Nanocellulose: a benefit for green food packaging

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Nanocellulose in green food packaging

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Abstract

The development of packaging materials with new functionalities and lower environmental impact is now an urgent requisite of our society. On one hand, the shelf-life extension of packaged products can be an answer to the exponential increase of worldwide demand for food. On the other hand, uncertainty of crude oil prices and reserves has imposed the necessity to find raw materials to replace oil-derived polymers. Additionally, consumers' awareness towards environmental issues increasingly pushes industries to look with renewed interest to "green" solutions. In response to these issues, numerous polymers have been exploited to develop biodegradable food packaging materials. Although the use of biopolymers has been limited due to their poor mechanical and barrier properties, these can be enhanced by adding reinforcing

nano-sized components to form nanocomposites. Cellulose is probably the most used and well-known renewable and sustainable raw material. The mechanical properties, reinforcing capabilities, abundance, low density and biodegradability of nanosized cellulose make it an ideal candidate for polymer nanocomposites processing. Here we review the potential applications of cellulose based nanocomposites in food packaging materials, highlighting the several types of biopolymers with nanocellulose fillers that have been used to form bio-nanocomposite materials. The trends in nanocellulose packaging applications are also addressed.

Keywords

Bionanocomposites, Food Contact Material; Nanocellulose.

Introduction

Food packaging evolves in response to the advances in materials science and technology, as well as the changes in consumers' demands. In today´s global economy, packaging is not only essential to enable an effective distribution and preservation of food, but also to simplify their end-use convenience and for communication with the final consumer. Plastics are, by far, the most used packaging materials due to their excellent properties and versatility, which allow them to be used in a wide range of applications. Global plastics production has shown continuous growth for more than 50 years, and globally it rose to 299 million tonnes in 2013 (PlasticsEurope- Association of Plastics manufactures, 2014). In Europe, packaging applications represent about 40% of the total plastics demand, representing the largest application sector (PlasticsEurope- Association of Plastics manufactures, 2014). Repeatedly, every year several hundred thousand tonnes of plastics are discarded into the environment and accumulate in the oceans. One of the options to decrease plastics waste accumulation is incineration but this is expensive and dangerous, releasing carbon dioxide and harmful chemicals to the atmosphere.

Significant advances are being made in the environmental performance of plastics in their production and end-of-life phases, to contribute for their sustainability (PlasticsEurope- Association of Plastics manufactures 2014). Therefore, there is an increasing tendency for the use of bio-based materials. Bioplastics can be made from renewable bio-based resources, and/or they can be biodegradable/compostable. The biodegradability/compostability of a material is critical for minimising environmental impact and it is an important element for claiming greater

sustainability of bioplastics over conventional plastics and for claiming enhanced functionality of one bioplastic over another.

Unfortunately, the use of biopolymers as food packaging materials has been limited by poorer mechanical, thermal and barrier properties, as compared to conventional materials. One way to overcome these limitations is by using nanocomposites and nanoparticles which have been shown to have better mechanical and barrier properties (Kanmani and Rhim, 2014; Reddy and Rhim, 2014; Sanuja *et al.*, 2014). Nanocomposites are multi-phase materials, in which the majority of the dispersed phase components have one or more dimensions of the order of 100 nm or less (EFSA-Q-2007-124a). The nano-sized fillers play a structural role, acting to improve the mechanical and barrier properties of the matrix. While the matrix tension can be transferred to the nanofillers through the interface increasing the material mechanical properties (Trovatti *et al.*, 2012; Arfat *et al.*, 2014; Kanmani and Rhim, 2014), the dispersed state of the nanofillers decreases the diffusion of gases through the material (Trovatti *et al.*, 2012; Arfat *et al.*, 2014; Kanmani and Rhim, 2014).

The incorporation of nanofillers of cellulose, chitosan or titanium dioxide (TiO_2) into biopolymers can improve, not only the biopolymers' mechanical and barrier properties, but also input additional functionalities such as antimicrobial, biosensor, oxygen scavenging, etc. (Rhim *et al*., 2007).

Finally, it is important to emphasize the Scientific Opinion adopted by the Scientific Committee of EFSA in 2009 (EFSA-Q-2007-124a), following a request from the European Commission, on potential risks arising from nanoscience and nanotechnologies on food and feed safety. This recommends; in particular, actions that should be taken to develop methods to detect and

measure engineered nanomaterials (ENMs) in food/feed and biological tissues, to survey the use of ENMs in these matrices, to assess the exposure of consumers and livestock, and to generate information on the toxicity of different ENMs.

Biopolymers

Biopolymers usually refer to biodegradable polymers and/or those derived from renewable sources. The first have the capability to be degraded or broken down through the action of naturally occurring organisms leaving behind organic by-products (Othman, 2014), while the second are derived or extracted from bio-renewable resources (plants, marine animals and microorganisms). During the growth cycles of some organisms, polymers are produced as biomass or by-products. They are considered environmentally friendly materials not only due to their source but also, in most cases, to their natural biodegradability. It should however be noted that there is a significant proportion of polymers produced from biological resources that are not 'biodegradable' according to the internationally accepted standards (SCS 2011). Figure 1 represents the four types of biopolymers based on their pathways and biodegradability (Kaplan 1998; Chandra and Rustgi, 1998*;* Steinbuchel, 2005; Kaith and Kaur, 2011; Kalia *et al.,* 2011).

The most common type of biopolymers suitable for food packaging applications are natural occurring biopolymers such as starch, cellulose, chitosan, and agar (derived from carbohydrate), as well as gelatine, gluten, alginate, whey protein, and collagen. More recently, synthetic biopolymers have been proposed, such as polylactic acid (PLA), polycaprolactone (PCL), polyglycolic acid (PGA), polyvinyl alcohol (PVA), and polybutylene succinate PBS (Rhim *et al.,* 2007). The advantages of synthetically produced biopolymers include the potential to create a

sustainable industry as well as the enhancement of various properties such as durability, flexibility, high gloss, clarity, and tensile strength (Rhim *et al*., 2007). The most common synthetic biopolymer studied is PLA (Jochen Weiss *et al.,* 2006), which is produced from lactic acid and can be produced by fermentation of carbohydrates from plant resources such as sugar beet and corn. The advantages of PLA include biodegradability and the possibility to tailor its lifespan (Goffin *et al.,* 2011; Fortunati *et al.,* 2012; Silvério *et al.,* 2013; Fortunati *et al.,* 2014; Fortunati *et al.,* 2015; Halász *et al.,* 2015).

Biopolymers have great potential in the commercial plastics market, in particular, for food packaging applications. However, there are significant impediments in converting them into real applications due to their poor properties (mechanical properties, thermal stability, water absorption and barrier properties) in comparison to their synthetic counterparts. One way to enhance biopolymers is by using 'nanocomposite materials' (Kaplan, 1998; Chandra and Rustgi, 1998; Steinbuchel, 2005; Kalia *et al.,* 2011; Kaith and Kaur, 2011). Among these, cellulose nanomaterials are expected to be less expensive than many other nanomaterials, show impressive strength-to-weight ratio and have demonstrated major environmental benefits because they are recyclable, biodegradable, and produced from renewable resources such as trees and other plants, algae or bacteria (Jorfi*, et al.* 2013).

Cellulose

Cellulose is a polydisperse linear homopolymer composed of D-glucopyranose units linked with a β-1,4-glycosidic bond, including free hydroxyl groups (-OH) at the C-2, C-3, and C-6 atoms.

Based on the -OH groups and the oxygen atoms of both the pyranose ring and the glycosidic bond, ordered hydrogen bond networks can be formed (Figure 2) (Ball, 2015)

Cellulose is the most abundant biopolymer in nature and it is derived from readily available biomass, is a homopolysaccharide, composed of (β-1,4) linked-glucopyranose units. In recent times, cellulose has attracted considerable attention as one of the most well-known renewable and ecological raw materials for obtaining environmentally friendly and biocompatible technological products. Biomass produced by photosynthetic organisms such as plants, algae, and some bacteria is made up of cellulose and for that reason it is the most abundant biopolymer on earth (Klemm, 2005). As a result, the use of cellulose-based materials in composites has increased over the last few years because of their relative low price compared to conventional materials, their recyclability, and their mechanical properties. Wood pulp remains the most important raw material for the processing of cellulose. The structure of wood is extremely complex due to the presence of lignin, a three-dimensional (3D) polymer network that binds to carbohydrates (hemicellulose and cellulose) to form a tight and compact structure from which cellulose is isolated by large-scale chemical pulping, separation and purification processes (Klemm, 2005). Wood is approximately 40-50 wt % cellulose, half in nanocrystal form, half in amorphous form (Figure 3).

Cellulose can be chemically modified to produce different derivatives. The hydrogen bonding patterns in cellulose are considered to be the main factor which determines its physical and chemical properties. Intra- and intermolecular bond formation affects directly the solubility, crystallinity and hydroxyl reactivity. Cellulose derivatives have been designed and adjusted to

obtain certain desired properties and the chemical functionalization of cellulose is done by changing the inherent hydrogen bonding network and by introducing different substituents (Ball, 2015).

Different raw materials, as well as different top-down and bottom-up production methods, including physical and chemical modification, lead to cellulose nanomaterials with different morphology and properties, such as size, aspect ratio, morphology, crystal structure and degree of crystallinity (Jorfi *et al.,* 2013).

