WALAILAK JOURNAL
http://wjst.wu.ac.th MiniReview

Nanocellulose-Reinforced "Green" Composite Materials

Nattakan SOYKEABKAEW*, Nattaya TAWICHAI,
Chuleeporn THANOMSILP and Orawan SUWANTONG

Materials for Energy and Environment (MEE) Research Group, School of Science,
Mae Fah Luang University, Chiang Rai 57000, Thailand

(*Corresponding author's e-mail: nattakan@mfu.ac.th)

Received: 23 December 2015, Revised: 28 March 2016, Accepted: 5 April 2016

Abstract

Today, the development of materials has to involve the consideration of environmental responsibility and sustainability. Therefore, more environmentally friendly products, which are biodegradable and derived from renewable resources, have been extensively established. However, in widespread applications, most bio-based polymers when used alone present limitations on their functions and are more costly when compared to their petroleum-based counterparts. One of the most effective ways to enhance the performance of bio-based materials is the incorporation of nanofillers or nanoreinforcements. Recently, cellulose nanofibers or nanocelluloses (NCs) have been paid a great deal of attention to, and incorporated within various biopolymer matrices, since NCs are renewable, biodegradable, carbon neutral, biocompatible, possess extraordinary reinforcing potential, etc. A significant improvement in key performances of the resulting NC-reinforced nanocomposites has been demonstrated, showing that they are comparable, or even better, than the more conventional materials and, thus, are a promising "green" alternative for various applications. Three types of NCs are classified in this review, including microfibrillated cellulose (MFC), cellulose nanowhisker (CNW), and bacterial cellulose (BC), and the NC-reinforced "green" composite systems are overviewed separately for each NC type. The details of their attempted processing techniques, improvements in the nanocomposite properties, dispersion problems in NCs, and remedies are discussed.

Keywords: Nanocellulose, biodegradable polymer, bio-based material, green nanocomposite

Introduction

New environmental and waste management policies, together with concerns over the reliable availability of petrochemicals in the future, have intensely forced the development of environmentally friendly, sustainable, and degradable products in the past decade [1-3]. Accordingly, biodegradable polymers and materials obtained from renewable resources have gained much attention. Based on their sources, biodegradable polymers can be classified into 3 main categories, as illustrated in **Figure 1**. Among them, some of the biodegradable polymers, for instance, thermoplastic starch (TPS), poly(lactic acid) (PLA), and polyhydroxyalkanoates (PHAs), have been extensively developed because of their similar mechanical properties to those of petroleum-based polymers, and also because of their ability to be processed by conventional plastics machinery [3-5].

The commercial use of these biodegradable polymers, however, has expanded slowly, due to the problems of their performances and their cost when compared to those of other common polymers or plastics such as polyolefins and polyethylene terephthalate (PET) [1]. Particularly, brittleness, low heat distortion temperature, and low gas barrier properties of biopolymers have strongly limited their uses [6,7]. Thus, there is an obvious requirement to improve some of their properties, so that they can compete with the current conventional plastics [4]. To compensate for the inherent inadequate properties of biopolymers, the incorporation of reinforcements has been proven to be one of the most effective ways to thus improve the properties [5,8-12]. Therefore, trends in researches have been harnessed to develop fully "green" composites, and much effort has been devoted to the use of natural fibers as an alternative to conventional inorganic fillers (e.g., glass, aramid, or carbon fibers). The advantages of natural fibers over traditional reinforcing materials are low cost, low density, renewable resource origin, acceptable specific strength properties, reduced tool wear, reduced dermal and respiratory irritation, good thermal properties, ease of separation, enhanced energy recovery, carbon dioxide sequestration, and biodegradability [13,14]. Nowadays, natural fiber-reinforced polymer composites with endurable mechanical properties have been manufactured and widely used in various applications, mainly in the automotive, construction, and packaging industries [12,15,16]. Deliberately, these "green" composite materials can provide several positive environmental benefits from raw material utilization, product manufacturing, and utility until ultimate disposability (fully degraded without releasing toxins into the environment) [17].

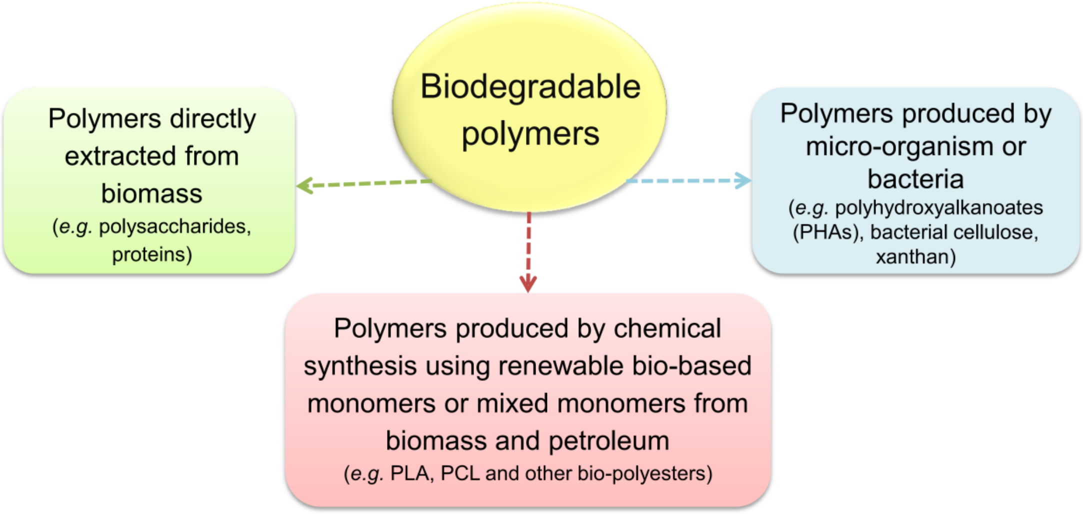


Figure 1 Three categories of biodegradable polymers, according to their sources.

Cellulose is the major constituent of natural fibers and the most abundant biopolymer on earth. Besides plants, it is also presented in other living species such as bacteria and animals. Cellulose is a linear polymer composed of β-1,4 linked glucopyranose units, in which each unit contains 3 alcoholic hydroxyl groups, allowing hydrogen bonds to form between their chains [15,18]. This bonding leads to the formation of bundles of crystalline nanofibrils, also called "cellulose microfibrils", which have a small width (2 - 20 nm), a high aspect ratio (> 300), and a high crystal modulus (130 - 150 GPa) of cellulose I polymorph. Because of their reinforcing potential and their wide applicability in products, considerable interest and effort have been drawn to the use of cellulose in fully degradable and renewable "green" composite and nanocomposite production [18-21].

