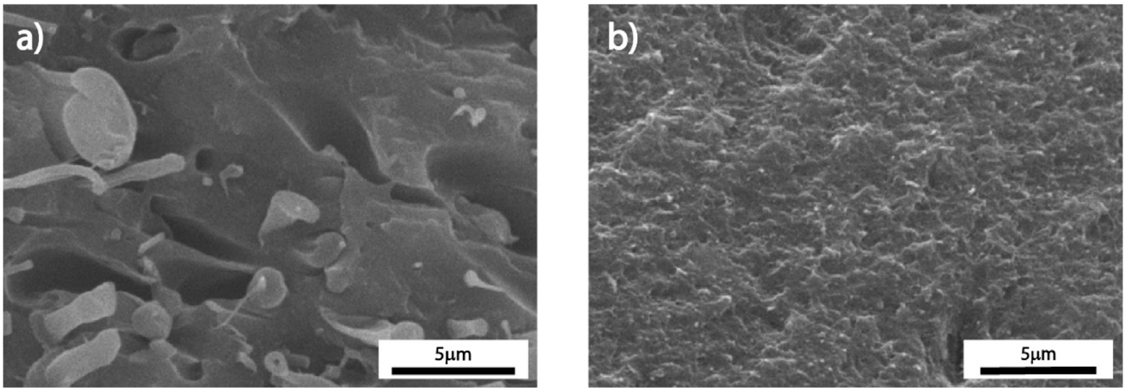


Fig. 14. **a)** SEM image of PLLA/PCL (1:1) polymer blend showing clear phase inhomogeneity between the two polymeric materials and **b)** a PLLA/PCL (1:1) blend with 2 wt.% of *rf*-CNC-SO_3^- showing a much more homogenous morphology [183]. Copyright 2012. Adopted with permission from the American Chemical Society.

of the CNCs with specific binding motifs and towards stripping the sequestered material in order to recover and reuse the filtration material [186–188]. In one example, Mathew and coworkers made a bio-based high flux membranes by vacuum filtration of a 1:1 gelatin/*w*-CNC-PO_3^- solution on a cellulose microfiber support followed by melt pressing at 80 °C [189]. The resulting uniform membrane was capable of high flux (almost 3000 L/h/m^2 at 1 bar) and high capacity uptake of metal ions such as Cu^{2+} (358 mg/g of CNC in the filter) and Fe^{3+}/Fe^{2+} (512 mg/g). For comparison, carbon nanotubes have a Cu^{2+} sorption capacity of 67.8 mg/g of filtration material.

3.3. Biomedical CNC-containing bio-based materials

CNCs have been investigated in a wide range of different biomedical materials. In this regard there are a few biomedical application areas for which fully bio-based composites have received some attention [190,191].

One area where CNC-containing bio-based hydrogels have been investigated is as drug delivery vehicles. For example, Dufresne and coworkers blended *c*-CNC-SO_3^- into a crosslinked alginate core and subsequently adsorbed additional alginate onto the surface to create double-layer hydrogel particles (Fig. 15) [192]. The pure alginate outer layer showed relatively rapid degradation and drug release while longer-term sustained release of the active pharmaceutical ingredient was observed from the inner alginate/ *c*-CNC-SO_3^- sphere, which degraded at a slower rate. It was also suggested that the CNCs may cause slower diffusion of the drug within the matrix.

Bio-based nanocomposites have also attracted interest in tissue engineering applications. For instance, CNCs have been shown to delay implant degradation, increasing the amount of time cells that can grow into the scaffold before losing mechanical support. For example, it has been shown that while cell proliferation in alginate/*c*-CNC-SO_3^- gel composites was slowed (relative to alginate gels), the improved mechanical strength and slower degradation rate made the material a promising candidate for bone stents for which rapid cellular growth is not required, but mechanical strength is needed [193]. In a related example, Yang et al. created hydroxyapatite/gelatin/*b*-CNC-COOH hydrogel composites where the amount of CNCs incorporated into the composite could be used to control the gel's degradation rate in simulated bodily fluid while maintaining the tensile strength [194].

CNC-based materials have also been investigated as antimicrobial agents. For example, CNCs have been grafted with a variety of molecules, such as rosin [195], porphyrin [196] and polyrhodanine [197] to create films and particles that have shown considerable success in reducing bacterial colony survival. While not composites, these functionalized CNC nanomaterials have been proposed to be incorporated into fabrics, papers, and coatings for the biomedical, food service and packaging industries to access more sustainable and biocompatible alternatives to the current solutions.

The future role of CNCs in the biomedical industry relies on the continued investigation of biological interactions with the many different forms of CNCs and in a wide range of environments. While some *in vitro* studies have been undertaken with CNC-based systems [198], we have only scratched the surface and a much better understanding of *in vivo* interactions is necessary. Additionally, further degradation studies need to be undertaken so that the long-term impact of CNCs on the body can be better understood.

3.4. Electronics

CNCs have been investigated in a range of electronic applications further highlighting their versatility as a nanomaterial. While not all of the materials used with the CNCs in this section are sustainable, the key goal is to replace actively toxic materials that are traditionally used in systems like batteries and solar cells, and as such, reducing the non-trivial contamination issues upon disposal [199,200].

In battery applications, nanocellulose based materials are interesting on account of their mechanical strength and permeability [201]. Accordingly, studies have investigated the potential of CNC composites as separators, electrolytes [202] and electrodes [203] in next-generation battery technologies. Dufresne and coworkers combined the needs of a separator and electrolyte by solvent casting *t*-CNC-SO_3^-s into a PEO film to create a robust, conductive nanocomposite [202]. The material exhibited less than half an order of magnitude loss in ionic conductivity at 60 °C when compared to neat PEO, while also achieving an order of magnitude increase in mechanical strength.

The complexity of electronic systems is one factor that makes fully sustainable devices difficult to design, but CNCs provide a foundation that can be built upon. Okahisa and coworkers used cellulose nanofiber mats dipped in various acrylic resins to create substrates with low coefficients of thermal expansion (CTE) for deposition of organic light-emitting diodes (OLEDs) [204]. The low CTE, 12.1 ppm/K in the best case, showed a 94 % decrease over the neat resin and was essential to prevent delamination during thermal cycles encountered in regular use. This idea was advanced by Kippelen and coworkers, who used a glycerol/*w*-CNC-SO_3^- substrate to create a fully recyclable OLED [205]. Building on this work, the same group went on to employ the same optically clear composite of glycerol and *w*-CNC-SO_3^- as a substrate for recyclable solar cells (Fig. 16), on top of which was deposited successive layers of silver, ethoxylated polyethyenimine, photoactive material, molyb-