The production of cellulose nanoparticles (CNs) is generally carried out in two steps. The first stage involves a pre-treatment of the raw material to obtain "purified" individual cellulosic fibers that can be further processed. Depending on the source of the raw material, different pre-treatments are applied, according to the desired size and morphology of the final CNs (Moon *et al*., 2011). The second stage (generally called "fibrillation") concerns the transformation of the individual cellulosic fibers into cellulose nanofibrils (CNF) or cellulose nanocrystals (CNC) (Rebouillat *et al*., 2013). The leading processes typically used for this transformation are mechanical treatment, acid hydrolysis or enzymatic hydrolysis, either used separately or combined (Hubbe *et al.*, 2008 and Stelte *et al.,* 2009). For example, in order to facilitate disintegration of the cellulosic fibers, enzymatic pre-treatments followed by mechanical treatments may be applied (Pääkkö *et al*., 2007). The pre-treatments allow opening of the structure of the material to facilitate access to the cellulose micro-structure during the second stage of the process. Thus, it is important to apply a sufficiently selective pre-treatment which

increases the access to the micro sites and still maintains a desired degree of polymerization (Rebouillat, *et al*., 2013).

Cellulose nanocrystals (CNCs) and cellulose nanofibrils (CNFs) can be obtained from the same cellulose source by two different methods. CNC can be produced by acid hydrolysis of wood fiber or other cellulosic materials, yielding rod-like nanoscale materials that are 3-20 nm wide and 50-500 nm in length (Jorfi *et al.,* 2013). CNF can be produced using mechanical processes, with or without chemical and biological treatments, yielding 4-50 nm wide and are longer than 500 nm of linear or branched chains (Jorfi*, et al.,* 2013). In addition to CNC and CNF, there are two more types of cellulose nanomaterials: microcrystalline cellulose (MCC) consisting of purified and partially depolymerized cellulose particles with an average degree of polymerization between 200 and 450, and microfibrillated cellulose (CMF), obtained when cellulose fibers are submitted to high mechanical shearing forces.

Figure 4 shows a schematic representation of different derivatization methods to convert macroscopic cellulosic fibres into nanoscale fibrils (Paakko, 2007):

− the conversion of cellulose macrofibers into highly crystalline and low aspect ratio fibrils (aggregates) *via* aggressive acid hydrolysis and sonication (Fortunati *et al.,* 2015);

− the disintegration or defibrillation of macrofibers into highly entangled connected fibrils and mechanically strong networks of CMF/CNF through the application of high shear forces (Siro and Plackett, 2010);

– the incorporation of an additional enzymatic hydrolysis which produces a mixture of predominantly cellulose/fibrils (about 5 nm thickness) and fibril aggregates (about 10-20 nm thickness) (Moon, 2011).

Cellulose nanoparticles have a strong tendency for self-association due to the interaction between surface hydroxyl groups. This is a desirable feature for the formation of "wall support" within the host polymer matrix. However, these inter-particle interactions can also cause aggregation during the preparation of the nanocomposite thus inducing the loss of the nanoscale and limit the potential of mechanical reinforcement. This aggregation phenomenon is more pronounced for smaller particles due to the increased specific surface area (Dufresne, 2013). Different strategies have been reported in the literature to homogeneously mix cellulose nanoparticles with the polymeric matrix. These different strategies are summarized in Figure 5 (Dufresne, 2012).

Nanocellulose has a large amount of hydroxyl groups on their surface, providing the possibility of extensive chemical modifications. Most of these modifications aim to improve two factors: the dispersibility (by reducing hydrogen bonding, which cause reaggregation of the crystals during processing, for example, spray-drying), and the compatibility with the different processing solvents or matrices that are suitable in the production of nanocomposites. The most used chemical modifications are esterification, silylation, cationization, carboxylation and polymer grafting (Morandi *et al, 2009*).

Cellulose Nanocrystals (CNC)

Cellulose nanocrystals are a novel class of nanomaterials with many promising applications. CNC are obtained in aqueous suspension from strong acid hydrolysis of cellulosic fibers. This

allows the dissolution of the amorphous areas, in the fibers by promoting the hydrolytic cleavage of the glycosidic bonds, thus releasing individual crystallites after mechanical treatment such as sonication (Fortunati *et al.*, 2012; Silvério *et al.*, 2013; Abdollahi *et al.*, 2013; Arrieta *et al.*, 2014; Reddy *et al.*, 2014; Arrieta *et al.*, 2015; Fortunati *et al.*, 2015; Nahla *et al.*, 2015; Alves *et al.*, 2015; Mondragon *et al.*, 2015; El Miri *et al.*, 2015). Different strong acids have been shown to successfully degrade cellulose fibers, but hydrochloric and sulphuric acids have been more extensively used (Fortunati *et al.*, 2012; Silvério *et al.*, 2013; Abdollahi *et al.*, 2013; Fortunati *et al.*, 2014; Reddy, 2014; Arrieta *et al.*, 2015; Fortunati *et al.*, 2015; Nahla *et al.*, 2015; Alves *et al.*, 2015; Mondragon *et al.*, 2015; Miri *et al.*, 2015). One of the major reasons for using sulphuric acid as hydrolysing agent is its reaction with the surface hydroxyl groups via an esterification process allowing the grafting of anionic sulphate ester groups. The presence of these negatively charged groups forms a negative electrostatic layer that covers the nanocrystals, promoting their dispersion in water. However, this compromises the thermostability of the nanoparticles (Moein *et al.*, 2014; Fortunati *et al.*, 2014; Halász *et al.*, 2015). To increase the thermal stability of nanocrystals produced by this process, neutralization of the nanoparticles by sodium hydroxide (NaOH) can be carried out (Moein *et al.*, 2014; Fortunati et al., 2014; Halász, *et al.*, 2015). These nanoparticles occur as high aspect ratio rod-like nanocrystals, or whiskers (Goffin *et al.*, 2011; Pereda *et al.*, 2011). Their geometrical dimensions depend on the origin of the cellulose substrate and hydrolysis conditions, each rod can be considered as a cellulose crystal (Moon *et al.*, 2011). CNC generally present a relatively broad distribution in length because of the diffusion-controlled nature of the acid hydrolysis. The average length is generally of the order of a few hundred nanometers and the width is of the order of a few nanometers

(Moon *et al.*, 2011). An important parameter for CNC is the aspect ratio, which is defined as the ratio of the length to the width. As reported by Moon *et al.* (2011), the surface chemistry of cellulose nanoparticles is influenced by the extraction procedure used to prepare the nanoparticles from the native cellulosic substrate. Since cellulose nanoparticles have very high surface area (usually of the order of few 100 $m^2.g^{-1}$) because of their nanoscale dimensions, they feature a very large amount of surface hydroxyl groups (2–3 $mmol.g^{-1}$) that allow surface modification to impart any desired surface functionality (Eyley and Thielemans, 2011). For example, the formation of sulphate ester groups on the surface of the nanoparticles is usually achieved by sulphuric acid hydrolysis, a severe but effective treatment to induce high stability of the modified nanocrystals is aqueous suspension. on the other hand, although hydrolysis with hydrochloric acid preserves the hydroxyl groups of the native fibers, it leads to less stable suspensions (Dufresne, 2012),

Cellulose nanoparticles suffer aggregation mainly because of their nanosized and fibrillar structure, characterized by hydrogens bonding between the (β-1,4) linked-glucopyranose units. In order to prevent self-aggregation of the nanoparticles and stimulate efficient dispersion in non-aqueous media, hydrophobic compounds can be used to modify the surface of cellulosic nanoparticles using covalent and non-covalent coupling techniques. A wide variety of chemical modification techniques, such as, coupling hydrophobic small molecules, grafting polymers and oligomers, and adsorbing hydrophobic compounds to the surface hydroxyl groups have been employed (Dufresne, 2012).

Chemical modification of nanocellulose have been used to improve the thermal, mechanical and migration properties of the bionanocomposites (Fortunati *et al.*, 2015; Nahla *et al.* 2015; Alves *et*

al. 2015; Mondragon *et al.* 2015 and El Miri *et al.* 2015). In these examples, CNC were extracted though an optimized chemical treatment, followed by sulphuric acid hydrolysis, and the bionanocomposite films were prepared by solvent casting. In Fortunati *et al.* (2015) the nanocrystals were added to neat PLA polymer at 1wt% and 3wt%, using a commercial surfactant to increase the dispersion of CNC in the biodegradadble matrix. All the nanocomposites maintained the optical transparency of the PLA matrix and the plasticization effect induced by the surfactant suggest the possibility of modulating mechanical properties of the composite. In Nahla *et al.* (2015) the bionanocomposites developed by casting/evaporation of wheat gluten (WG), cellulose nanocrystals (CNC), and TiO2 nanoparticles showed an improvement in TS, Young´s modulus and water sensitivity, with a significant enhancement in breaking length and burst index. Alves *et al.* (2015) showed that increasing the CNC concentration , in corn plasticized films, increases the values found for the thickness, puncture force and elongation at break variables. Mondragon *et al.* (2015) reported that bionanocomposites of gelatine matrix and nanocellulose, showed a lower tensile strength and an improvement of the thermal stability. El Miri *et al.* (2015) verified that the WVP was significantly reduced and the elastic modulus and tensile strength were increased in bionanocomposites films reinforced with cellulose nanocrystals (these are the main properties required for packaging applications).