"Green" nanocomposite materials

Nanocomposite describes a 2 or more constituent material where one of the phases has at least one dimension of less than 100 nm [19]. Since Toyota researchers in the late 1980s found that mechanical, thermal, and barrier properties of nylon-clay composite material improved substantially by reinforcing it with less than 5 % of nanoclay, extensive research works have been performed in the study of nanocomposites for various applications [22]. Several researches have reported very unusual properties of such nanocomposite materials, which are very different from their microscale counterparts. The improvements in mechanical properties, their stability towards UV-VIS, thermal, and chemical attacks, self-extinguishing behavior, processability, oxygen and water vapor barrier, and tunable biodegradability have been demonstrated in many nanocomposite systems [1,4,10,22-24].

Undoubtedly, for biobased and biodegradable polymers, the integration of nanofillers or nanoreinforcements would bring significant opportunities to lessen their drawbacks and enhance the final product key performance for use. Some of the most extensively studied renewable reinforcements in this field are, of course, nanocelluloses, since they exhibit a number of interesting properties, such as renewability, biodegradability, biocompatibility, a wide variety of sources, non-food agricultural based economy, carbon neutrality, low density, and high specific strength and modulus [4]. Certainly, the use of nanocellulose to reinforce biopolymers creates completely biobased formulation nanocomposites that are fully renewable and degradable; so called "green" nanocomposite materials. [10,22]. This approach results in "green" materials with various attractive properties which encouraging their use in a wide range of applications, hence, leading towards their large-scale production and the sustainability of these NC-reinforced nanocomposites, as depicted in **Figure 2**.

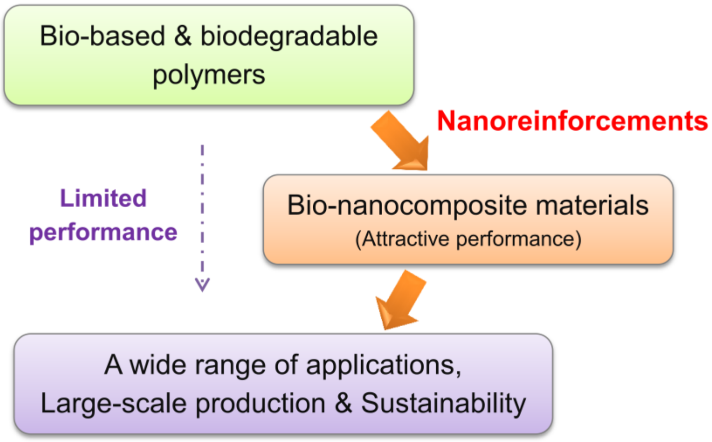


Figure 2 Application of nanoreinforcements, leading towards sustainability of bio-based materials.

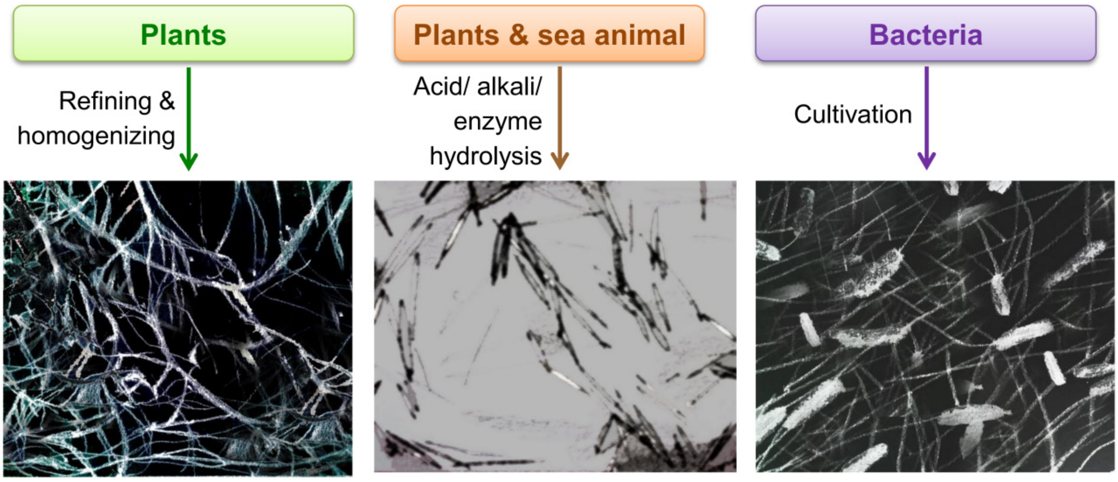
Nanoreinforcement: Nanocelluloses (NCs)

Several nanofillers have been recognized as possible reinforcements for enhancing polymer performance. Among the various existing nanoreinforcements, the ones that have attracted most attention in the biobased polymers field are nanoclay-based nanocomposites. It has been extensively reported in the scientific literature that the addition at low contents of nanolayered clay particles to biopolymers can have a major enhancing effect on several properties of the composite material [22]. Nevertheless, a minor disadvantage of nanoclays on polymers has been reported, in that there is a reduction in transparency [25].

More recently, nanocelluloses (NCs) have also received a great deal of interest for incorporation into biopolymer matrices. Many researches have studied nanocomposite materials reinforced by NCs and discovered a significant improvement in mechanical properties, thermal stability, and/or gas barrier performance of the resulting products, while high transparency is retained [10,12,15,26]. Currently, the 3 main forms of nanoreinforcements obtained from cellulose that have been extensively studied are microfibrillated cellulose (MFC), cellulose nanowhiskers (CNW), and bacterial cellulose (BC).