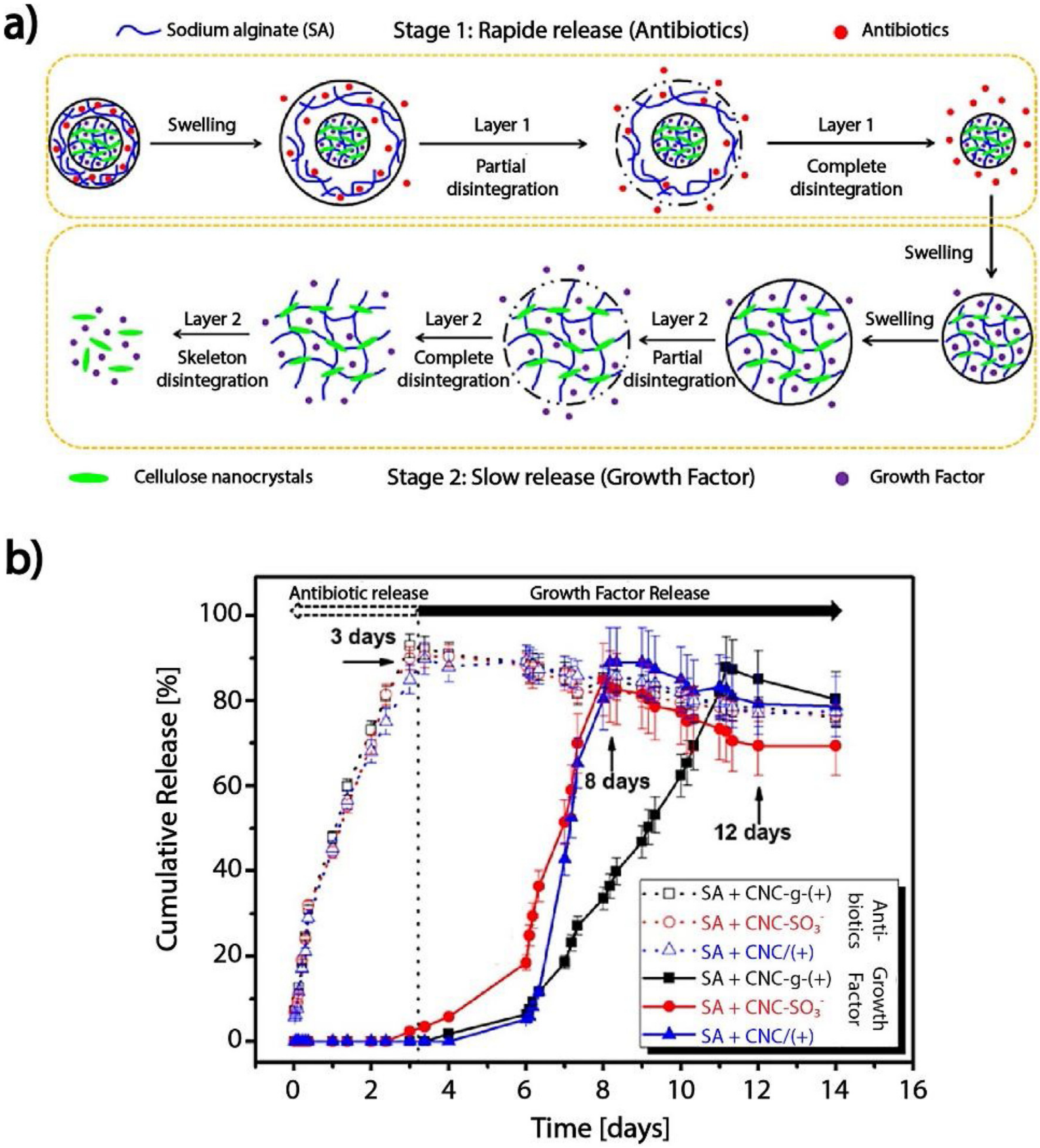


Fig. 15. a) Drug release schematic for the release of the antibiotic ceftazidime hydrate loaded into the sodium alginate (SA) outer layer and human epidermal growth factor in the SA/CNC inner layer from double membrane alginate hydrogel particles. **b)** Graph of drug release times showing rapid release of the antibiotic from the outer layer, and a delayed onset release of growth factor . CNCs used were neat *w*-CNC-SO3-, CNCs modified by chemical grafting of a positively charged small molecule (CNC-*g*-(+)), and CNCs modified by physical adsorption of a positively charged polyelectrolyte polymer (CNC/(+)) [192]. Copyright 2016. Adopted with permission from the American Chemical Society.

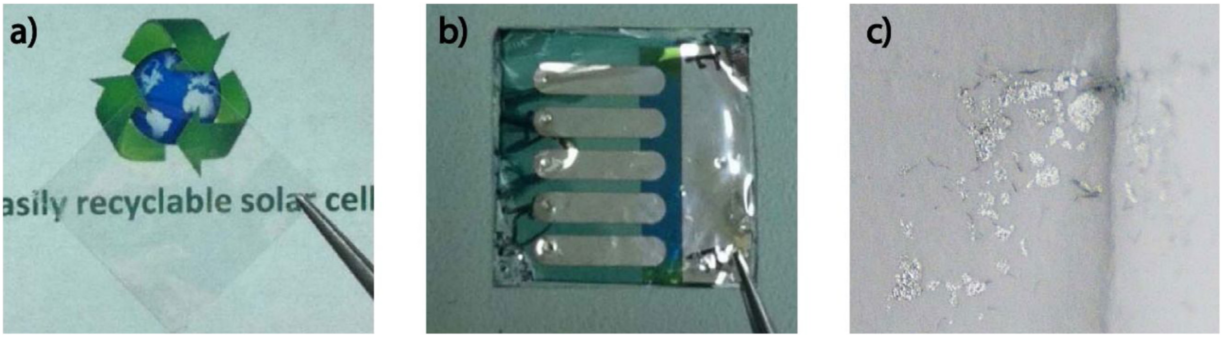


Fig. 16. a) Transparent *w*-CNC-SO$_3^-$ film used as the substrate for the recyclable solar cell, **b)** the fully assembled and recyclable solar cell on the CNC substrate and **c)** the solid remains (mainly consisting of Ag and MoO$_3$) after dissolving the solar cell into its constituent components through a series of washes in deionized water and chlorobenzene [206]. Copyright 2013. Adopted with permission from the Nature Group.

Please cite this article as: C. Calvino, N. Macke, R. Kato et al., Development, processing and applications of bio-sourced cellulose nanocrystal composites, Prog Polym Sci, https://doi.org/10.1016/j.progpolymsci.2020.101221

denum oxide (MoO_3) and finally another layer of silver [206]. While the achieved power conversion efficiency of 2.7 % is nowhere near to the state-of-the-art solar cells, ca. 25 %, these cells were able to be completely recycled, showing that fully-recyclable solar cells are a legitimate possibility.

4. Conclusion

The incorporation of bio-based cellulose nanocrystals into sustainable polymer matrices allows access to improvements in a number of important material properties, from mechanical strength and thermal resistance to barrier properties, without detracting from the materials sustainability. Although, it is important to note that while CNCs are components of many natural systems (in particular within trees and plants), more work is needed to better understand the environmental and biological impacts of isolated and functionalized CNCs. This critical aspect aside, the key to improved materials properties is the ability to access composites where the CNCs are well- dispersed within the host matrix. If the polymer matrix is soluble in water (or even polar organic solvents such as DMF), e.g. alginate and chitosan, then it is relatively easy to access CNC composites that show greatly enhanced properties by standard solution casting processes. The real challenge comes when the polymer matrix in question is not soluble in a solvent that disperses the CNCs. Numerous methods have been tried to get around this problem, including transferring the CNCs into less polar solvents, to limited success. Additives (e.g. surfactants or dispersing agents) can be used to enhance CNC dispersion in the matrix. However, such molecules usually facilitate the dispersion by localizing at the CNC surfaces and as such, stress transfer between the CNCs themselves as well as between CNCs and the matrix is diminished, reducing the effectiveness of the reinforcement. To improve stress transfer, covalent grafting of the dispersing agent, usually a short-chain polymer, to the CNC surface has been conducted. The resulting materials exhibit some of the best properties of any CNC composites currently reported. Nonetheless, improvements in the large-scale synthesis and processing of such materials need to be made before commercial implementation will be achieved.