Since the dispersion level of cellulose nanoparticles in water is good, this is obviously the most suitable processing medium. Both water-soluble polymers and polymer aqueous dispersions (latex) can be used to obtain nanocomposites with CNC. After mixing the cellulose nanoparticle dispersion with the polymer solution/dispersion, a solid nanocomposite film can be obtained by simple casting and water evaporation. This mode of processing allows the preservation of the

individualization state of the nanoparticles resulting from their colloidal dispersion in water (Fortunati *et al.,* 2015; Nahla *et al.,* 2015; Alves *et al.,* 2015; Mondragon *et al.,* 2015; El Miri *et al.,* 2015). Water has been extensively used as a processing medium, although stable suspensions of negatively charged CNCs can be obtained in various polar liquid media. Casting from a mixture of solvents can also be used to prepare nanocellulose-reinforced nanocomposites. By this method, the aqueous suspension of nanoparticles is mixed with the polymer dissolved in a solvent miscible with water, for example, tetrahydrofuran (THF) (Kalia *et al.,* 2011).

Stable cellulose nanoparticle dispersions in apolar or low polarity solvent, can be obtained by physically coating the surface with a surfactant (Fortunati *et al.*, 2012; Arrieta *et al.*, 2014; Arrieta *et al.*, 2015; Fortunati *et al.*, 2015) or chemically grafting apolar moieties onto the surface (Huang *et al.*, 2014). The two methods allow the tuning of the surface and a decrease of the surface energy of the nanoparticle. Experimental conditions should avoid swelling media and the peeling effect of surface-grafted chains inducing their dissolution in the reaction medium. Therefore, the chemical grafting process has to be soft to preserve the integrity of the nanoparticle. The most common surface chemical modifications of CNCs are summarized in Figure 6. They can be categorized into three distinctive groups: (1) substitution of hydroxyl groups with small molecules; (2) polymer grafting based on the 'grafting onto' strategy with different coupling agents; and (3) polymer grafting based on the 'grafting from' approach with a radical polymerization involving ring opening polymerization (ROP) (Goffin *et al.*, 2011), atom transfer radical polymerization (ATRP) (Matyjaszewski *et.al.*, 2001) and single-electron transfer living radical polymerization (SET-LP) (Zhang *et al.*, 2009).

Graft copolymerization is a commonly used method to modify the physical and/or chemical properties of the polymers and their surfaces, (Kalia and Sabaa, 2013; Bhattacharya,. *et al.*, 2004). This method is used to produce copolymers with a branched structure, where the side chains are covalently bonded to the main polymer backbone or substrate (Kalia and Sabaa, 2013). Grafting methods are classified as:

1 - "grafting from", where the growth of the side chains is initiated from the polymer backbonethat contains appropriate active sites. In this method the grafting is performed either with a single monomer (usually in a single step) or with a monomer mixture (either by simultaneous or sequential addition of two monomers) (Kalia and Sabaa, 2013);

2 - "grafting to", where a polymer with reactive end groups is linked to functional groups of the polymer backbone or substrate (Bhattacharya. *et al.*, 2004);

3 - "grafting through", a methoid used to modify cellulose, in which a vinyl derivative of the cellulose is polymerized with the same or another vinyl monomer (Roy *et al.*, 2009).

Cellulose nanocrystals (CNCs), remaining after acid hydrolysis of microcrystalline cellulose (MCC), or CNF (Moein *et al.,* 2014; Arrieta *et al.,* 2015; Mondragon *et al.,* 2015), exhibit a strong tendency to aggregate due to their higher specific surface area and energy. This can limit their potential technological application in most organic media and polymer matrices (Capadona, 2007; van den Berg, 2007). The most usual pathways for the preparation of polymers nanocomposites/ CNC are:

- the solvent method in which the CNC are first dispersed in a solvent in which the host polymer is also soluble or dispersible in latex form, followed by casting and drying (Hajji, 1996);

- melt blending, in which CNC are mixed with a melted polymer whose softening or melting temperature is below 200 °C. To promote dispersion, surfactants or compatibilizers are very often used, especially with most common nonpolar or hydrophobic polymer matrices (Fortunati *et al.*, 2012; Arrieta *et al.*, 2014; Arrieta. *et al.*, 2015; Fortunati *et al.,* 2015).

For *in situ* polymerization, CNC are dispersed in a mixture of precursors or prepolymers (with or without solvent) and subsequently polymerized further to obtain the nanocomposites (Goffin *et al.,* 2011). In the so-called solvent exchange sol-gel process, a template percolating network of CNC is first formed (the gelation of a dispersion of well-individualized CNCs through a solvent exchange) and then the gelled nanofiber template is saturated with a solution of a polymer of choice, before the nanocomposite is dried and shaped (Oksman *et al.,* 2014). These methods have been shown to yield composites with improved mechanical properties, indicating strong interactions between polymer and CNC, owing to the chemical structural similarities between the filler and the matrix.

All-cellulose nanocomposites have been also described, prepared by partially dissolving the cellulose matrix and/or linking the nanocrystals (undissolved cellulose). The matrix and reinforcement phases of all-cellulose composites are completely compatible with each other, allowing efficient stress transfer and good interfacial adhesion (Moein *et al.,* 2014). These biobased and biodegradable new composites have been demonstrated to be highly resistant. Table S1 (supporting information) summarizes the preparation, characterization, properties, and applications of cellulose reinforced bio-nanocomposites.

Physico-chemical properties of cellulose biopolymer nanocomposites

The design and manufacture of packaging materials are multistep processes and involve careful and numerous considerations to engineer the final package successfully with all the required properties (Webert *et al.,* 2002). There are several properties of interest for evaluating the application of bio-nanocomposites in food packaging such as mechanical, barrier, thermal, and rheological properties (Azeredo, 2009).

Mechanical properties of attention are tensile modulus (TM), tensile strength (TS), and percent elongation (%E) at break. TM is a measure of the resistance of a material to deformation, TS is the maximum tensile stress a film can support, and %E is the flexibility of the film. Abdollahi *et al*. (2013), determined the mechanical properties, of the neat alginate film and its nanocomposites reinforced with various contents of NC. They verified that the TS value of the composite films increased from 18.0 to 22.4 MPa with increasing nanoparticles content from 0 to 5 wt.%, while the E% value decreased from 11.5 to 8.2%. The improvement observed in the TS of the nanocomposite by increasing the filler content up to 5% was attributed to the reinforcement effect of homogeneously dispersed high-strength cellulose nanoparticles in the biopolymer matrix. Alves *et al*. (2015) studied the mechanical properties of starch/gelatine/CNC films, with the increase in gelatine and CNC concentration driving an increase in the puncture resistance. This behaviour is desirable because a larger resistance to puncture indicates better film resistance, and resistant film is better suited for applications in the packaging industry. Nassima *et al*. (2015) developed bio-nanocomposite films of carboxymethyl cellulose and starch

(CMC/ST) matrix, reinforced with CNC, verifying that the elastic modulus and TS were increased gradually with the addition of CNC.

Barrier properties of the packaging material play a major role in determining the shelf life of a food product. There properties indicate the material resistance to sorption and diffusion of moisture and gases across the packaging material. Barrier properties of interest in food packaging are water vapour permeability (WVP) and oxygen permeability (OP) (Yam *et al.,* 2012). According to Paralikar, CNC provide a physical barrier in the nanocomposite films, creating a tortuous path for moisture that permeates the membrane (Paralikar *et al.,* 2008). This increases the effective path length for diffusion, thereby improving the barrier properties (Rhim, 2007). Silvério *et al.* (2013) shows that PVA nanocomposite films with 3%, 6%, and 9% filler with CNC have increasing improvement in reducing WVP, by 7%, 20% and 29%, respectively. Mondragon *et al.* (2015) used cellulose nanofibres (CNF) and CNC to develop bionanocomposite films based on a protein matrix (gelatine). To analyse the effect of nanocellulose addition to gelatine matrix, they carried out oxygen and water vapour permeability tests, and observed that nanocellulose contributes to improve the excellent oxygen gas barrier properties of gelatine, with the oxygen transmission rate (measurement of the amount of oxygen gas that passes through a substance over a given period - OTR) values decreasing in nanocomposites especially for 5 and 10 wt.% nanocellulose content. Large fractions of nanocellulose have been found to contribute to film impermeability (Aulin *et al.,* 2010). by creating longer diffusion paths for oxygen permeation (Belbelchouche *et al.,* 2011). Fortunati, Armentano *et al.* (2012) reported the impact of the addition of CNC and silver nanoparticles on the morphological, mechanical, thermal and antibacterial response of PLA. These authors

prepared the nanocomposite films by melt compounding, with the films maintaining the transparency of PLA and increased crystallinity. The presence of surfactant on the nanocrystal surface favoured the dispersion of the nanocellulose in the PLA and the nucleation effect was greatly improved, highlighting the effect of the crystals and of their surface modification on the thermal and mechanical properties of the nanocomposites. Nanocomposites also showed bactericidal effect on *S. aureus* and *E. coli* showing excellent perspectives of application by the food industry in applications that require an overtime effect. Fortunati, Peltzer *et al.* (2012) reported the effect of the addition of CNC on the barrier properties and on the migration behaviour of PLA. The nano-biocomposites were prepared by solvent casting. Both pristine (CNC) and surfactant-modified cellulose nanocrystals (s-CNC) were used. Moreover, the effect of the cellulose modification and content in the nano-biocomposites was also evaluated. The presence of surfactant on the nanocrystal surface favoured the dispersion of CNC in the PLA. Electron microscopy showed good dispersion of s-CNC indicating that the surfactant allowed a better interaction between the cellulose structures and the PLA matrix. The water permeability was reduced in 34 % for the films containing 1 wt.% of s-CNC and good oxygen barrier properties were found for nano-biocomposites with 1 wt.% and 5 wt.% of modified and un-modified CNC. The migration level of the studied nano-biocomposites was below the overall migration limits required by the for food packaging materials legislation.