Microfibrillated cellulose (MFC)

Microfibrillated cellulose (MFC) comes in the form of fine nano-sized fibrils, expanded to high-volume, with a web-like structure of a considerably high surface area [27]. It can be obtained by mechanical treatment, primarily a combination of shearing and impact forces, of pulp fibers through the refining and high-pressure homogenizing processes. In these procedures, cellulose fibers in the plant cell wall are fibrillated or split into smaller fibrils and microfibrils, in which the latter have diameters in the range of the nano-scale [1]. The repeated mechanical forces on cellulose fibers promote a high degree of microfibrillation; however, the processes are quite energy and time consuming [2]. Depending on the pretreatment, process, and source of cellulose, individual fibrils can be about 5 - 10 nm in diameter, with a long length (varying from 100 nm to several micrometers) (**Figure 3(a)**) [1,11,28]. Sometimes, enzymatic pretreatment using endoglucanase is firstly performed to increase the efficiency of the refining and homogenizing process [29].



(a) (b) (c)

Figure 3 Schematic structures of (a) microfibrillated cellulose (MFC), (b) cellulose nanowhiskers (CNW) and (c) bacterial cellulose (BC).

Cellulose nanowhisker (CNW)

The main method for preparation of cellulose nanowhisker (CNW) is the acid hydrolysis of cellulose sources using strong acids such as hydrochloric and sulfuric acids. This harsh chemical process basically removes the amorphous regions present in the fibrils, leaving the crystalline regions intact as a fine crystal (**Figure 3(b)**). After acid hydrolysis, variation of the CNW dimension is of 4 - 20 nm in diameter and 50 - 500 nm in length, with an aspect ratio in the range of 6 - 40 [7,18,25,26]. Various sources of plants, sea animal (tunicate) and, more recently, agro-wastes have been investigated as sources for CNW preparation [30,31].

In general, sulfuric acid hydrolysis has been often used, since it can provide negative charges of the sulfate groups on the surfaces of CNWs. This can effectively hinder their agglomeration and allow a well-dispersion of CNWs within polymer matrices, which maximizes the reinforcing effect [12,32,33]. Alkaline and enzymatic hydrolysis by using sodium hydroxide and cellulase, respectively, were also attempted for CNW extraction [30,34]. Nevertheless, for industrial practices, all of these preparation procedures are considered time consuming, with very low yields and high costs, are commercially unavailable, and/or mostly involve the use of harsh chemicals [35].

Bacterial cellulose (BC)

Apart from plants, which are the main producers of it, cellulose can also be produced by several microorganisms, particularly Gluconacetobacter xylinus bacteria [36]. Cellulose derived from bacteria, so called “bacterial cellulose (BC)”, has the advantage of being a pure-cellulose network free from wax, lignin, hemicellulose, and pectin, which are present in plant-based cellulosic materials. Furthermore, BC exists naturally as nanosized ribbon-shaped fibers (between 24 - 86 nm in diameter and several micrometers in length) (**Figure 3(c)**), possessing a high degree of crystallinity and mechanical strength [10,16]. Since BC naturally occurs as nanosized fibers, there is no need for the tedious size-reducing steps as per the previous MFC and CNW preparations; however, cultivation of BC is typically a batchwise process, with low yield and high cost, and is time-consuming.

Nanocellulose-reinforced “green” composites

Despite all the difficulties and inconveniences in the preparation and extraction of NCs, during the last decade, a number of research groups have started preparing and investigating various systems of biodegradable polymer nanocomposites reinforced by all NC types. However, since NCs have strong hydrophilic characters and considerably high energetic surfaces, the common problem encountered is their tendency to flocculate through hydrogen bonding. Therefore, gaining the full reinforcing potential of NCs by means of their uniform dispersion and distribution within the less polar polymer matrix is usually challenging, especially in the design for composite processing [15,37]. The next parts of this section review each “green” nanocomposite, classified by the different types of reinforcing NCs; MFC, CNW, and BC, respectively.

“Green” nanocomposites: MFC reinforcement

Earlier, MFC was incorporated into hydrophilic biopolymers such as polyvinyl alcohol (PVA) [2,38], TPS [39,40], wood fibers [41], and pectin and carboxymethyl cellulose (CMC) [42,43]. Due to the similarity in their nature, a homogeneous dispersion and excellent reinforcing effect of MFC on the tensile properties of these nanocomposites were reported (see **Table 1**). The typical 3 tensile values were presented in the table, including tensile strength (σ), tensile strain (ε) and Young’s modulus (E), which can be calculated as follows;

$$\sigma = F/A \tag{1}$$

where F is the force (N), and A is the original unreformed cross-sectional area (m^2);

$$\varepsilon = \frac{\Delta l}{l_{\circ}} \tag{2}$$

where Δl is the change in length (m), and l_o is the original length (m);

$$E = \sigma/\varepsilon \tag{3}$$

Later on, the reinforcing ability of MFC in other biopolymers which are less hydrophilic, i.e., PLA [1,44-46], chitosan [8], and cellulose acetate butyrate (CAB) [47], were investigated. However, difficulties in MFC dispersion in the hydrophobic matrices were found. To solve this problem, the preparation process of the nanocomposites, therefore, had to be well-designed and more complicated, with several steps needed to ensure good MFC dispersion. One inspiring example, Nakagaito *et al.* used a papermaking-like process, followed by compression molding to elaborately prepare the PLA/MFC films [1]. A dramatic improvement in the mechanical and thermal properties of these nanocomposites was presented, with MFC contents of 10 wt% and more. Furthermore, the addition of MFC was reported to improve toughness and also decrease oxygen transmission in some other PLA-based nanocomposite materials [28]. MFC was also observed to act as a nucleating agent, increasing the crystallization rate and crystallinity of PLA, while decreasing the processing time [44,48]. In contrast, another work reported that adding MFC was found to decrease crystallinity in PVA systems [2,38].

If MFC was poorly dispersed in some systems, their agglomerates within a matrix phase were usually observed; in particular, the nanocomposites that were processed by melt mixing or compounding; however, after several additional steps in processing, for instance, (1) MFC/PLA master batch preparation, (2) extrusion compounding the master batch and PLA, and (3) injection molding of the nanocomposites, this problem could be somewhat relieved, and some improvements in the material properties were observed [45] (see **Table 1**). Recently, another modification, using liquid feeding of MFC together with a plasticizer, was reported by Herrera *et al*. [46]. PLA-based films, with well-dispersed MFC, were successfully prepared by a co-rotating twin-screw extruder (attached with liquid feeding) and then compression molding. Interestingly, a positive effect on this film’s toughness was also found in the presence of MFC together with the plasticizer. It was suggested that the combination of slippage of the nanofiber–matrix interface and a massive crazing effect led to the PLA toughening.