Solvent casting-based processes are currently the most frequently employed because they offer the advantage of maximizing dispersion of the CNCs. However, such processing involves large amounts of solvent and, from a sustainability and commercialization point of view, any solution-based processing is not ideal. Unfortunately, melt processing of CNC composites is a major challenge, as it is with most nanocomposites, given their tendency to aggregate/phase separate and the fact that they can start to decompose at high temperatures. Most of the aforementioned strategies (functionalization of CNCs, addition of surfactants and plasticizers) are viable options, but as of yet, a scalable, cost effective process still needs to be developed.

The possibilities of commercialization are diverse, and work has been done in the areas of packaging, compatibilization, water purification, biomedical and electronics (amongst others). The sustainability and ability to functionalize the CNC's surface with a wide variety of chemistries are part of what makes their appeal so broad. For example, grafting of binding sites allows sequestration of ions in contaminated water, attachment of antibacterial agents helps to prevent disease in biomedical applications and grafting of conductive materials improves electronic or ionic conduction, opening the door to potentially accessing wholly sustainable systems that can impact fields ranging from energy storage to flexible bio-electronics. As such, while there are still unresolved challenges that need to be addressed, the potential of CNCs (and other nanocelluloses) to help expand the sustainable materials portfolio is clear.

Authors contribution

All the authors contributed in surveying the literature and writing this review.

Declaration of Competing Interest

None.

Acknowledgments

The authors gratefully acknowledge financial support through the National Science Foundation (NSF)Center for Sustainable Polymers (CSP) (CHE-1901635) and the Swiss National Science Foundation (SNSF) (P2FRP2_181437).

References

[1] Über Polymerisation Staudinger H. Ber Dtsch Chem Ges A, B Ser 1920;53:1073–85.
[2] Ritchie H, Roser N. Global plastic production statistics. Our world in data; 2019 https://ourworldindata.org/plastic-pollution/.
[3] Schneiderman DK, Hillmyer MA. 50th anniversary perspective: there is a great future in sustainable polymers. Macromolecules 2017;50:3733–49.
[4] Geyer R, Jambeck JR, Law KL. Production, use, and fate of all plastics ever made. Sci Adv 2017;3:e1700782/1-5.
[5] Nguyen HTH QP, Rostagno M, Feteha A, Miller SA. The quest for high glass transition temperature bioplastics. J Mater Chem A Mater Energy Sustain 2018;6:9298–331.
[6] Jambeck JR, Geyer R, Wilcox C, Siegler TR, Perryman M, Andrady A, et al. Plastic waste inputs from land into the ocean. Science 2015;347:768–71.
[7] Ellen MacArthur foundation. The new plastics economy: rethinking the future of plastics. World Economic Forum; 2016, 120 pp.
[8] Anonymous. G20 implementation framework for actions on marine plastic litter. G20 2019 Japan 2019 (4 pp). Accessed 2019.
[9] Miller SA. Sustainable polymers: opportunities for the next decade. ACS Macro Lett 2013;2:550–4.
[10] Rose M, Palkovits R. Cellulose-based sustainable polymers: state of the art and future trends. Macromol Rapid Commun 2011;32:1299–311.
[11] Hong M, Chen EYX. Towards truly sustainable polymers: a metal-free recyclable polyester from biorenewable non-strained γ-butyrolactone. Angew Chem Int Ed 2016;55:4188–93.
[12] Fortman DJ, Brutman JP, De Hoe GX, Snyder RL, Dichtel WR, Hillmyer MA. Approaches to sustainable and continually recyclable cross-linked polymers. ACS Sustain Chem Eng 2018;6:11145–59.
[13] Zhu Y, Romain C, Williams CK. Sustainable polymers from renewable resources. Nature 2016;540:354–62.
[14] Nakajima H, Dijkstra P, Loos K. The recent developments in biobased polymers toward general and engineering applications: polymers that are upgraded from biodegradable polymers, analogous to petroleum-derived polymers, and newly developed. Polymers 2017;9, 523/1-26.
[15] Laycock B, Nikolic M, Colwell JM, Gauthier E, Halley PJ, Bottle S, et al. Lifetime prediction of biodegradable polymers. Prog Polym Sci 2017;71:144–89.
[16] Chen L, Pelton REO, Smith TM. Comparative life cycle assessment of fossil and bio-based polyethylene terephthalate (PET) bottles. J Clean Prod 2016;137:667–76.
[17] Ritchie H, Roser N. Plastic pollution. Our world in data; 2018 https://ourworldindata.org/plastic-pollution/.
[18] Wallace T. Cosmos Magazine Global plastic waste totals 4.9 billion tonnes; 2017 https://cosmosmagazine.com/society/global-plastic-waste-totals-4-9-billion-tonnes/.
[19] Mohanty AK, Vivekanandhan S, Pin JM, Misra M. Composites from renewable and sustainable resources: challenges and innovations. Science 2018;362:536–42.
[20] Storz H, Vorlop KD. Bio-based plastics: status, challenges and trends. Appl Agric Forestry Res 2013;63:321–32.
[21] Lee SY, Hong SH, Lee SH, Park SJ. Fermentative production of chemicals that can be used for polymer synthesis. Macromol Biosci 2004;4:157–64.
[22] Garlotta D. A literature review of poly(Lactic acid). J Polym Environ 2001;9:63–84.
[23] Suriyamongkol P, Weselake R, Narine S, Moloney M, Shah S. Biotechnological approaches for the production of polyhydroxyalkanoates in microorganisms and plants—a review. Biotechnol Adv 2007;25:148–75.
[24] Lu DR, Xiao CM, Xu SJ. Starch-based completely biodegradable polymer materials. Express Polym Lett 2009;3:366–75.
[25] Peelman N, Ragaert P, De Meulenaer B, Adons D, Peeters R, Cardon L, et al. Application of bioplastics for food packaging. Trends Food Sci Technol 2013;32:128–41.
[26] Anonymous. Bioplastics market data. Eur Bioplast; 2017. Accessed October 2019 https://www.european-bioplastics.org/market/.