The thermal stability of polymeric materials can be studied by Thermogravimetric Analysis (TGA) used to assess changes in the mass of a material as the temperature is increased. Dynamic mechanical analysis (DMA) and Differential scanning calorimetry (DSC) can be used to determine the glass transition temperature (Tg), the temperature at which an amorphous solid

changes from a relatively brittle (glassy) to a softer (rubbery) material. At the Tg, there is an abrupt change in properties such as storage modulus, specific heat, and coefficient of expansion (Menard, 2008). Arrieta *et al.* (2015) shows the improvement of thermal stability on the multifunctional PLA-PHB/cellulose nanocrystal films when compared with PLA–PHB blends. TGA showed that while plasticized PLA–PHB sample degraded in two-step process, the reinforced CNC materials degraded in one-step as a consequence of the better interaction among all components in the nanocomposites. These results suggest that multifunctional plasticized PLA–PHB blends reinforced with modified CNC are promising materials for food packaging. Alves *et al.* (2015) investigated the thermal properties of starch/gelatine/cellulose nanocrystals (CNC) films and they concluded that films with low levels of gelatine and CNC presented the maximum degradation temperature. Mondragon *et al.* (2015) used CNF and CNC to develop bionanocomposite films based on a protein matrix (gelatine). They also verified that the addition of CNC to gelatine matrix improved the thermal stability of nanocomposites.

The rheological properties of a packaging material are also important because they determine its processability. Rheological measurements such as dynamic shear measurement and extensional measurement can be used to predict the melt-processing behaviour of bio-nanocomposites during unit operations such as injection moulding and film blowing (Bhattacharya *et al.*, 2007). Nassima *et al.* (2015) developed bio-nanocomposite films of a CMC/starch matrix reinforced with CNC. The steady shear viscosity and dynamic viscoelastic measurements of film-forming solutions of neat CMC, CMC/ST blend and CMC/ST-CNC bio-nanocomposites could be used to predict which solutions form solid films with high quality and a smooth surface.

Application of Nanocellulose-based composites in food packaging

Most papers reporting the development of nanocellulose-based composites for packaging present results on their barrier and mechanical properties (Table S1 - Supporting Information), with some testing their antimicrobial properties and also the quality of foodstuffs coated with the nanocellulose-based composites.

Among the publications that have been reviewed regarding the application of nanocellulose-based composites to foods, Dong *et al.* (2015), Dehnad *et al.* (2014) and El-Wakil *et al.* (2015) do not mention if the CNC were functionalised, while El-Wakil *et al.* (2015), Salmieri *et al.* (2014a, b) and Azeredo *et al.* (2012) treated the extracted CNC by sulphuric acid hydrolysis.

For example, El-Wakil *et al.* (2015) evaluated the antimicrobial activity of coated papers against *Saccharomyces cervisiae*, *Escherichia coli*, *Staphylococcus aureus* and concluded that the coated kraft paper with WG/CNC 7.5%/0.6% TiO_2 presented excellent antimicrobial activities for 3 layers paper after 2 h of exposure to UVA light illumination. However, they did not validate the antimicrobial efficiency of the paper with food systems under real storage conditions.

Few studies have evaluated the improvement of quality and/or shelf life of foodstuffs packaged with nanocellulose-based composites. Azeredo *et al.* (2012) have reinforced edible films (based on alginate-acerola puree) with cellulose whiskers or MMT. The application of these coatings to fresh acerolas decreased fruit weight loss, decay incidence, ripening rates and favoured the retention of ascorbic acid. However, the nanocomposite coating was the most effective in maintaining red colour and visual acceptance, as well as in reducing weight loss.

Salmieri *et al.* (2014a, b) studied the inactivation of *Listeria monocytogenes* in cooked ham and mixed vegetables. In the case of a compression-moulded PLA-CNC-nisin nanocomposite film used to pack cooked ham, the growth of L. monocytogenes was retarded up to day 14. The solvent-cast PLA-CNC-oregano essential oil nanocomposite film, used to pack mixed vegetable, showed a quasi-total inhibition of *L. monocytogenes* when the vegetables were stored for 14 days at 4 °C.

Dehnad *et al.* (2014) have applied a chitosan-nanocellullose biocomposite to extend the shelf life of ground meat, observing a decrease in lactic acid bacteria population, compared with nylon packaged samples at 3 and 25 °C after 6 days of storage.

Coating of blueberries with aqueous slurries of cellulose nanofibrils and nanoparticles of calcium carbonate revealed that leakage of anthocyanin pigments from the blueberries during thermal processing was virtually eliminated (Zhao *et al.*, 2014).

Dong *et al.* (2015) were able to improve the shelf life and quality of strawberries by applying a mixture of 1% chitosan and 5% nanocellulose. In fact, the weight loss and decay rate of the coated strawberries was decreased, due to a decrease in senescence and metabolism. The coating also allowed to maintained total phenols and total anthocyanins, and improved visual appearance.

Conclusions

Bionanomaterials are a promising alternative for use in food packaging applications, substituting conventional plastics, especially those made from oil. However, poor mechanical and water vapour barrier properties of these materials limit their widespread use in the food packaging

industry. Techniques developed to improve the properties of these biodegradable materials, include modification of biopolymers, and their use in nanocomposites. The utilization of nanoparticles generally improves the mechanical, thermal, and barrier properties of biopolymers, and can also introduce other desired functions in food packaging materials, such as antimicrobial, biosensing, and oxygen scavenging. The excellent properties of nanocellulose materials and the fact that they can be considered green nanomaterials because they are carbon neutral, sustainable, recyclable and non-toxic, open excellent prospects for the increase of their use in the design of novel high performance food packaging materials. The safety issues of nanocellulose should, however, be monitored and controlled in order to confirm whether it has no harmful effects on human´s health and on environment. Although few studies have evaluated the improvement of quality and/or shelf life of foodstuffs packaged with nanocellulose-based composites, these have been successfully applied to fruits, meat and vegetables.

The next generation of packaging materials will be able to fit the requirements of preserving fruits, vegetables, beverages and other foods. Research and development of different types of new bio-based materials, such as edible and biodegradable nanocomposite films and their commercial applications in packaging, are expected to have an exponential growth in the next decade. Nanocomposites of biopolymers and nanocellulose offer excellent opportunities to play an important role in this development.

Nomenclature

3HHx hydroxyhexanoate

ACNC All-cellulose nanocomposite film

AFM   Atomic Force Microscopy

ATBC acetyl (tributylcitrate)

CA   Static Contact Angle Measurements

CH - chitosan

CMC - carboxymethyl

CNC - cellulose nanocrystals

CNC_{60} with an acid hydrolysis time of 60 minutes

CNF   cellulose nanofibres

CNW cellulose nanowiskers

DMTADynamic Mechanical Analysis

DSC   Differential Scanning Colorimetry

E%   Percentage Elongation at Break

EB   Elongation Break

FESEM   Field Emission Scanning Electron Microscope

FTIR   Fourier Transformed Infrared Spectroscopy

HB   hydroxybutyrate

HV   hydroxyvalerate

lcl   long chain length

LDHs layered double hydroxides

MAC methyl adipoyl chloride

MC   Moisture Content

MCC Microcrystalline cellulose

mcl   medium chain length

MMT montmorillonite

MWCNTs   multi-walled carbon nanotubes

Op   Opacity

OTR   Oxygen Transmission Rate

PA   poly(amide)

PCL   poly(caprolactones)

PE   poly(ethylene)

PET   poly (ethylene terephthalate)

PF   Puncture Force

PHA   poly(hydroxyalkanoates)

PHB   poly(hydroxybutyrate)

PHBHx   poly(3-hydroxybutyrate-co-3-hydroxyhexanoate)

PHBV poly(hydroxybutyrate-co-hydroxyvalerate)

PHO   poly(3-hydroxyoctanoate)

PLA   poly (lactic acid)

PP   poly(propylene)

PS   poly(styrene)

PVA   poly (vynil alcohol)

PVC   poly(vinylchloride)

PVOH poly(vinyl alcohol)

QCM   Quartz/Crystals Microbalance

scl   short chain length

s-CNC surfactant-modified cellulose nanocrystales

SEM   Scanning Electron Microscopy

ST   starch

TEM   Transmission Electron Microscopy

Tg   glass transition temperature, °C

TGA   Thermogravimetric Analysis

TiO$_2$ titanium dioxide

TM   Thickness Measurements

Tr   Light Transmission

TS   Thermal Stabilities

UTS   Ultimate tensile Strength

WAXS Wide Angle X-ray Scattering

WS   Water Solubility

WVP - Water Vapor Permeability

WVTR Moisture Vapor Transmission Rate

WVU Water Vapor Uptake

YM   Young´s Modulus

Acknowledgments

References

Abdollahi, M., Alboofetileh, M., Behrooz, R., Rezaei, M., and Miraki, R. (2013). Reducing water sensitivity of alginate bio-nanocomposite film using cellulose nanoparticles. *Int. J. Biol. Macromol.* **54**: 166–173. DOI: 10.1016/j.ijbiomac.2012.12.016

Alves, J. S., Reis, K. C., Menezes, E. G. T., Pereira, F. V., and Pereira, J. (2015). Effect of cellulose nanocrystals and gelatin in corn starch plasticized films. *Carbohyd. Polym.*, **115**: 215-222. DOI: 10.1016/j.carbpol.2014.08.057

Annamalai, P. K. and Singh, R. P. Biopolymeric nanocomposites as environment benign materials. **In**: Cellulose Fibers: Bio- and Nano-Polymer Composites, pp. 519-535., Eds., Springer Berlin Heidelberg, Berlin.