“Green” nanocomposites: CNW reinforcement

In 1995, Favier *et al*. showed that a well-dispersion of the tunicin whiskers in styrene butyl acrylate copolymer matrix led to an unusual reinforcing effect within the nanocomposite materials [32]. With a very high surface area of the nano-sized whisker, the percolation threshold (by the hydrogen-bonding system) could be reached with the additional content as low as 1.5 wt%. This was expected to be responsible for the unusual increase in mechanical properties of their nanocomposite system. Since then, CNW has received a great deal of interest and been integrated in many biopolymer matrices. CNW was also added into hydrophobic PLA, either by extrusion compounding or solution casting [19,20,49,50]. However, poor dispersion and CNW aggregation were apparent in most of the subsequent composite structures, and minimal enhancement in mechanical properties was observed. One more problem usually found in using CNWs is their low thermal stability as a result of the prior acid treatment, which also led to an inferior thermal stability of the nanocomposites in many cases. Gas barrier properties of some PLA-based films, however, have been reported to increase in the presence of CNW [49].

Afterwards, a higher potential for CNW dispersibility in melts of PLA and polypropylene (PP), via the use of a spray freeze drying technique to produce porous CNW agglomerate structures, was reported by Kamal and Khoshkava [51]. Furthermore, a good adhesion between CNW and PLA was also found to be achievable in the work of Martine-Sanz *et al*. [52] via electrospinning PLA fibers onto the CNW film and then hot pressing to melt and homogenize the PLA phase and create the sandwich structure of PLA/CNW/PLA films. A pronounced increase in the mechanical properties of these PLA/CNW films, together with a great reduction in water and oxygen permeability, was demonstrated. It should be noted that reported performances of this nanocomposite film were comparable to, or even better than, those of the conventional packaging plastics, such as PET. Also, after the elaborated processing steps in the work of Oksman *et al*. [19], an impressive mechanical property improvement was obtained (**Table 1**).

In more hydrophilic biopolymers, e.g., PVA [18,53,54], ethylene vinyl alcohol copolymer (EVOH) [55], TPS [30,56-60], hydroxypropyl methyl cellulose (HPMC) [61], regenerated cellulose [62], natural rubber [63,64], gelatin [65,66], and agar [67,68], the nanocomposites with CNW were mostly prepared by a film casting technique from aqueous suspension. Well-dispersion of CNW (particularly at < 5 wt% addition), strong interaction between CNW and these polymer matrices, and high reinforcing effect were observed (see **Table 1** for an example). For higher CNW loading systems (e.g., 10 wt%), Santos *et al*. found that sonication treatment could significantly enhance CNW dispersibility in the gelatin matrix [65]. Therefore, a great improvement in mechanical, thermal, and gas barrier properties in some of these film materials were gained, while good transparency could also be retained. However, a higher degree of water vapor permeability was reported in some CNW reinforced films [53,63] and, in ductile polymer like HMPC, the films combined with CNW were found to be more brittle [61].

“Green” nanocomposites: BC reinforcement

BC was first intended to be used as a modifier to enhance properties of fibrous paper-like sheets. The composites were prepared by blending BC with various micro-size pulps (e.g., apple, radish, birch, pine, and softwood) and then hot pressed [69-71]. The BC contents in these sheets ranged from 1 wt% to as high as 100 wt%. It was found that, with increasing BC content, density, tear index, tensile index, burst index, and stiffness of these sheets were heightened, while their porosity and water absorption were reduced.

Soon after, BC drew attention as a reinforcement in other biopolymers, for instance, PVA [9,72,73], TPS [12,74,75], PLA [76-78], poly(hydroxyl butyrate) (PHB) [79], polycaprolactone (PCL) [80], regenerated cellulose [81], chitosan [82], xyloglucan [83], novo aloe vera [84], and hyaluronan [85]. The bionanocomposites were created by many techniques, such as film casting, in situ BC cultivation in media containing polymer solution, partial dissolution of BC fibers, polymer solution impregnation, compounding, and injection or compression molding. With these preparation methods, BC contents in some of these nanocomposites were as high as 50 - 80 wt% [72,80,84], resulting in considerably high mechanical properties of these BC-reinforced materials, approaching that of the neat BC sheet (**Table 1**). Since BC is highly biocompatible, some systems have also been developed for use in the biomedical field, for example, as a wound dressing material and as a drug controlled release host [82,85]. It should be noted that it is very important to clarify the impurities contained in these composite materials prior to use in such a field.

On the other hand, for systems incorporated with the low BC contents (≤ 10 wt%) such as in some of the starch-based materials [12,75], all performances of these nanocomposites were found to be visibly advanced due to a great reinforcing capability of BC and good adhesion between them. In addition, the light transmittance of some BC-reinforced PLA films was observed to be maintainable at the adequate level applicable for uses in food packaging and so on [77].

Approaches for solving NCs' agglomeration problem

In most researches on biopolymers, PLA is now considered to be the most attractive choice. However, a poor dispersion of NCs in the PLA matrix (and other hydrophobic polymers), and a weak interfacial adhesion between the 2 phases due to the difference in their nature, has often been reported. No improvement in the properties of the prepared nanocomposite materials was usually shown as a consequence. This problem has been paid attention to by many researchers, and it has been found that it can be solved by various approaches.

The addition of compatibilizers such as maleic anhydride (MA) [35], poly(ethylene glycol) (PEG) [86], and carbohydrate derived copoly(lactide) [87] has been formerly used to enhance the interaction between NCs and polymer matrices. Improvement in NC dispersion in the polymer phase and, hence, an increase in the mechanical properties of some nanocomposites were reported (a few examples are shown in **Table 2**). However, the thermal properties of some of these materials seemed to be diminished by the presence of compatibilizers [35].

Various surface modifications of NCs via grafting reactions have also been reported. Grafting CNWs with poly(glycidylmethacrylate) [5], n-octadecyl-isocyanate [88], amino-terminated PEG [21], butyl acrylate hydrophobic monomer [89], PLA-chains [90], lactic acid oligomers [37], and long alkyl chain amine [91] have been attempted. Better CNW dispersibility and stronger adhesion with the polymer matrices were obtained, leading to nanocomposites with enhanced mechanical performances (see **Table 2**). Good transparency and improved barrier properties towards water vapor and/or oxygen in these films were also reported in some works [37,88,89,92]. Nevertheless, the thermal properties and/or transparency of some of these nanocomposite films were observed to decrease [5,21,90].