[27] Kuilla T, Bhadra S, Yao D, Kim NH, Bose S, Lee JH. Recent advances in graphene based polymer composites. Prog Polym Sci 2010;35:1350–75.
[28] Sreekumar PA, Al-Harthi MA, De SK. Reinforcement of starch/polyvinyl alcohol blend using nano-titanium dioxide. J Compos Mater 2012;46:3181–7.
[29] Jiang L, Zhang J, Wolcott MP. Comparison of polylactide/nano-sized calcium carbonate and polylactide/montmorillonite composites: reinforcing effects and toughening mechanisms. Polymer 2007;48:7632–44.
[30] Reynaud E, Jouen T, Gauthier C, Vigier G, Varlet J. Nanofillers in polymeric matrix: a study on silica reinforced PA6. Polymer 2001;42:8759–68.
[31] Saba N, Tahir P, Jawaid M. A review on potentiality of nano filler/natural fiber filled polymer hybrid composites. Polymers 2014;6:2247–73.
[32] Siqueira G, Bras J, Dufresne A. Cellulosic bionanocomposites: a review of preparation, properties and applications. Polymers 2010;2:728–65.
[33] Moon RJ, Martini A, Nairn J, Simonsen J, Youngblood J. Cellulose nanomaterials review: structure, properties and nanocomposites. Chem Soc Rev 2011;40:3941–94.
[34] Khalil HPSA, Davoudpour Y, Saurabh CK, Hossain MS, Adnan AS, Dungani R, et al. A review on nanocellulosic fibres as new material for sustainable packaging: Process and applications. Renew Sustain Energ Rev 2016;64:823–36.
[35] Khalil HPSA, Bhat AH, Yusra AFI. Green composites from sustainable cellulose nanofibrils: a review. Carbohydr Polym 2012;87:963–79.
[36] Al-Oqla FM, Sapuan SM. Natural fiber reinforced polymer composites in industrial applications: feasibility of date palm fibers for sustainable automotive industry. J Clean Prod 2014;66:347–54.
[37] Kargarzadeh H, Huang J, Lin N, Ahmad I, Mariano M, Dufresne A, et al. Recent developments in nanocellulose-based biodegradable polymers, thermoplastic polymers, and porous nanocomposites. Prog Polym Sci 2018;87:197–227.
[38] Dufresne A, Cavaillé J, Vignon MR. Mechanical behavior of sheets prepared from sugar beet cellulose microfibrils. J Appl Polym Sci 1997;64:1185–94.
[39] Saito T, Kimura S, Nishiyama Y, Isogai A. Cellulose nanofibers prepared by TEMPO-mediated oxidation of native cellulose. Biomacromolecules 2007;8:2485–91.
[40] Habibi Y, Goffin AL, Schiltz N, Duquesne E, Dubois P, Dufresne A. Bionanocomposites based on poly (ε-caprolactone)-grafted cellulose nanocrystals by ring-opening polymerization. J Mater Chem 2008;18:5002–10.
[41] Lin N, Dufresne A. Nanocellulose in biomedicine: current status and future prospect. Eur Polym J 2014;59:302–25.
[42] Bondeson D, Mathew AP, Oksman K. Optimization of the isolation of nanocrystals from microcrystalline cellulose by acid hydrolysis. Cellulose 2006;13:171–80.
[43] Cudjoe E, Hunsen M, Xue Z, Way AE, Barrios E, Olson RA, et al. Miscanthus Giganteus: a commercially viable sustainable source of cellulose nanocrystals. Carbohydr Polym 2017;155:230–41.
[44] Yang H, Zhang Y, Kato R, Rowan SJ. Preparation of cellulose nanofibers from Miscanthus x. Giganteus by ammonium persulfate oxidation. Carbohydr Polym 2019;212:30–9.
[45] Araki J, Wada M, Kuga S, Okano T. Flow properties of microcrystalline cellulose suspension prepared by acid treatment of native cellulose. Colloids Surf A Physicochem Eng Asp 1998;142:75–82.
[46] Beck-Candanedo S, Roman M, Gray DG. Effect of reaction conditions on the properties and behavior of wood cellulose nanocrystal suspensions. Biomacromolecules 2005;6:1048–54.
[47] Dong XM, Kimura T, Revol JF, Gray DG. Effects of ionic strength on the isotropic– chiral nematic phase transition of suspensions of cellulose crystallites. Langmuir 1996;12:2076–82.
[48] Heux L, Chauve G, Bonini C. Nonflocculating and chiral-nematic self-ordering of cellulose microcrystals suspensions in nonpolar solvents. Langmuir 2000;16:8210–2.
[49] De Menezes AJ, Siqueira G, Curvelo AAS, Dufresne A. Extrusion and characterization of functionalized cellulose whiskers reinforced polyethylene nanocomposites. Polymer 2009;50:4552–63.
[50] Angles MN, Dufresne A. Plasticized starch/tunicin whiskers nanocomposites. 1. Structural analysis. Macromolecules 2000;33:8344–53.
[51] Elazzouzi-Hafraoui S, Nishiyama Y, Putaux JL, Heux L, Dubreuil F, Rochas C. The shape and size distribution of crystalline nanoparticles prepared by acid hydrolysis of native cellulose. Biomacromolecules 2007;9:57–65.
[52] Brito BSL, Pereira FV, Putaux JL, Jean B. Preparation, morphology and structure of cellulose nanocrystals from bamboo fibers. Cellulose 2012;19:1527–36.
[53] Singla R, Soni S, Kulurkar PM, Kumari A, Mahesh S, Patial V, et al. In situ functionalized nanobiocomposites dressings of bamboo cellulose nanocrystals and silver nanoparticles for accelerated wound healing. Carbohydr Polym 2017;155:152–62.
[54] Grunert M, Winter WT. Nanocomposites of cellulose acetate butyrate reinforced with cellulose nanocrystals. J Polym Environ 2002;10:27–30.
[55] Araki J, Wada M, Kuga S. Steric stabilization of a cellulose microcrystal suspension by poly (ethylene glycol) grafting. Langmuir 2001;17:21–7.
[56] Fortunati E, Puglia D, Monti M, Peponi L, Santulli C, Kenny JM, et al. Extraction of cellulose nanocrystals from Phormium tenax fibres. J Polym Environ 2013;21:319–28.