Arrieta, M. P., Fortunati, E., Dominici, F., Rayón, E., López J., and Kenny, J. M. (2014). PLA-PHB/cellulose based films: Mechanical, barrier and disintegration properties *Polym. Degrad. Stabil.*. **107**: 119-149.DOI: 10.1016/j.polymdegradstab.2014.05.010

Arrieta, M. P., Fortunati, E., Dominici, F., Rayón, E., López J., and Kenny, J. M. (2014). Multifunctional PLA-PHB/cellulose nanocrystal films: processing, structural and thermal properties. *Carbohyd. Polym.*, **107**: 16-24. DOI: 10.1016/j.carbpol.2014.02.044

Arrieta, M. P., Fortunati, E., Dominici, F., Rayón, E., López J., and Kenny, J. M. (2015). Bionanocomposite films based on plasticized PLA-PHB/cellulose nanocrystal blends. *Carbohyd. Polym.*, **121**: 265-275. DOI: 10.1016/j.carbpol.2014.12.056

Aulin, C., Gallsted, M., and Lindstrom, T. (2010). Oxygen and oil barrier properties of microfibrillated cellulose films and coating. *Cellulose* **17** :559-74. DOI : 10. 1007/s10570-009-9393-y

Azeredo H. M. C., Miranda K. W. E., Ribeiro H. L., Rosa M. F., & Nascimento D. M. (2012). Nanoreinforced alginate – acerola puree coatings on acerola fruits. *J Food Eng*., 113(4), 505–510 DOI:10.1016/j.jfoodeng.2012.08.006

Azeredo H. M. C., Miranda K. W. E., Rosa M. F., Nascimento D. M., & Moura, M. R. De. (2012). LWT - Food Science and Technology Edible fi lms from alginate-acerola puree reinforced with cellulose whiskers. *LWT – Food Sci. Technol.* 46: 294–297. DOI:10.1016/j.lwt.2011.09.016

Azeredo, H. M. C. (2009). Nanocomposites for food packaging applications. *Food Res. Int.* , **42**: 1240-1253. DOI: 10.1016/j.foodres.2009.03.019

Ball, D. W. (2015). In: Introductory Chemistry, v. 1.0 ©2015, Eds. Flat World Education, Inc.

Belbelchouche, S., Bras, J., Sequeira, G., Chappey, C., Lebrun, L., and Khelifi, B. (2011). Water sorption behaviour and gas barrier properties of cellulose whiskers and microfibrils films. *Carbohydr Polym* **83** : 1740-8 DOI : 10.1016/j.carbpol.2010.10.036

Bhattacharya, S. N., Kamal, M. R., and Gupta, R. K. (2007). Rheology of Nanocomposites In : Polymeric nanocomposites: theory and practice, pp.145-231 Bhattacharya, S. N., Kamal, M. R., and Gupta, R. K., Eds., Carl Hanser Verlag GmbH & Co. KG, Cincinnati DOI: 10.3139/9783446418523

Bhattacharyaa and B.N. Misrab, (**2004**). Grafting: a versatile means to modify polymers Techniques, factors and applications. *Prog. Polym. Sci*. 29:767–814. DOI: 10.1016/j.progpolymsci.2004.05.002

Biodegradable Certification Standard. (2011). Eds., Scientific Certification Systems.

Capadona, J. R., Berg, O., Capadona, L. A., Schroeter, M., Rowan, S. J., Tyler, D. J., and Weder, C. (2007). A versatile approach for the processing of polymer nanocomposites with self-assembled nanofibretemplates. *Nat. Nanotechnol*. **2:** 765-769

Capadona, J. R., Shanmuganathan, K., Tyler, D. J., Rowan, S. J., and Weder, C. (2008) Stimuli-responsive polymer nanocomposites inspired by the sea cucumber dermis. *Science* **319**: 1370-1374. DOI: 10.1126/science.1153307

Chandra, R., and Rustgi, R. (1998). Biodegradable Polymers. *Prog. Polym. Sci.*. **23**: 1273-1335.

Dufresne, A. (2012). **In**: Nanocellulose: From Nature to High Performance Tailored Materials, Eds., De Gruyter

Dufresne, A. (2013). Nanocellulose: a new ageless bionanomaterial. Mater. Today.. **16**: 220–227DOI: 10.1016/j.mattod.2013.06.004

Dehnad D., Mirzaei H., Emam-djomeh Z., & Jafari S. (2014). Thermal and antimicrobial properties of chitosan – nanocellulose films for extending shelf life of ground meat. *Carbohyd. Polym*, *109*, 148–154. DOI:10.1016/j.carbpol.2014.03.063

El-Wakil, N. A., Hassan, E. A., Abou-Zeid R. E. and Dufresne, A. (2015). Development of wheat gluten/nanocellulose/titanium dioxide nanocomposites for active food packaging. *Carbohyd. Polym.* **124**: 337-346 DOI: 10.1016/j.carbpol,2015,01,076

El Miri N., Abdelouahdi K., Barakat A., Zahouilya M., Fihri A., Solhye A., Achabye E. M., (2015). Bio-nanocomposite films reinforced with cellulose nanocrystals: Rheology of film-forming solutions, transparency, water vapor barrier and tensile properties of films. *Carbohydrate Polymers*, **129**: 156–167. DOI: 10.1016/j.carbpol.2015.04.051

Eyley, S. and Thielemans, W. (2011). Imidazolium grafted cellulose nanocrystals for ion exchange applications. *Chem. Comm.* 47, 4177–4179. **DOI:** 10.1039/C0CC05359G

European Food Safety. (2008b). Draft opinion of the scientific committee on potencial risks arising from nanoscience and nanotechnologies on food and feed safe (Question No EFSA-Q-2007-124). European Food Safety Authority, Endorsed for public consultation 14 October 2008

Fortunati, E., Armentano, I., Zhou, Q., Iannoni, A., Saino, E., Visa, L., Berglund L. A., and Kenny, J. M. (2012). Multifunctional bionanocomposite films of poly (lactic acid), cellulose nanocrystals and silver nanoparticles. *Carbohyd. Polym.* **87:** 1596-1605. DOI: 10.1016/j.carbpol.2011.09.066

Fortunati, E., Luzi, F., Puglia, D., Dominici, F., Santulli, C., Kenny, J. M., and Torre, L. (2014). Investigation of thermo-mechanical, chemical and degradative properties of PLA-limonene films reinforced with cellulose nanocrystals extracted from Phormium tenax leaves. *European Polymer Journal.* **56 :** 77-91.DOI: 10.1016/j.europolym.2014.03.030

Fortunati, E., Luzi, F., Puglia, D., Petrucci, R., Kenny, J. M., and Torre, L. (2015). Processing of PLA nanocomposites with cellulose nanocrystals extracted from Posidonia oceanica waste: Innovative reuse of coastal plant. *Ind Crop Prod*, **67**: 439-447. Doi: 10.1016/j.indcrop.2015.01.075

Fortunati, E., Peltzer, M., Armentano, I., jimenez, A., and Kenny, J. M. (2012). Effects of modified cellulose nanocrystals on the barrier and migration properties of PLA nano-biocomposites. *Carbohyd. Polym*. **90**: 948-956. DOI: 10.1016/j.carbpol.2012.06.025

Fortunati, E., Puglia, D., Monti, M., Santulli, C., Maniruzzaman M., and Kenny, J. M. (2012). Cellulose nanocrystals extracted from okra fibers in PVA nanocomposites. *Journal of Aplied Polymer Science*. **128** : 3220–3230 DOI : 10.1002/app.38524

Ghaderi, M., Mousavo, M., Yousefi H., and Labbafi, M. (2014). All-cellulose nanocomposite film made from bagasse cellulose nanofibers for food packaging application. *Carbohyd. Polym*. **104**: 59-65. DOI: 10.1016/j.carbpol.2014.01.013

Goffin, A. L., Raquez, J. M., Duquesne, E., Siqueira, G., Habibi, Y., Dufresne, A., and Dubois, P. (2011). From Interfacial Ring-Opening Polymerization to Melt Processing of Cellulose Nanowhisker - Filled Polylactide - Based Nanocomposites. *Biomacromolecules*. **12**: 2456–2465. DOI: 10.1021/bm200581h.

Gómez H.C., Serpa A., Velásquez-Cock J., Gañán P., Castro C., Vélez L. and Zuluaga R. (**2016**). Vegetable nanocellulose in food science: A review. *Food Hydrocoloids* 178-186. DOI**:** 10.1016/j.foodhyd..2016.01.023

Hajji, P., Cavaillé, J. Y., Favier, V., Gauthier C., and Vigier, G. (1996). Tensile behavior of nanocomposites from latex and cellulose whiskers. *Polym Composite* **17** : 612–619 DOI : 10.1002/pc.10651.