A number of researchers have focused on surface modification of NCs via acetylation (using acids or anhydrides) [11,15,92-94], silylation (using various types of silanes) [26,95,96], chemical treatment with tert-butanol [50], or functionalization with methyl adipoyl chloride [97]. These approaches have appeared to be very interesting, since some of these works reported an improvement in all key performances of the resulting nanocomposites [11,92,97] (see **Table 2**). In addition, an effective enhancement of CNW dispersion in PLA and PLA/PHB blend systems was also observed when a CNW surface was functionalized with an acid phosphate ester of ethoxylated nonylphenol (a commercial surfactant) [98-103]. The good dispersion of CNWs in these systems was confirmed by a high light transmission in the visible region and by good film transparency. For the blended system, the modified CNWs also contributed to an increase in the interfacial adhesion between PLA and PHB, which consequently enhanced the thermal properties of the materials. In addition, the films developed in these researches were formed simply after a melt blending. However, masterbatches were first prepared to improve CNW dispersion in the polymer melts. Interestingly, it was found that both the stiffness and stretchability of the obtained nanocomposite films were increased, while water vapor permeability and oxygen and UV-light transmission were reduced [101-103]. The migration levels for these films were also well below the European legislative limits required for their use as food packaging materials [99,100] (**Table 2**). Considering all results together, it was suggested that these films are very promising for industrial application as short-term flexible food packaging.

Table 1 Tensile properties and processing steps of some selected NC-reinforced “green” nanocomposites.

Sample	Tensile properties			Processing steps	Ref.
	σ (MPa)	ε (%)	E (MPa)		
TPS	8.8	23.0	455	▪ Melt compounding using twin-screw extruder	[40]
TPS/MFC 5 %	11.8	8.9	623	▪ Compression molding into thin films	
TPS/MFC 10 %	16.4	8.8	915		
PVA	34.1	331.0	248	▪ Mechanical stirring & sonication for mixing PVA & MFC	[2]
PVA/MFC 1 %	43.3	34.7	687	▪ Film casting at room temperature	
PVA/MFC 5 %	53.5	25.2	1033	▪ Hot pressing to form the final composites	
PLA	58.9	3.4	2900	▪ PLA & MFC Master batch preparation using acetone:chloroform	[45]
PLA/MFC 1 %	63.1	2.8	3300	▪ Master batch film casting & crushing into particles	
PLA/MFC 5 %	71.2	2.7	3600	▪ Compounding (twin-screw extrusion) & Injection molding into specimens	
TPS	2.8	44.9	112	▪ Ultrasonication for mixing and dispersion CNW in starch solution	[30]
TPS/CNW 3 %	17.4	9.1	520	▪ Composite film casting at 35 °C	
PVA	38.5	61.0	2522	▪ PVA solution preparation	[18]
PVA/CNW 1 %	42.1	96.1	2570	▪ Mixing CNW suspension into PVA solution	
PVA/CNW 3 %	46.0	74.3	2940	▪ Composite film casting	
PLA	40.9	1.9	2900	▪ Swelling CNW in DMAc/0.5 % LiCl & Extrusion compounding with PLA	[19]
PLA/CNW 5 %	77.9	2.7	3900	▪ Compression molding into composite sheets	
TPS	2.5	36	20	▪ Shredding BC pellicle into a slurry using a home blender	[75]
TPS/BC 10 %	8.0	17	170	▪ Mixing BC suspension with starch solution & Film casting at 40 °C	
PVA	60.1	83.2	2200	▪ Shredding BC pellicle into a slurry using a home blender	[72]
PVA/BC 51 %	130.9	2.6	6000	▪ Mixing BC slurry with PVA solution & Composite film casting	
PLA	27.7	23.5	2000	▪ PLA film & BC strip preparation	[76]
PLA/BC 18 %	115.2	3.4	4000	▪ Compression molding the PLA/BC/PLA sandwich into composite films	

Table 2 Tensile and barrier properties of some selected modified NC-reinforced "green" nanocomposites.

Sample	**Approach to improve NC dispersion**	**Tensile properties**			**Barrier properties**			**Ref.**
		***σ* (MPa)**	***ε* (%)**	***E* (MPa)**	**O_2 permeability ($\times 10^{18}$ $m^3\ m\ m^{-2}\ s^{-1}\ Pa^{-1}$)**	**H_2O permeability ($\times 10^{14}$ $kg\ m\ s^{-1}\ m^{-2}\ Pa$)**	**Migration ($mg\ kg^{-1}$)**	
PLA	-	50.9	2.3	4500	-	-	-	[35]
PLA/CNW 5 %	Maleic anhydride	51.7	2.1	4800	-	-	-	
PLA	-	63.1	1.7	4080	-	-	-	[87]
PLA/MFC 5 %	Carbohydrate derived copoly(lactide)	67.4	1.9	4710	-	-	-	
PLA	-	45.0	20	910	-	-	-	[11]
PLA/CNW 2 %	Acetic anhydride	55.0	12	970	-	-	-	
PLA	-	48.3	31.1	1100	-	-	-	[26]
PLA/CNW 2 %	*n*-dodecyldimethylchlorosilane	53.8	7.1	1400	-	-	-	
PLA	-	40.0	4.3	-	2.9[a]	2.2[b]	-	[88]
PLA/CNW 2.5 %	*n*-octadecyl-isocyanate	51.0	5.6	-	3.2[a]	2.4[b]		
PLA	-	45.3	4.1	2410	2.15[a]	-	-	[5]
PLA/CNW 3 %	Poly(glycidyl methacrylate)	55.2	4.1	2790	1.62[a]	-	-	
PLA	-	45.4	5.9	1363	1.73[d]	1.59[a]	-	[37]
PLA/CNW 5 %	Lactic acid oligomers	30.2	1.9	1661	1.31[d]	1.28[a]	-	
PLA	-	15.2	40	1170	-	1.9[c]	-	[92]
PLA/MFC 3 %	Acetic acid and anhydride	33.1	189	1200	-	2.6[c]	-	
PLA	-	16.5	278	1205	-	-	0.06[e]	[100]
PLA/CNW 3 %	Acid phosphate ester of ethoxylated nonylphenol	25.7	210	800	-	-	0.11[e]	