[57] Fortunati E, Luzi F, Puglia D, Dominici F, Santulli C, Kenny JM, et al. Investigation of thermo-mechanical, chemical and degradative properties of PLA-limonene films reinforced with cellulose nanocrystals extracted from Phormium tenax leaves. Eur Polym J 2014;56:77–91.
[58] Cao X, Dong H, Li CM. New nanocomposite materials reinforced with flax cellulose nanocrystals in waterborne polyurethane. Biomacromolecules 2007;8:899–904.
[59] Chen Y, Cao X, Chang PR, Huneault MA. Comparative study on the films of poly(vinyl alcohol)/pea starch nanocrystals and poly(vinyl alcohol)/native pea starch. Carbohydr Polym 2008;73:8–17.
[60] Habibi Y, Lucia LA, Rojas OJ. Cellulose nanocrystals : chemistry, self-assembly, and applications. Chem Rev 2010;110:3479–500.
[61] Trache D, Hussin MH, Haafiz MKM, Thakur VK. Recent progress in cellulose nanocrystals: sources and production. Nanoscale 2017;9:1763–86.
[62] Einchhorn SJ, Dufresne A, Aranguren MM, Capadona JR, Rowan SJ, Weder C, et al. Review: current international research into cellulose nanofibres and composites. J Mater Sci 2010;45:1–33.
[63] Rahman IA, Padavettan V. Synthesis of silica nanoparticles by sol-gel : size-dependent properties, surface modification, and aplications in silica-polymer nanocomposites — a review. J Nanomater 2012;2012, 132424/1-15.
[64] Al-Saleh MH, Sundararaj U. Composites : part A Review of the mechanical properties of carbon nanofiber / polymer composites. Compos Part A Appl Sci Manuf 2011;42:2126–42.
[65] Albdiry MT, Yousif BF, Ku H, Lau KT. A critical review on the manufacturing processes in relation to the properties of nanoclay / polymer composites. J Compos Mater 2012;47:1093–115.
[66] Moon RJ, Schueneman GT, Simonsen J. Overview of cellulose nanomaterials, their capabilities and applications. JOM 2016;68:2383–94.
[67] Favier V, Cavaillé J, Canova GR, Shrivastava SC. Mechanical percolation in cellulose whisker nanocomposites. Polym Eng Sci 1997;37: 1732–9.
[68] Oksman K, Aitomäki Y, Mathew AP, Siqueira G, Zhou Q, Butylina S, et al. Review of the recent developments in cellulose nanocomposite processing. Compos Part A Appl Sci Manuf 2016;83:2–18.
[69] Favier V, Canova GR, Cavaillé J, Chanzy H, Dufresne A, Gauthier C. Nanocomposite materials from latex and cellulose whiskers. Polym Adv Technol 1995;6:351–5.
[70] Dufresne A, Cavaillé J, Helbert W. New nanocomposite materials: microcrystalline starch reinforced thermoplastic. Macromolecules 1996;29:7624–6.
[71] Favier V, Chanzy H, Cavaillé J. Polymer nanocomposites reinforced by cellulose whiskers. Macromolecules 1995;28:6365–7.
[72] Dufresne A, Cavaillé J, Helbert W. Thermoplastic nanocomposites filled with wheat straw cellulose whiskers. Part II: effect of processing and modeling. Polym Compos 1997;18:198–210.
[73] Tang J, Sisler J, Grishkewich N, Tam KC. Functionalization of cellulose nanocrystals for advanced applications. J Colloid Interface Sci 2017;494:397–409.
[74] Vartiainen T, Pöhler T, Sirola K, Pylkkänen L, Alenius J, Hokkinen J, et al. Health and environmental safety aspects of friction grinding and spray drying of microfibrillated cellulose. Cellulose 2011;18:775–86.
[75] Kovacs T, Naish V, O'Connor B, Blaise C, Gagne F, Hall L, et al. An ecotoxicological characterization of nanocrystalline cellulose (NCC). Nanotoxicology 2010;4:255–70.
[76] Roman M. Toxicity of cellulose nanocrystals: a review. Ind Biotechnol (New Rochelle N Y) 2015;11:25–33.
[77] Clift MJD, Foster EJ, Vanhecke D, Studer D, Wick P, Gehr P, et al. Investigating the interaction of cellulose nanofibers derived from cotton with a sophisticated 3D human lung cell coculture. Biomacromolecules 2011;12:3666–73.
[78] Yanamala N, Farcas MT, Hat MK, Kisin ER, Kagan VE, Geraci CL, et al. In vivo evaluation of the pulmonary toxicity of cellulose nanocrystals: a renewable and sustainable nanomaterial of the future. ACS Sustain Chem Eng 2014;2:1691–8.
[79] Mohanty AK, Misra M, Hinrichsen GI. Biofibres, biodegradable polymers and biocomposites: an overview. Macromol Mater Eng 2000;276:1–24.
[80] Jayakumar R, Menon D, Manzoor K, Nair SV, Tamura H. Biomedical applications of chitin and chitosan based nanomaterials — a short review. Carbohydr Polym 2010;82:227–32.
[81] Smith PJ, Wu L-Q, Embree HD, Balgley BM, Payne GF. Utilizing renewable Resources to create functional polymers : chitosan-based associative thickener. Environ Sci Technol 2002;36:3446–54.
[82] No H, Meyers W, Prinyawiwatkul ZX. Applications of chitosan for improvement of quality and shelf life of foods : a review. J Food Sci 2007;72:87–100.
[83] Khan A, Khan RA, Salmieri S, Le C, Riedl B, Bouchard J, et al. Mechanical and barrier properties of nanocrystalline cellulose reinforced chitosan based nanocomposite films. Carbohydr Polym 2012;90:1601–8.
[84] Mao H, Wei C, Gong Y, Wang S, Ding W. Mechanical and water-resistant properties of eco-friendly chitosan membrane reinforced with cellulose nanocrystals. Polymers 2019;11, 166/1-15.
[85] Mujtaba M, Salaberria AM, Andres MA, Kaya M, Gunyakti A, Labidi J. Utilization of flax (Linum usitatissimum) cellulose nanocrystals as reinforcing material for chitosan films. Int J Biol Macromol 2017;104:944–52.
[86] Abo-Elseoud WS, Hassan ML, Sabaa MW, Basha M, Hassan EA, Fadel SM. Chitosan nanoparticles/cellulose nanocrystals nanocomposites as a carrier