Huang, J., Chang, P. R., Lin, N., and Dufresne, A. (2014). In: *Polysaccharide-Based Nanocrystals: Chemistry and Applications,* John Wiley & Sons.

Hubbe, M. A., Rojas, O. J., Lucia, L. A., and Sain, M. (2008). Cellulosic nanocomposites: a review. *Bioresources*. **3**: 929–80.

ISO 20200:2004 - *Plastics -- Determination of the degree of disintegration of plastic materials under simulated composting conditions in a laboratory-scale test*

Jorfi, M., Amiralian, N., Biyani M. V., and Annamalai, P. K. (2013). *In book: Biomass-based Biocomposites,* **14**:.277-304 Thakur, V. K., Singha,A. S., Eds., Smithers Rapra Technology .

Kalia S. and Sabaa M.W. (eds.) (2013) Polysaccharide Based Graft Copolymers, Chapter 2. DOI: 10.1007/978-3-642-36566-9_2

Kalia, S., Kaith, B. S., and Kaur, I. (2011). Green Chemistry and Technology. **In**: Cellulose Fibers: Bio- and Nano-Polymer Composites., **Kalia**, S., **Kaith**, B. S., **Kaur**, I., Eds., Springer-Verlag, Berlin.

Kanmani, P., and Rhim, J. W. (2014). Physicochemical properties of gelatin/silver nanoparticle antimicrobial composite films. *Food Chem* **148**:162-169. DOI: 10.1016/j.foodchem.2013.10.047

Kaplan, D. L. (1998) **In:** Biopolymers from Renewable Resources, Eds., Springer-Verlag, Berlin.

Khan A., Huq T., Khan R.A., Rield B. And Lacroix M. (2014). Nanocellulose-Based Composites and Bioactive Agents for Food Packaging, Critical Reviews in Food Science and Nutrition, 54:2, 163-174, DOI: 10.10180/10408398.2011.578765

Klemm, D., Heublein, B., Fink, H. P., and Bohn, A. (2005). In: Angew Chem Int Ed **44**: 3358, 2005

Kumar, P., Sandeep, K. P., Alavi, S., and Truong, V. D. (2011). *J Food Sci*,**76**

Li, B. F., Mascheroni, E., and Piergiovanni, L. (2015). The Potential of NanoCellulose in the Packaging Field : A Review. **In** : Packaging Technology and Science, **28**, pp. 475–508. DOI : 10.1002/pts.2121

Matyjaszewski, K., and Xia, J. (2001). Atom Transfer Radical Polymerization. *Chem. Rev.* **101** (9): 2921–2990. DOI**:** 10.1021/cr940534g

Menard K. P. (2008). *Dynamic mechanical analysis a practical introduction, Second Edition*, Eds., CRC Press.

Miri, N. E., Abdelouahdi, K. Barakat, A., Zahouily, M., Fihi, A., Solhy A., and Achaby, M. E. (2015). Bio-nanocomposite films reinforced with cellulose nanocrystals: Rheology of film-forming solutions, transparency, water vapor barrier and tensile properties of films. . *Carbohyd. Polym* **129**: 156-167. DOI: 10.1016/j.carbpol.2015.04.051

Mondragon, G., Peña-Rodriguez, C., González, A., Eceiza, A., and Arbelaiz, A. (2015). Bionanocomposites based on gelatin matrix and nanocellulose. *Eur Polym J* . **62**:1-9. DOI: 10.1016/j.europolymj.2014.11.003

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

Morandi, G., Heath, L., and Thielemans, W. (2009). Cellulose Nanocrystals Grafted with Polystyrene Chains through Surface-Initiated Atom Transfer Radical Polymerization (SI-ATRP). *Langmuir*. **25:** 8280- 8286. DOI:10.1021/la900452a

Oksman, K., Mathew, A. P., Bismarck, A., Rojas, O., and Sain, M. (2014). **In**: *Handbook of Green Materials: Processing Technologies, Properties and Applications*, Eds., World Scientific Publishing Company Pte Limited

Othman, S. H. (2014). Bio-nanocomposite Materials for Food Packaging Applications: Types of Biopolymer and Nano-sized Filler. *Agriculture and Agricultural Science Procedia,* **2**: 296-303. DOI: 10.1016/j.aaspro.2014.11.042

Paralikar, S. A., Simonsen, J., and Lombardi, J. (2008). Poly (vinyl alcohol)/cellulose nanocrystal barrier membranes. . *J Membrane Sci* **320**: 248–258,

Pereda, M., Amica, G., Rácz, I., and Marcovich, N. E. (2011). Structure and properties of nanocomposite films based on sodium caseinate and nanocellulose fibers. *J Food Eng* ,, **103**: 76–83. DOI: 10.1016/j.jfoodeng.2010.10.001

PăăkkÖ, M. (2007). Enzymatic hydrolysis combined with mechanical shearing and high-pressure homogenization for nanoscale cellulose fibrils and strong gels. *Biomacromolecules*. **8** : 1934–1941. DOI: 10.1021/bm061215p

Plastics – the Facts (2014) - An analysis of European plastics production, demand and waste data. PlasticsEurope- Association of Plastics manufactures.

Postek, M. T., Vladar, A., Dagata, J., Farkas, N., and Ming, B. (2008) Cellulose nanocrystals the next big nano-thing? *Instrumentation, Metrology and Standards for Nanomanufacturing III*, **7042**:7042oD-1. DOI: 10.1117/12.797575

Rebouillat, S., and Pla, F. (2013). State of the Art Manufacturing and Engineering of Nanocellulose: A Review of Available Data and Industrial Applications. *Journal of Biomaterials and Nanobiotechnology*, **4**: 165-188. DOI: 10.4236/jbnb.2013.42022

Reddy, J. P., Rhim, J. W. (2014). Characterization of bionanocomposite films prepared with agar and paper-mulberry pulp nanocellulose. *Carbohyd. Polym,* **110**: 480-488. DOI: 10.1016/j.carbpol.2014.04.056

Rhim, J. W., Ng P. K. W. (2007). Natural Biopolymer-Based Nanocomposite Films for Packaging Applications. *Crit Rev Food Sci Nutr*. **47**: 411–433. DOI: 10.1080/10408390600846366

Roy D, Semsarilar M, Guthriea J.T. and Perrier S (2009) Cellulose modification by polymer grafting: a review. *Chem. Soc. Rev.* 38:2046-2064. DOI: 10.1039/B808639G

Salmieri S, Islam F, & Khan R. A. (2014) Antimicrobial nanocomposite films made of poly (lactic acid) – cellulose nanocrystals (PLA – CNC) in food applications — part B: effect of oregano essential oil release on the inactivation of Listeria monocytogenes in mixed vegetables. *Cellulose* 21:4271–4285. DOI:10.1007/s10570-014-0406-0

Salmieri S, Islam F, Khan R. A., Hossain F. M., & Lacroix M. (2014) Antimicrobial nanocomposite films made of poly (lactic acid) -cellulose nanocrystals (PLA-CNC) in food applications: part A

— effect of nisin release on the inactivation of Listeria monocytogenes in ham. *Cellulose* 21:1837–1850. DOI:10.1007/s10570-014-0230-6

Santos M.T., Souza Filho M.S., Caceres C.A., Rosa M.F., Morais J.P.S., et al. (2014). Fish gelatin films as affected by celulose whiskers and sonication. *Food Hydrocolloid* 41:113-118 DOI: 10.1016/j.foodhyd.2014.04.001

Sanuja, S., Agalya, A., Umapathy, M. J. (2014). Studies on Magnesium Oxide Reinforced Chitosan Bionanocomposite Incorporated with Clove Oil for Active Food Packaging Application. *Journal of Polymeric Materials and Polymeric Biomaterials.* **63**: 733-740. DOI: 10.1080/00914037.2013.879445

Savadekar N.R., Karande V.S., Vigneshwaran N., Bharimalla A.K. and Mhaske S.T. (**2012)** Preparation of nano cellulose fibers and its application in Kappa-carrageenan based film. *Int J Biol Macromol* 51:1008-1013 DOI: 10.1016/j.ijbiomac.2012.08.014

Silvério, H. A., Neto, W. P. F., and Pasquini, D. (2013). Effect of Incorporating Cellulose Nanocrystals from Corncob on the Tensile, Thermal and Barrier Properties of Poly (Vinyl Alcohol) Nanocomposites. *J Nanomater*, **2013**: Article ID 289641, 9 pages, DOI: 10,1155/2013/289641

Siro, I., and Plackett, D. (2010). MicroÞbrillated cellulose and new nanocomposite materials: a review. *Cellulose*. **17**: 459-494. DOI: 10.1007/s10570-010-9405-y

Steinbuchel, A. (2005). Non-biodegradable biopolymers from renewable resources: perspectives and impacts. *Current Opinion in Biotechnology.* **16**: 607-613.