[*] tested at [a] 0 %RH, [b] 50 %RH, [c] 75 %RH, [d] 80 %RH; [e] the EU migration limits for food contact materials = 60 mg kg^{-1} (ethanol 10 % v/v)

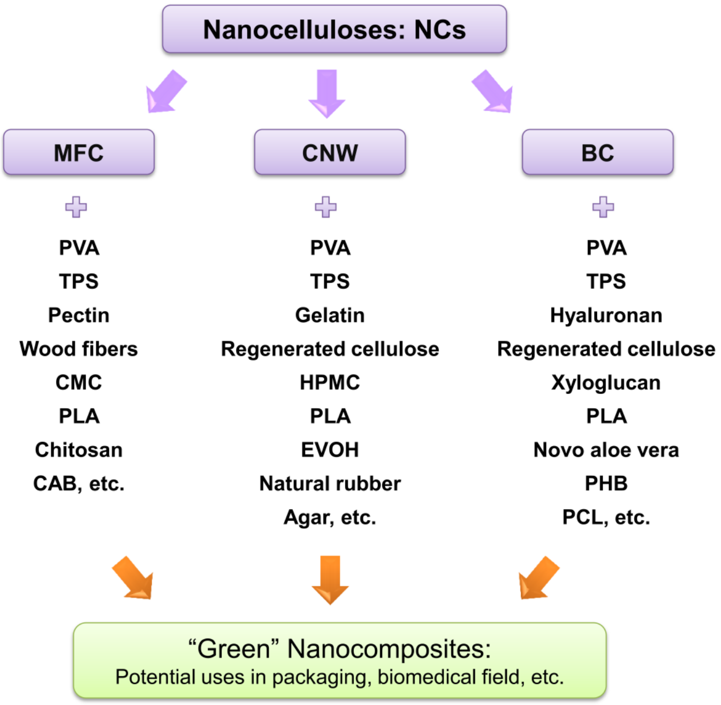


Figure 4 Researches in NC-reinforced “green” composite materials in the last decade.

Summary

Nanocelluloses, classified into 3 types in this review, being microfibrillated cellulose, cellulose nanowhisker, and bacterial cellulose, have attracted a great deal of interest in their use as reinforcements in various biobased and biodegradable polymers. Due to the NCs’ extraordinary reinforcing capacity, renewability, biodegradability, biocompatibility, and so on, many attractive characters are, therefore, integrated into these NC reinforced “green” composite materials. Hence, they are now considered to be promising alternatives, or interesting new choices, for widespread applications, particularly in the packaging and biomedical fields.

In fact, the physical and mechanical properties of these composites could be explained in terms of the properties of each composite material based on their compositions, method of processing, dispersion of nanofillers, and chemical or physical bonding between phases within the materials. For all NCs (MFC, CNW, and BC), it should be noted that their reinforcing capacity (at similar NC content) to enhance mechanical properties in nanocomposite systems are quite similar. When NCs are incorporated into more hydrophilic polymers, a good NC dispersion, and their impressive reinforcing effects, is usually demonstrated. Among the most studied biopolymers, PLA is currently of greatest interest. Nonetheless, the difference in polarity between hydrophobic polymers and hydrophilic NCs is well known; thus, their poor dispersion in the polymer matrix, and weak interaction between them, were often found. Several approaches, such as the use of a well-designed processing technique, the addition of compatibilizers, and the surface modification of NCs (via acetylation, silylation, grafting or using surfactant, etc.) have been experimented with, in an attempt to solve this problem. Some of these approaches were proven to be very effective in enhancing NC dispersion and strengthening the interfacial adhesion with a matrix phase. This led to a great enhancement in the mechanical, thermal, and gas barrier properties of the resulting “green” nanocomposite materials, while also retaining their high optical transparency. In many systems, it has been shown that the performance of these newly created materials can easily compete with conventional polymers and, thus, they can be considered for use as promising "green" alternatives.

However, a challenge still remains for all aspects in the large-scale manufacturing of these NC-reinforced "green" composite materials. Firstly, in the preparation of all types of NCs, the processes are costly, time-consuming, and sometimes involve harsh chemical treatments. Secondly, there are only a few feasible biobased and biodegradable polymers that are commercially available at present. Thirdly, an industrially prevalent technique for the processing of a well-dispersed NC within polymer matrices has been only limitedly successful and reported. Therefore, in order to drive forward a wider commercial opportunity and sustainability of these "green" nanocomposite materials, further researches and developments in all involved technologies must be carried out concurrently.

Acknowledgements

The authors wish to thank Mae Fah Luang University for facilities during the draft manuscript preparation. We are greatly thankful to Assoc. Prof. Dr. Darunee Wattanasiriwech and the reviewers of this article for their comments and suggestions. We also very much appreciate the hand-drawn schematic structures of the 3 different types of nanocelluloses provided by Miss Phattharasaya Rattanawongkun.

References

[1] AN Nakagaito, A Fujimura, T Sakai, Y Hama and H Yano. Production of microfibrillated cellulose (MFC)-reinforced polylactic acid (PLA) nanocomposites from sheets obtained by a papermaking-like process. *Compos. Sci. Tech.* 2009; **69**, 1293-7.

[2] K Qiu and AN Netravali. Fabrication and characterization of biodegradable composites based on microfibrillated cellulose and polyvinyl alcohol. *Compos. Sci. Tech.* 2012; **72**, 1588-94.

[3] E Ten, J Turtle, D Bahr, L Jiang and M Wolcott. Thermal and mechanical properties of poly(3-hydroxybutyrate-co-3-hydroxyvalerate)/cellulose nanowhiskers composites. *Polymer* 2010; **51**, 2652-60.

[4] MD Sanchez-Garcia, A Lopez-Rubio and JM Lagaron. Natural micro and nanobiocomposites with enhanced barriers properties and novel functionalities for food biopackaging applications. *Trends Food Sci. Tech.* 2010; **21**, 528-36.

[5] M Martínez-Sanz, MA Abdelwahab, A Lopez-Rubio, JM Lagaron, E Chiellini, TG Williams, DF Wood, WJ Orts and SH Imam. Incorporation of poly(glycidylmethacrylate) grafted bacterial cellulose nanowhiskers in poly(lactic acid) nanocomposites: Improved barrier and mechanical properties. *Eur. Polym. J.* 2013; **49**, 2062-72.