Please cite this article as: C. Calvino, N. Macke, R. Kato et al., Development, processing and applications of bio-sourced cellulose nanocrystal composites, Prog Polym Sci, https://doi.org/10.1016/j.progpolymsci.2020.101221

system for the controlled release of repaglinide. Int J Biol Macromol 2018;111:604–13.
[87] Li F, Biagioni P, Finazzi M, Tavazzi S, Piergiovanni L. Tunable green oxygen barrier through layer-by-layer self-assembly of chitosan and cellulose nanocrystals. Carbohydr Polym 2013;92:2128–34.
[88] Karim Z, Mathew AP, Grahn M, Mouzon J, Oksman K. Nanoporous membranes with cellulose nanocrystals as functional entity in chitosan: removal of dyes from water. Carbohydr Polym 2014;112:668–76.
[89] Huq T, Salmieri S, Khan A, Khan RA, Le Tien C, Riedl B, et al. Nanocrystalline cellulose (NCC) reinforced alginate based biodegradable nanocomposite film. Carbohydr Polym 2012;90:1757–63.
[90] Szekalska M, Sosnowska K, Czajkowska-Kósnik A, Winnicka K. Calcium chloride modified alginate microparticles formulated by the spray drying process: a strategy to prolong the release of freely soluble drugs. Materials 2018;11:1–14.
[91] De France KJ, Hoare T, Cranston ED. Review of hydrogels and aerogels containing nanocellulose. Chem Mater 2017;29:4609–31.
[92] Smyth M, M'Bengue MS, Terrien M, Picart C, Bras J, Foster EJ. The effect of hydration on the material and mechanical properties of cellulose nanocrystal-alginate composites. Carbohydr Polym 2018;179:186–95.
[93] Ma X, Li R, Zhao X, Ji Q, Xing Y, Sunarso J, et al. Biopolymer composite fibres composed of calcium alginate reinforced with nanocrystalline cellulose. Compos Part A Appl Sci Manuf 2017;96:155–63.
[94] Lin N, Bruzzese C, Dufresne A. TEMPO-oxidized nanocellulose participating as crosslinking aid for alginate-based sponges. ACS Appl Mater Interfaces 2012;4:4948–59.
[95] Mohammed N, Grishkewich N, Berry RM, Tam KC. Cellulose nanocrystal–alginate hydrogel beads as novel adsorbents for organic dyes in aqueous solutions. Cellulose 2015;22:3725–38.
[96] Shaghaleh H, Xu X, Wang S. Current progress in production of biopolymeric materials based on cellulose, cellulose nano fibers, and cellulose derivatives. RSC Adv 2018;8:825–42.
[97] Edgar KJ, Buchanan CM, Debenham JS, Rundquist PA, Seiler BD, Shelton MC, et al. Advances in cellulose ester performance and application. Prog Polym Sci 2001;26:1605–88.
[98] Ayuk JE, Mathew AP, Oksman K. The effect of plasticizer and cellulose nanowhisker content on the dispersion and properties of cellulose acetate butyrate nanocomposites. J Appl Polym Sci 2009;114:2723–30.
[99] Khan B, Bilal Khan Niazi M, Samin G, Jahan Z. Thermoplastic Starch: A Possible Biodegradable Food Packaging Material—A Review. J Food Process Eng 2017;40, e12447/1-17.
[100] Ogunsona E, Ojogbo E, Mekonnen T. Advanced material applications of starch and its derivatives. Eur Polym J 2018;108:570–81.
[101] Sanyang ML, Sapuan SM, Jawaid M, Ishak MR, Sahari J. Effect of plasticizer type and concentration on tensile, thermal and barrier properties of biodegradable films based on sugar palm (Arenga pinnata) starch. Polymers 2015;7:1106–24.
[102] Ge X, Yu L, Liu Z, Liu H, Chen Y, Chen L. Developing acrylated epoxidized soybean oil coating for improving moisture sensitivity and permeability of starch-based film. Int J Biol Macromol 2019;125:370–5.
[103] Le Corre D, Bras J, Dufresne A. Starch nanoparticles: a review. Biomacromolecules 2010;11:1139–53.
[104] Liu H, Xie F, Yu L, Chen L, Li L. Thermal processing of starch-based polymers. Prog Polym Sci 2009;34:1348–68.
[105] Abdullah ZW, Dong Y. Recent advances and perspectives on starch nanocomposites for packaging applications. J Mater Sci 2018;53:15319–39.
[106] Lu Y, Weng L, Cao X. Biocomposites of plasticized starch reinforced with cellulose crystallites from cottonseed linter. Macromol Biosci 2005;5:1101–7.
[107] Slavutsky AM, Bertuzzi MA. Water barrier properties of starch films reinforced with cellulose nanocrystals obtained from sugarcane bagasse. Carbohydr Polym 2014;110:53–61.
[108] Cao X, Chen Y, Chang PR, Muir AD, Falk G. Starch-based nanocomposites reinforced with flax cellulose nanocrystals. Express Polym Lett 2008;2:502–10.
[109] Forssell PM, Mikkilä JM, Moates GK, Parker R. Phase and glass transition behaviour of concentrated barley starch-glycerol-water mixtures, a model for thermoplastic starch. Carbohydr Polym 1998;34:275–82.
[110] Fishman ML, Coffin DR, Konstance RP, Onwulata CI. Extrusion of pectin/starch blends plasticized with glycerol. Carbohydr Polym 2000;41:317–25.
[111] Forssell P, Mikkilä J, Suortti T, Seppälä J, Poutanen K. Plasticization of barley starch with glycerol and water. J Macromol Sci Part A Pure Appl Chem 1996;33:703–15.
[112] Ma X, Yu J, Wang N. Glycerol plasticized-starch/multiwall carbon nanotube composites for electroactive polymers. Compos Sci Technol 2008;68:268–73.
[113] Angles MN, Dufresne A. Plasticized starch/tunicin whiskers nanocomposite materials. 2. Mechanical behavior. Macromolecules 2001;34: 2921–31.
[114] Mathew AP, Dufresne A. Morphological investigation of nanocomposites from sorbitol plasticized starch and tunicin whiskers. Biomacromolecules 2002;3:609–17.
[115] Mathew AP, Thielemans W, Dufresne A. Mechanical properties of nanocomposites from sorbitol plasticized starch and tunicin whiskers. J Appl Polym Sci 2008;109:4065–74.
[116] Castro-Aguirre E, Iñiguez-Franco F, Samsudin H, Fang X, Auras R. Poly (lactic acid)—mass production, processing, industrial applications, and end of life. Adv Drug Deliv Rev 2016;107:333–66.
[117] Chen Y, Geever LM, Killion JA, Lyons JG, Higginbotham CL, Devine DM. Review of multifarious applications of poly (lactic acid). Polym Plast Technol Eng 2016;55:1057–75.
[118] Di Lorenzo ML, Androsch R, editors. Industrial applications of poly (lactic acid). Adv Polym Sci; 2018, 228 pp.
[119] Jacobsen S, Fritz HG, Degée P, Dubois P, Jérôme R. Polylactide (PLA)—a new way of production. Polym Eng Sci 1999;39:1311–9.
[120] Vink ETH, Rábago KR, Glassner DA, Gruber PR. Applications of life cycle assessment to NatureWorksTM polylactide (PLA) production. Polym Degrad Stab 2003;80:403–19.
[121] Dhar P, Tarafder D, Kumar A, Katiyar V. Effect of cellulose nanocrystal polymorphs on mechanical, barrier and thermal properties of poly(lactic acid) based bionanocomposites. RSC Adv 2015;5:60426–40.
[122] Lange BJ, Wyser Y. Recent innovations in barrier yechnologies for plastic packaging - a review. Packag Technol Sci 2003;16:149–58.
[123] Anderson KS, Schreck KM, Hillmyer MA. Toughening polylactide. Polym Rev (Phila Pa) 2008;48:85–108.
[124] Li Z, Tan BH, Lin T, He C. Recent advances in stereocomplexation of enantiomeric PLA-based copolymers and applications. Prog Polym Sci 2016;62:22–72.
[125] Tan BH, Muiruri JK, Li Z, He C. Recent progress in using stereocomplexation for enhancement of thermal and mechanical property of polylactide. ACS Sustain Chem Eng 2016;4:5370–91.
[126] Meng QK, Hetzer M, De Kee D. PLA/clay/wood nanocomposites: nanoclay effects on mechanical and thermal properties. J Compos Mater 2011;45:1145–58.
[127] Sanchez-Garcia MD, Lagaron JM. On the use of plant cellulose nanowhiskers to enhance the barrier properties of polylactic acid. Cellulose 2010;17:987–1004.
[128] Dufresne A, Kellerhals MB, Witholt B. Transcrystallization in Mcl-PHAs/cellulose whiskers composites. Macromolecules 1999;32:7396–401.
[129] Martínez-Sanz M, Lopez-Rubio A, Lagaron JM. Optimization of the dispersion of unmodified bacterial cellulose nanowhiskers into polylactide via melt compounding to significantly enhance barrier and mechanical properties. Biomacromolecules 2012;13:3887–99.
[130] Fortunati E, Peltzer MA, Armentano I, Torre L, Jiménez A, Kenny JM. Effects of modified cellulose nanocrystals on the barrier and migration properties of PLA nano-biocomposites. Carbohydr Polym 2012;90:948–56.
[131] Lagaron JM, Catalá R, Gavara R. Structural characteristics defining high barrier properties in polymeric materials. Mater Sci Technol 2004;20:1–7.
[132] Fortunati E, Armentano I, Zhou Q, Puglia D, Terenzi A, Berglund LA, et al. Microstructure and nonisothermal cold crystallization of PLA composites based on silver nanoparticles and nanocrystalline cellulose. Polym Degrad Stab 2012;97:2027, -20.
[133] Azeredo HMC, Miranda KWE, Rosa MF, Nascimento DM, de Moura MR. Edible films from alginate-acerola puree reinforced with cellulose whiskers. LWT Food Sci Technol 2012;46:294–7.
[134] Azeredo HMC, Mattoso LHC, Wood D, Williams TG, Avena-Bustillos RJ, McHugh TH. Nanocomposite edible films from mango puree reinforced with cellulose nanofibers. J Food Sci 2009;74:N31–5.
[135] Yu H, Yan C, Yao J. Fully biodegradable food packaging materials based on functionalized cellulose nanocrystals/poly(3-hydroxybutyrate-co-3-hydroxyvalerate) nanocomposites. RSC Adv 2014;4:59792–802.
[136] Dufresne A, Vignon MR. Improvement of starch film performances using cellulose microfibrils. Macromolecules 1998;31:2693–6.
[137] Abdollahi M, Alboofetileh M, Behrooz R, Rezaei M, Miraki R. Reducing water sensitivity of alginate bio-nanocomposite film using cellulose nanoparticles. Int J Biol Macromol 2013;54:166–73.
[138] Petersson L, Kvien I, Oksman K. Structure and thermal properties of poly (lactic acid)/cellulose whiskers nanocomposite materials. Compos Sci Technol 2007;67:2535–44.
[139] Labuza TP. Effect of water activity on reaction kinetics of food deterioration. Food Technol 1980;34:36–41.
[140] Fortunati E, Armentano I, Zhou Q, Iannoni A, Saino E, Visai L, et al. Multifunctional bionanocomposite films of poly(lactic acid), cellulose nanocrystals and silver nanoparticles. Carbohydr Polym 2012;87:1596–605.
[141] Ho KG, Pometto AL, Hinz PN. Effects of temperature and relative rumidity on polylactic acid plastic degradation. J Environ Polym Degrad 1999;7:83–92.
[142] Mathew AP, Oksman K, Sain M. Mechanical properties of biodegradable composites from poly lactic acid (PLA) and microcrystalline cellulose (MCC). J Appl Polym Sci 2005;97:2014–25.
[143] Arrieta MP, Fortunati E, Dominici F, Rayón E, López J, Kenny JM. PLA-PHB/cellulose based films: mechanical, barrier and disintegration properties. Polym Degrad Stab 2014;107:139–49.
[144] Fortunati E, Peltzer MA, Armentano I, Jiménez A, Kenny JM. Combined effects of cellulose nanocrystals and silver nanoparticles on the barrier and migration properties of PLA nano-biocomposites. J Food Eng 2013;118:117–24.
[145] Oksman K, Mathew AP, Bondeson D, Kvien I. Manufacturing process of cellulose whiskers/polylactic acid nanocomposites. Compos Sci Technol 2006;66:2776–84.