Stelte, W.,and Sanadi, A. R. (2009). Preparation and Characterization of Cellulose Nanofibers from Two Commercial Hardwood and Softwood Pulps. *Industrial and Engineer Chemistry Research*. **48**: 11211-11219. DOI: 10.1021/ie9011672

Trovatti, E., Fernandes, S. C. M., Rubatat, L., Freire, C. S. R., Silvestre, A. J. D., and Neto, C. P. (2012). Sustainable nanocomposite films based on bacterial cellulose and pullulan. *Cellulose* **19**: 729-737. DOI: 10.1007/s.10570-012-9673-9

Vigneshwaran, N., Ammayappan, L., and Huang, Q. (2011). Effect of Gum arabic on distribution behavior of nanocellulose fillers in starch film. *Applied Nanoscience*, **1**:137-142. DOI: 10.1007/s13204-011-0020-5

Visanko, M., Limatainen, H., Sirvio, J. A., Mikkonen, K. S., Tenkanen, M., Siiz, R., Hormi O., and Niinimaki, J. (2015). Butylamino-functionalized cellulose nanocrystal films: barrier properties and mechanical strength. *The Royal Society of Chemistry - RSC Advances*, **5**: 15140–1514. DOI: 10.1039/c4ra15445b

Webert, C. J., Haugaard, V., Festersen, R., and Bertelsen, G. (2002). Production and applications of biobased packaging materials for the food industry. Food Additives and Contaminants, **19**, pp. 172-177. DOI: 10.1080/026500301 1008748.3

Yam, K. L., and Lee, D. S. (2012). In: *Emerging Food Packaging Technologies: Principles and Practice*. Eds.*,* Elsevier

Zhang, Z., Wang, W., Xia, H., Zhu, J., Zhang, W., and Zhu, X. (2009). Single-Electron Transfer Living Radical Polymerization (SET-LRP) of Methyl Methacrylate (MMA) with a Typical RAFT Agent as an Initiator. *Macromolecules*. **42**: 7360–7366. DOI: 10.1021/ma901064h

Zhao Y., Simonsen J., Cavender G., Jung J. and Fuchigami L.H. (2014). Patent: Nano-cellulose coatings to prevent damage in foodstuffs, nº publication: US 20140272013 A1.
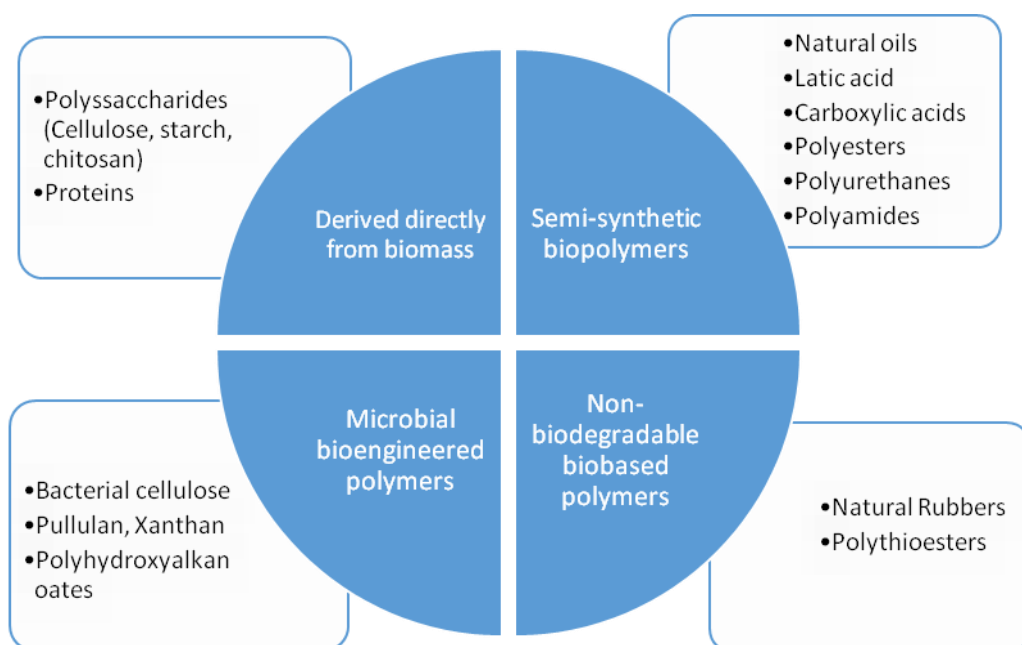
Figure 1. Polymers from biomass a renewable resource. (Adapted from P.K. Annamalai and R.P. Singh, in Cellulose Fibers*: Bio- and Nano-Polymer Composites, Eds.;* S. Kalia, B.S. Kaith and I. Kaur, *Springer-Verlag Berlin Heidelberg,* Germany, 2011, p.519)
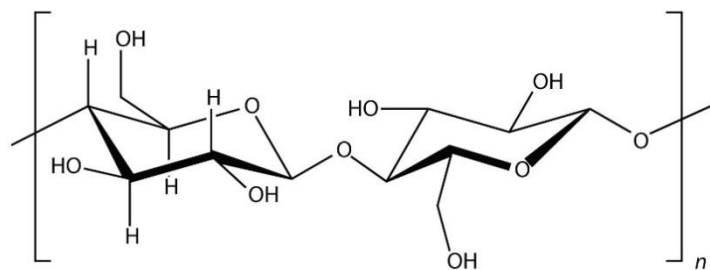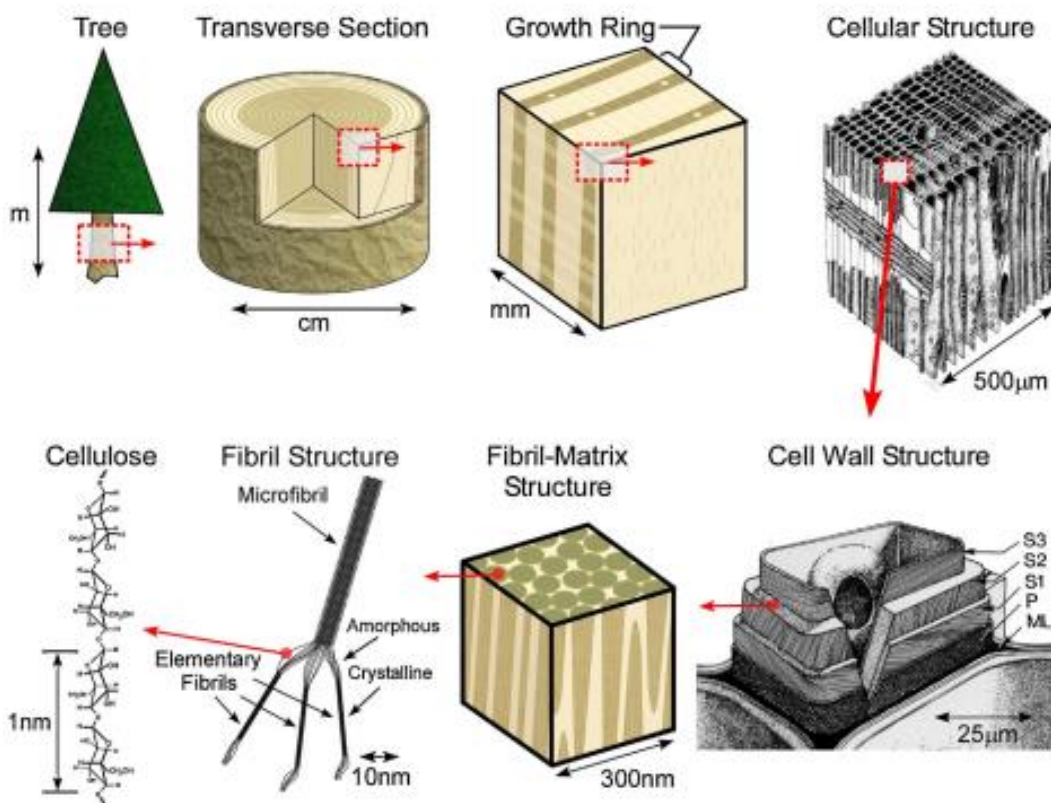
Figure 2. Structure of cellulose