[6] A Sorrentino, G Gorrasi and V Vittoria. Potential perspectives of bio-nanocomposites for food packaging applications. *Trends Food Sci. Tech.* 2007; **18**, 84-95.

[7] MD Sanchez-Garcia and JM Lagaron. On the use of plant cellulose nanowhiskers to enhance the barrier properties of polylactic acid. *Cellulose* 2010; **17**, 987-1004.

[8] SCM Fernandes, CSR Freier, AJD Silvestre, CP Neto, A Gandini, LA Berglund and L Salmén. Transparent chitosan films reinforced with a high content of nanofibrillated cellulose. *Carbohyd. Polym.* 2010; **81**, 394-401.

[9] S Gea, E Bilotti, CT Reynolds, N Soykeabkeaw and T Peijs. Bacterial cellulose-poly(vinyl alcohol) nanocomposites prepared by an in-situ process. *Mater. Lett.* 2010; **64**, 901-4.

[10] KY Lee, JJ Blaker and A Bismarck. Surface functionalisation of bacterial cellulose as the route to produce green polylactide nanocomposites with improved properties. *Compos. Sci. Tech.* 2009; **69**, 2724-33.

[11] N Lin, J Huang, PR Chang, J Feng and J Yu. Surface acetylation of cellulose nanocrystal and its reinforcing function in poly(lactic acid). *Carbohyd. Polym.* 2011; **83**, 1834-42.

[12] IMG Martins, SP Magina, L Oliveira, CSR Freire, AJD Silvestre, CP Neto and A Gandini. New biocomposites based on thermoplastic starch and bacterial cellulose. *Compos. Sci. Tech.* 2009; **69**, 2169-8.

[13] AK Mohanty, M Misra and LT Drzal. Sustainable bio-composites from renewable resources: Opportunities and challenges in the green materials world. *J. Polym. Environ.* 2002; **10**, 19-26.
[14] K-Y Lee, Y Aitomaki, LA Berglund, K Oksman and A Bismarck. On the use of nanocellulose as reinforcement in polymer matrix composites. *Compos. Sci. Tech.* 2014; **105**, 15-27.
[15] P Tingaut, T Zimmermann and F Lopez-Suevos. Synthesis and characterization of bionanocomposites with tunable properties from poly(lactic acid) and acetylated microfibrillated cellulose. *Biomacromolecules* 2010; **11**, 454-64.
[16] HS Barud, JL Souza, DB Santos, MS Crespi, CA Ribeiro, Y Messaddeq and SJL Ribeiro. Baterial cellulose/poly(3-hydroxybutyrate) composite membranes. *Carbohyd. Polym.* 2011; **83**, 1279-84.
[17] AK Mohanty, M Misra and G Hinrichsen. Biofibres, biodegradable polymers and biocomposites: An overview. *Macromol. Mater. Eng.* 2000; **276/277**, 1-24.
[18] ALS Pereira, DM Nascimento, MMS Filho, JPS Morais, NF Vasconcelos, JPA Feitosa, AIS Brígida and MF Rosa. Improvement of polyvinyl alcohol properties by adding nanocrystalline cellulose isolated from banana pseudostems. *Carbohyd. Polym.* 2014; **112**, 165-72.
[19] K Oksman, AP Mathew, D Bondeson and I Kvien. Manufacturing process of cellulose whiskers/polylactic acid nanocomposites. *Compos. Sci. Tech.* 2006; **66**, 2776-84.
[20] D Bondeson and K Oksman. Polylactic acid/cellulose whisker nanocomposites modified by polyvinlyl alcohol. *Compos. Appl. Sci. Manuf.* 2007; **38**, 2486-92.
[21] S Fujisawa, T Saito, S Kimura, T Iwata and A Isogai. Comparison of mechanical reinforcement effects of surface-modified cellulose nanofibrils and carbon nanotubes in PLLA composites. *Compos. Sci. Tech.* 2014; **90**, 96-101.
[22] JM Lagaron and A Lopez-Rubio. Nanotechnology for bioplastics: Opportunities, challenges and strategies. *Trends Food Sci. Tech.* 2011; **22**, 611-7.
[23] A Iwatake, M Nogi and H Yano. Cellulose nanofiber-reinforced polylactic acid. *Compos. Sci. Tech.* 2008; **68**, 2103-6.
[24] M Zenkiewicz and J Richert. Permeability of polylactide nanocomposite films for water vapour, oxygen and carbon dioxide. *Polym. Test.* 2008; **27**, 835-40.
[25] HMC Azeredo. Nanocomposites for food packaging applications. *Food Res. Int.* 2009; **42**, 1240-53.
[26] A Pei, Q Zhou and LA Berglund. Functionalized cellulose nanocrystals as biobased nucleation agents in poly(L-lactide) (PLLA) - Crystallization and mechanical property effects. *Compos. Sci. Tech.* 2010; **70**, 815-21.
[27] SJ Eichhorn, A Dufresne, M Aranguren, NE Marcovich, JR Capadona, SJ Rowan, C Weder, W Thielemans, M Roman, S Renneckar, W Gindl, S Veigel, J Keckes, H Yano, K Abe, M Nogi, AN Nakagaito, A Mangalam, J Simonsen, AS Benight, A Bismarck, LA Berglund and T Peijs. Review: Current international research into cellulose nanofibres and nanocomposites. *J Mater. Sci.* 2010; **45**, 1-33.
[28] K Okubo, T Fujii and ET Thostenson. Multi-scale hybrid biocomposite: Processing and mechanical characterization of bamboo fiber reinforced PLA with microfibrillated cellulose. *Compos. Appl. Sci. Manuf.* 2009; **40**, 469-75.
[29] N Lavoine, C Givord, N Tabary, I Desloges, B Martel and J Bras. Elaboration of a new antibacterial bio-nano-material for food-packaging by synergistic action of cyclodextrin and microfibrillated cellulose. *Innovat. Food. Sci. Emerg. Tech.* 2014; **26**, 330-40.
[30] AM Slavutsky and MA Bertuzzi. Water barrier properties of starch films reinforced with cellulose nanocrystals obtained from sugarcane bagasse. *Carbohyd. Polym.* 2014; **110**, 53-61.
[31] E Fortunati, F Luzi, D Puglia, F Dominici, C Santulli, JM Kenny and L Torre. 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.
[32] V Favier, H Chanzy and JY Cavaillé. Polymer nanocomposites reinforced by cellulose whiskers. *Macromolecules* 1995; **28**, 6365-7.
[33] MF Rosa, ES Medeiros, JA Malmonge, KS Gregorski, DF Wood, LHC Mattoso, G Glenn, WJ Orts and SH Imam. Cellulose nanowhiskers from coconut husk fibers: Effect of preparation conditions on their thermal and morphological behavior. *Carbohyd. Polym.* 2010; **81**, 83-92.