Please cite this article as: C. Calvino, N. Macke, R. Kato et al., Development, processing and applications of bio-sourced cellulose nanocrystal composites, Prog Polym Sci, https://doi.org/10.1016/j.progpolymsci.2020.101221

[146] Bondeson D, Kvien I, Oksman K. Strategies for preparation of cellulose whiskers from microcrystalline cellulose as reinforcement in nanocomposites. ACS Symp Ser 2006;938:10–25.
[147] Potthast A, Rosenau T, Sartori J, Sixta H, Kosma P. Hydrolytic processes and condensation reactions in the cellulose solvent system N, N-dimethylacetamide/lithium chloride. Part 2: degradation of cellulose. Polymer 2003;44:7–17.
[148] Kuan CF, Kuan HC, Ma CCM, Chen CH. Mechanical and electrical properties of multi-wall carbon nanotube/poly(lactic acid) composites. J Phys Chem Solids 2008;69:1395–8.
[149] Pereda M, Kissi NE, Dufresne A. Extrusion of polysaccharide nanocrystal reinforced polymer nanocomposites through compatibilization with poly(ethylene oxide). ACS Appl Mater Interfaces 2014;6:9365–75.
[150] Helbert W, Cavaillé J, Dufresne A. Thermoplastic nanocomposites filled with wheat straw cellulose whiskers. Part I: processing and mechanical behavior. Polym Compos 1996;17:604–11.
[151] Ray SS, Okamoto M. Biodegradable polylactide and its nanocomposites: opening a new dimension for plastics and composites. Macromol Rapid Commun 2003;24:815–40.
[152] Arrieta MP, López J, Ferrándiz S, Peltzer MA. Characterization of PLA-limonene blends for food packaging applications. Polym Test 2013;32:760–8.
[153] Halász K, Csóka L. Plasticized biodegradable poly (lactic acid) based composites containing cellulose in micro-and nanosize. J Eng (Stevenage) 2013;2013, 329379/1-9.
[154] Wohlhauser S, Delepierre G, Labet M, Morandi G, Thielemans W, Weder C, et al. Grafting polymers from cellulose nanocrystals: synthesis, properties, and applications. Macromolecules 2018;51:6157–89.
[155] Braun B, Dorgan JR, Hollingsworth LO. Supra-molecular ecobionanocomposites based on polylactide and cellulosic nanowhiskers: synthesis and properties. Biomacromolecules 2012;13:2013–9.
[156] Goffin AL, Raquez JM, Duquesne E, Siqueira G, Habibi Y, Dufresne A, et al. From interfacial ring-opening polymerization to melt processing of cellulose nanowhisker-filled polylactide-based nanocomposites. Biomacromolecules 2011;12:2456–65.
[157] Bitinis N, Verdejo R, Bras J, Fortunati E, Kenny JM, Torre L, et al. Poly (lactic acid)/natural rubber/cellulose nanocrystal bionanocomposites Part I. Processing and morphology. Carbohydr Polym 2013;96:611–20.
[158] Lizundia E, Fortunati E, Dominici F, Vilas JL, León LM, Armentano I, et al. PLLA-grafted cellulose nanocrystals: role of the CNC content and grafting on the PLA bionanocomposite film properties. Carbohydr Polym 2016;142:105–13.
[159] Carlmark A, Larsson E, Malmström E. Grafting of cellulose by ring-opening polymerisation - A review. Eur Polym J 2012;48:1646–59.
[160] Clarke CJ, Jones RAL, Edwards JL, Shull KR, Penfold J. The structure of grafted polystyrene layers in a range of matrix polymers. Macromolecules 1995;28:2042–9.
[161] Lönnberg H, Larsson K, Lindström T, Hult A, Malmström E. Synthesis of polycaprolactone-grafted microfibrillated cellulose for use in novel bionanocomposites–influence of the graft length on the mechanical properties. ACS Appl Mater Interfaces 2011;3:1426–33.
[162] Pei A, Zhou Q, Berglund LA. Functionalized cellulose nanocrystals as biobased nucleation agents in poly (l-lactide)(PLLA)–Crystallization and mechanical property effects. Compos Sci Technol 2010;70:815–21.
[163] Siqueira G, Bras J, Dufresne A. Cellulose whiskers versus microfibrils: influence of the nature of the nanoparticle and its surface functionalization on the thermal and mechanical properties of nanocomposites. Biomacromolecules 2008;10:425–32.
[164] Braun B, Dorgan JR. Single-step method for the isolation and surface functionalization of cellulosic nanowhiskers. Biomacromolecules 2008;10:334–41.
[165] Sobkowicz MJ, Dorgan JR, Gneshin KW, Herring AM, McKinnon JT. Renewable cellulose derived carbon nanospheres as nucleating agents for polylactide and polypropylene. J Polym Environ 2008;16:131–40.
[166] Fukushima K, Kimura Y. Stereocomplexed polylactides (Neo-PLA) as high-performance bio-based polymers: their formation, properties, and application. Polym Int 2006;55:626–42.
[167] Wu H, Nagarajan S, Zhou L, Duan Y, Zhang J. Synthesis and characterization of cellulose nanocrystal-graft-poly(D-lactide) and its nanocomposite with poly(L-lactide). Polymer 2016;103:365–75.
[168] Jaratrotkamjorn R, Khaokong C, Tanrattanakul V. Toughness enhancement of poly(lactic acid) by melt blending with natural rubber. J Appl Polym Sci 2010;124:5027–36.
[169] Muiruri JK, Liu S, Teo WS, Kong J, He C. Highly biodegradable and tough polylactic acid–cellulose nanocrystal composite. ACS Sustain Chem Eng 2017;5:3929–37.
[170] Chen GQ, Zhang G, Park SJ, Lee SY. Industrial scale production of poly(3-hydroxybutyrate-co-3-hydroxyhexanoate). Appl Microbiol Biotechnol 2001;57:50–5.
[171] Zinn M, Witholt B, Egli T. Occurrence, synthesis and medical application of bacterial polyhydroxyalkanoate. Adv Drug Deliv Rev 2001;53:5–21.
[172] Kai D, Loh XJ. Polyhydroxyalkanoates: chemical modifications toward biomedical applications. ACS Sustain Chem Eng 2014;2:106–19.
[173] Bucci DZ, Tavares LBB, Sell I. PHB packaging for the storage of food products. Polym Test 2005;24:564–71.
[174] Yeo JCC, Muiruri JK, Thitsartarn W, Li Z, He C. Recent advances in the development of biodegradable PHB-based toughening materials: approaches, advantages and applications. Mater Sci Eng C 2018;92:1092–116.
[175] Seoane IT, Manfredi LB, Cyras VP, Torre L, Fortunati E, Puglia D. Effect of cellulose nanocrystals and bacterial cellulose on disintegrability in composting conditions of plasticized PHB nanocomposites. Polymers 2017;9, 561/1-16.
[176] Seoane IT, Cerrutti P, Vazquez A, Manfredi LB, Cyras VP. Polyhydroxybutyrate-based nanocomposites with cellulose nanocrystals and bacterial cellulose. J Polym Environ 2017;25:586–98.
[177] Patrício P, Pereira FV, dos Santos MC, de Souza PP, Roa JPB, Orefice RL. Increasing the elongation at break of polyhydroxybutyrate biopolymer : effect of cellulose nanowhiskers on mechanical and thermal properties. J Appl Polym Sci 2013;127:3613–21.
[178] Arrieta MP, Samper MD, Aldas M, López J. On the use of PLA-PHB blends for sustainable food packaging applications. Materials 2017;10, 1008/1-26.
[179] Arrieta MP, Fortunati E, Dominici F, López J, Kenny JM. Bionanocomposite films based on plasticized PLA–PHB/cellulose nanocrystal blends. Carbohydr Polym 2015;121:265–75.
[180] Arrieta MP, Fortunati E, Dominici F, Rayón E, López J, Kenny JM. Multifunctional PLA–PHB/cellulose nanocrystal films: processing, structural and thermal properties. Carbohydr Polym 2014;107:16–24.
[181] Eagan JM, Xu J, Di Girolamo R, Thurber CM, Macosko CW, La Pointe AM, et al. Combining polyethylene and polypropylene: enhanced performance with PE/iPP multiblock polymers. Science 2017;355:814–6.
[182] Zhuo C, Levendis YA. Upcycling waste plastics into carbon nanomaterials : a review. J Appl Polym Sci 2014;131:1–14.
[183] Goffin AL, Habibi Y, Raquez JM, Dubois P. Polyester-grafted cellulose nanowhiskers: a new approach for tuning the microstructure of immiscible polyester blends. ACS Appl Mater Interfaces 2012;4:3364–71.
[184] Yong C, Mei C, Guan M, Wu Q, Sun X, Xu B, et al. Interfacial modification mechanism of nanocellulose as a compatibilizer for immiscible binary poly(vinyl alcohol)/poly(ethylene oxide) blends. J Appl Polym Sci 2018;135:1–11.
[185] Saito T, Isogai A. Ion-exchange behavior of carboxylate groups in fibrous cellulose oxidized by the TEMPO-mediated system. Carbohydr Polym 2005;61:183–90.
[186] Wang D. A critical review of cellulose-based nanomaterials for water purification in industrial processes. Cellulose 2019;26:687–701.
[187] Lu J, Jin RN, Liu C, Wang YF, Ouyang XK. Magnetic carboxylated cellulose nanocrystals as adsorbent for the removal of Pb(II) from aqueous solution. Int J Biol Macromol 2016;93:547–56.
[188] Hokkanen S, Repo E, Sillanpää M. Removal of heavy metals from aqueous solutions by succinic anhydride modified mercerized nanocellulose. Chem Eng J 2013;223:40–7.
[189] Karim Z, Mathew AP, Kokol V, Wei J, Grahn M. High-flux affinity membranes based on cellulose nanocomposites for removal of heavy metal ions from industrial effluents. RSC Adv 2016;6:20644–53.
[190] Lam E, Male KB, Chong JH, Leung ACW, Luong JHT. Applications of functionalized and nanoparticle-modified nanocrystalline cellulose. Trends Biotechnol 2012;30:283–90.
[191] Jorfi M, Foster EJ. Recent advances in nanocellulose for biomedical applications. J Appl Polym Sci 2015;132:1–19.
[192] Lin N, Gèze A, Wouessidjewe D, Huang J, Dufresne A. Biocompatible double-membrane hydrogels from cationic cellulose nanocrystals and anionic alginate as complexing drugs codelivery. ACS Appl Mater Interfaces 2016;8:6880–9.
[193] Wang K, Nune KC, Misra RDK. The functional response of alginate-gelatin-nanocrystalline cellulose injectable hydrogels toward delivery of cells and bioactive molecules. Acta Biomater 2016;36: 143–51.
[194] Yang M, Zhen W, Chen H, Shan Z. Biomimetic design of oxidized bacterial cellulose-gelatin-hydroxyapatite nanocomposites. J Bionic Eng 2016;13:631–40.
[195] de Castro DO, Bras J, Gandini A, Belgacem N. Surface grafting of cellulose nanocrystals with natural antimicrobial rosin mixture using a green process. Carbohydr Polym 2016;137:1–8.
[196] Feese E, Sadeghifar H, Gracz HS, Argyropoulos DS, Ghiladi RA. Photobactericidal porphyrin-cellulose nanocrystals: synthesis, characterization, and antimicrobial properties. Biomacromolecules 2011;12:3528–39.
[197] Tang J, Song Y, Tanvir S, Anderson WA, Berry RM, Tam KC. Polyrhodanine coated cellulose nanocrystals: a sustainable antimicrobial agent. ACS Sustain Chem Eng 2015;3:1801–9.
[198] Shi Q, Zhou C, Yue Y, Guo W, Wu Y, Wu Q. Mechanical properties and in vitro degradation of electrospun bio-nanocomposite mats from PLA and cellulose nanocrystals. Carbohydr Polym 2012;90:301–8.
[199] Binek A, Petrus ML, Huber N, Bristow H, Hu Y, Bein T, et al. Recycling perovskite solar cells to avoid lead waste. ACS Appl Mater Interfaces 2016;8:12881–6.
[200] Rydh CJ. Environmental assessment of vanadium redox and lead-acid batteries for stationary energy storage. J Power Sources 1999;80:21–9.
[201] Jabbour L, Bongiovanni R, Chaussy D, Gerbaldi C, Beneventi D. Cellulose-based Li-ion batteries: a review. Cellulose 2013;20:1523–45.