Figure 3. Structure of wood from the tree to the CNCs (Reprinted with permission from Postek, M. T., et al. 2011- Development of the metrology and imaging of cellulose nanocrystals. *Measurement Science and Technology* - 22 (2011), IOP Publishing - DOI: 10.1088/0957/22/2/024005)
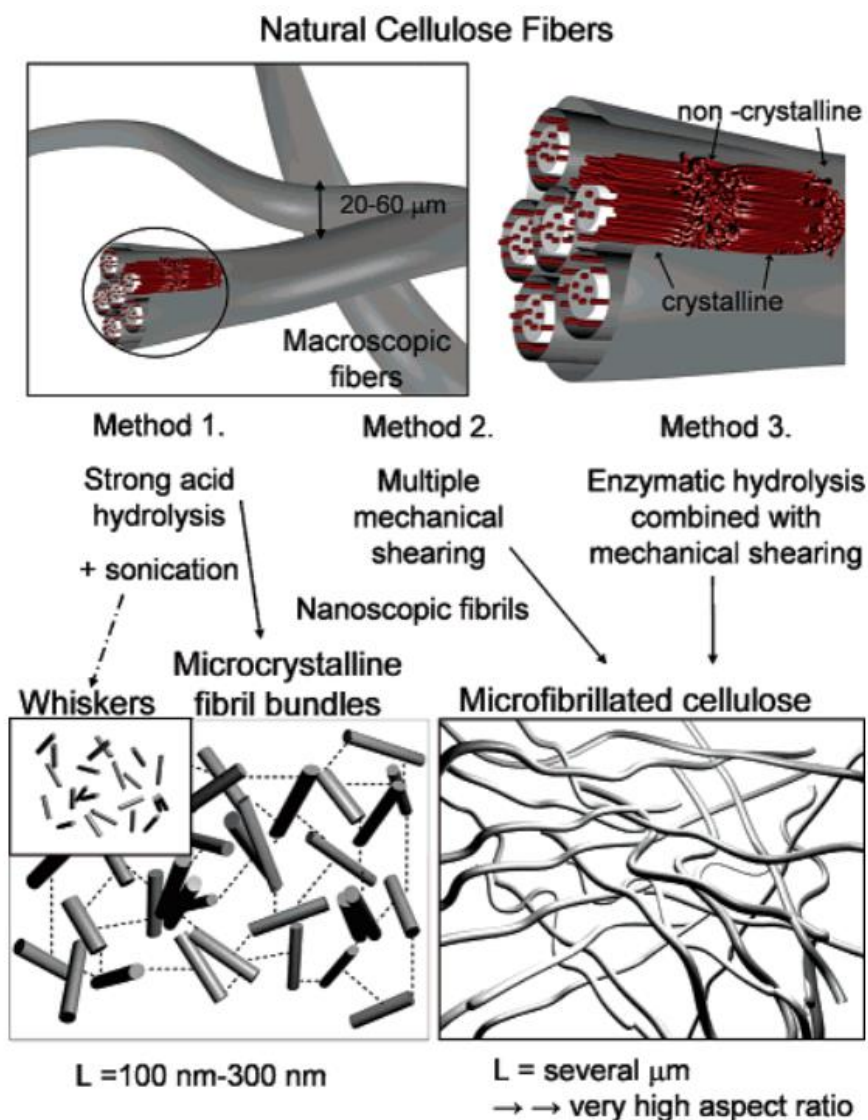
Figure 4. Schematic representation of derivatisation of macroscopic cellulosic fibres into nanoscale fibrils. L is the length and the two arrows represent higher aspect ratio. (Reproduced with permission from M. Paakko, M. Ankerfors, H. Kosonen, A. Nykanen, S. Ahola, M. Osterberg, J. Ruokolainen, J. Laine, P.T. Larsson, O. Ikkala and T. Lindstrom, *Biomacromolecules*, 2007, 8, 6)
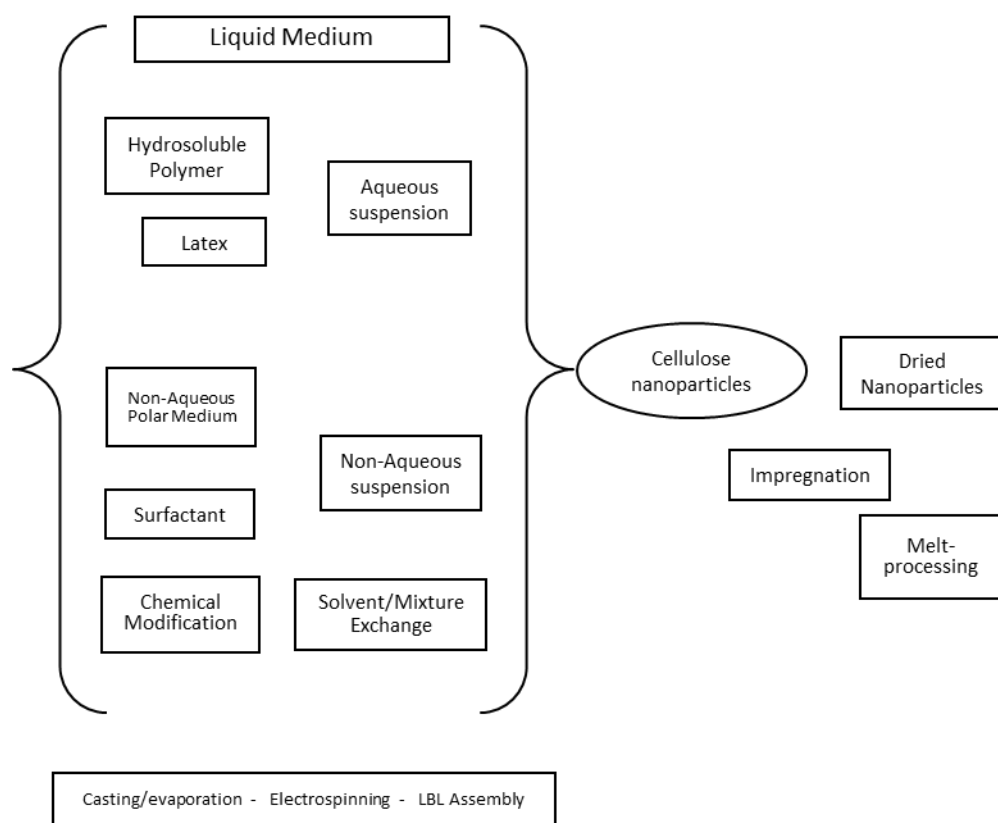
Figure 5. The different strategies applied for the processing of nanocellulose reinforced polymer nanocomposites. (Adapted from Dufresne, A. (2013). Nanocellulose: a new ageless bionanomaterial. *Materials Today*. **16**: 220–227)
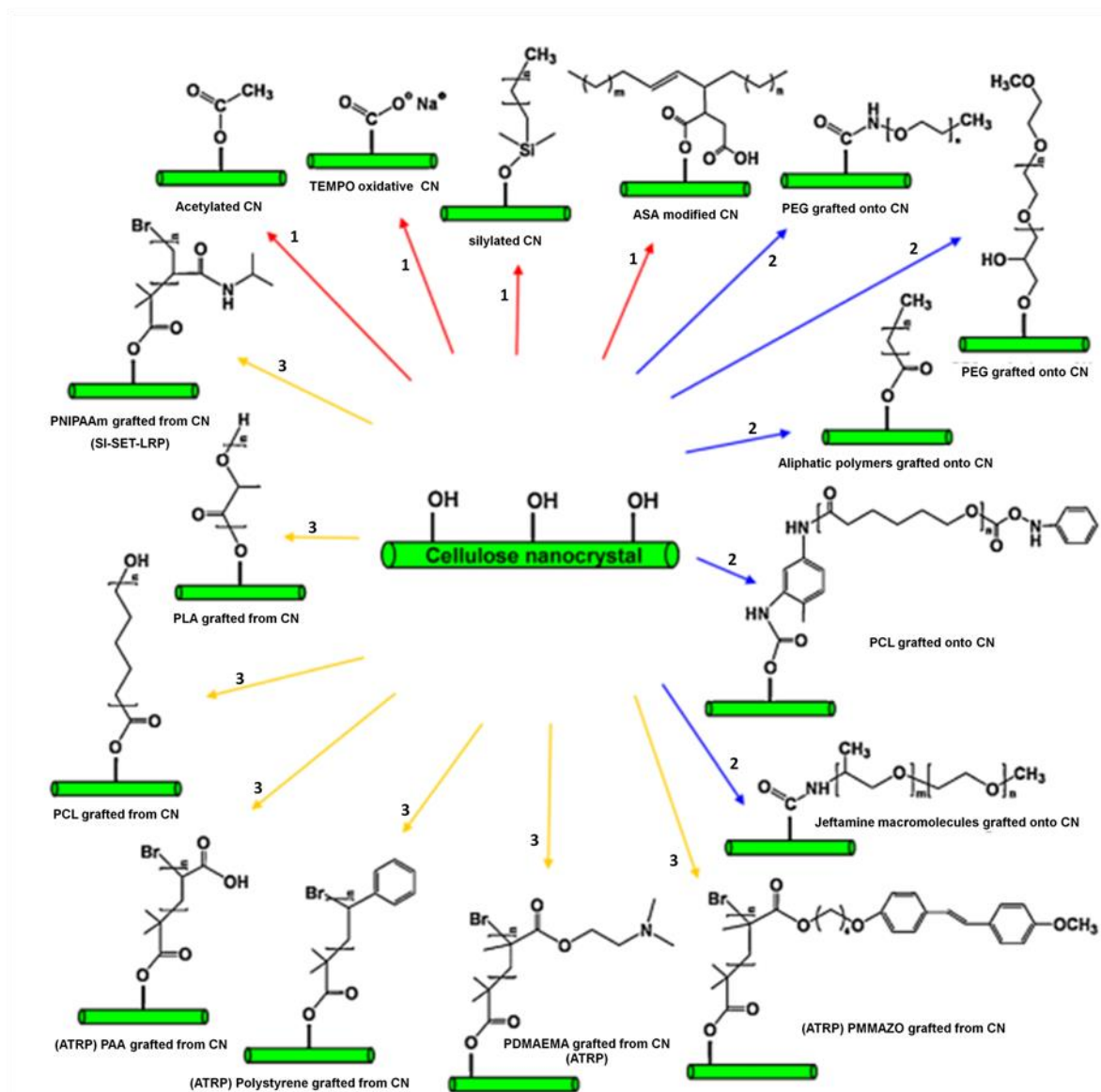
Figure 6. Common surface chemical modifications of cellulose nanocrystals. Poly (ethylene glycol) (PEG); poly (ethylene oxide) (PEO); poly (lactic acid) (PLA); poly (acrylic acid) (PAA); poly(N-isopropylacrylamide) (PNiPAAm); poly (N,Ndimethylaminoethylmethacrylate) (PDMAEMA). (Reproduced with permission from Alain Dufresne, *Materials Today,* 2013, 16, 220-227.)