Please cite this article as: C. Calvino, N. Macke, R. Kato et al., Development, processing and applications of bio-sourced cellulose nanocrystal composites, Prog Polym Sci, https://doi.org/10.1016/j.progpolymsci.2020.101221

[202] Samir MASA, Alloin F, Gorecki W, Sanchez JY, Dufresne A. Nanocomposite polymer electrolytes based on poly(oxyethylene) and cellulose nanocrystals. J Phys Chem B 2004;108:10845–52.
[203] Wu X, Chabot VL, Kim BK, Yu A, Berry RM, Tam KC. Cost-effective and scalable chemical synthesis of conductive cellulose nanocrystals for high-performance supercapacitors. Electrochim Acta 2014;138:139–47.
[204] Okahisa Y, Yoshida A, Miyaguchi S, Yano H. Optically transparent wood-cellulose nanocomposite as a base substrate for flexible organic light-emitting diode displays. Compos Sci Technol 2009;69: 1958–61.
[205] Najafabadi E, Zhou YH, Knauer KA, Fuentes-Hernandez C, Kippelen B. Efficient organic light-emitting diodes fabricated on cellulose nanocrystal substrates. Appl Phys Lett 2014;105, 063305/1-4.
[206] Zhou Y, Fuentes-Hernandez C, Khan TM, Liu JC, Hsu J, Shim JW, et al. Recyclable organic solar cells on cellulose nanocrystal substrates. Sci Rep 2013;3:24–6.

Please cite this article as: C. Calvino, N. Macke, R. Kato et al., Development, processing and applications of bio-sourced cellulose nanocrystal composites, Prog Polym Sci, https://doi.org/10.1016/j.progpolymsci.2020.101221