[34] S Kampangkaew, C Thongpin and O Santawtee. The synthesis of cellulose nanofibers from Sesbania Javanica for filler in thermoplastic starch. *Energ. Proc.* 2014; **56**, 318-25.
[35] JK Pandey, WS Chu, CS Kim, CS Lee and SH Ahn. Bio-nano reinforcement of environmentally degradable polymer matrix by cellulose whiskers from grass. *Compos. Part B: Eng.* 2009; **40**, 676-80.
[36] M Iguchi, S Yamanaka and A Budhiono. Review bacterial cellulose-a masterpiece of nature's arts. *J. Mater. Sci.* 2000; **35**, 261-70.
[37] J Ambrosio-Martin, MJ Fabra, A Lopez-Rubio and JM Lagaron. Melt polycondensation to improve the dispersion of bacterial cellulose into polylactide via melt compounding: Enhanced barrier and mechanical properties. *Cellulose* 2015; **22**, 1201-26.
[38] J Lu, T Wang and LT Drzal. Preparation and properties of microfibrillated cellulose polyvinyl alcohol composite materials. *Compos. Appl. Sci. Manuf.* 2008; **39**, 738-46.
[39] NR Savadekar and ST Mhaske. Synthesis of nano cellulose fibers and effect on thermoplastics starch based films. *Carbohyd. Polym.* 2012; **89**, 146-51.
[40] M Hietala, AP Mathew and K Oksman. Bionanocomposites of thermoplastic starch and cellulose nanofibers manufactured using twin-screw extrusion. *Eur. Polym. J.* 2013; **49**, 950-6.
[41] H Sehaqui, M Allais, Q Zhou and LA Berglund. Wood cellulose biocomposites with fibrous structures at micro- and nanoscale. *Compos. Sci. Tech.* 2011; **71**, 382-7.
[42] N Ninan, M Muthiah, IK Park, A Elain, S Thomas and Y Grohens. Pectin/carboxymethyl cellulose/microfibrillated cellulose composite scaffolds for tissue engineering. *Carbohyd. Polym.* 2013; **98**, 877-85.
[43] N Ninan, M Muthiah, IK Park, N Kalarikkal, A Elain, TW Wong, S Thomas and Y Grohens. Wound healing analysis of pectin/carboxymethyl cellulose/microfibrillated cellulose based composite scaffolds. *Mater. Lett.* 2014; **132**, 34-7.
[44] L Suryanegara, AN Nakagaito and H Yano. Thermo-mechanical properties of microfibrillated cellulose-reinforced partially crystallized PLA composites. *Cellulose* 2010; **17**, 771-8.
[45] M Jonoobi, J Harun, AP Mathew and K Oksman. Mechanical properties of cellulose nanofiber (CNF) reinforced polylactic acid (PLA) prepared by twin screw extrusion. *Compos. Sci. Tech.* 2010; **70**, 1742-7.
[46] N Herrera, AP Mathew and K Oksman. Plasticized polylactic acid/cellulose nanocomposites prepared using melt-extrusion and liquid feeding: Mechanical, thermal and optical properties. *Compos. Sci. Tech.* 2015; **106**, 149-55.
[47] M Jonoobi, Y Aitomäki, AP Mathew and K Oksman. Thermoplastic polymer impregnation of cellulose nanofibre networks: Morphology, mechanical and optical properties. *Compos. Appl. Sci. Manuf.* 2014; **58**, 30-5.
[48] A Suryanegara, AN Nakagaito and H Yano. The effect of crystallization of PLA on the thermal and mechanical properties of microfibrillated cellulose-reinforced PLA composites. *Compos. Sci. Tech.* 2009; **69**, 1187-92.
[49] L Petersson and K Oksman. Biopolymer based nanocomposites: Comparing layered silicates and microcrystalline cellulose as nanoreinforcement. *Compos. Sci. Tech.* 2006; **66**, 2187-96.
[50] L Petersson, I Kvien and K Oksman. Structure and thermal properties of poly(lactic acid)/cellulose whiskers nanocomposite materials. *Compos. Sci. Tech.* 2007; **67**, 2535-44.
[51] MR Kamal and V Khoshkava. Effect of cellulose nanocrystals (CNC) on rheological and mechanical properties and crystallization behavior of PLA/CNC nanocomposites. *Carbohyd. Polym.* 2015; **123**, 105-14.
[52] M Martínez-Sanz, A Lopez-Rubio and JM Lagaron. High-barrier coated bacterial cellulose nanowhiskers films with reduced moisture sensitivity. *Carbohyd. Polym.* 2013; **98**, 1072-82.
[53] E Fortunati, D Puglia, F Luzi, C Santulli, JM Kenny and L Torre. Binary PVA bio-nanocomposites containing cellulose nanocrystals extracted from different natural sources: Part I. *Carbohyd. Polym.* 2013; **97**, 825-36.

[54] N Rescignano, E Fortunati, S Montesano, C Emiliani, JM Kenny, S Martino and I Armentano. PVA bio-nanocomposites: A new take-off using cellulose nanocrystals and PLGA nanoparticles. *Carbohyd. Polym.* 2014; **99**, 47-58.

[55] M Martínez-Sanz, RT Olsson, A Lopez-Rubio and JM Lagaron. Development of electrospun EVOH fibres reinforced with bacterial cellulose nanowhiskers: Part I, characterization and method optimization. *Cellulose* 2011; **18**, 335-47.

[56] Y Chen, C Liu, PR Chang, X Cao and DP Anderson. Bionanocomposites based on pea starch and cellulose nanowhiskers hydrolyzed from pea hull fibre: Effect of hydrolysis time. *Carbohyd. Polym.* 2009; **76**, 607-15.

[57] EM Teixeira, D Pasquini, AAS Curvelo, E Corradini, MN Belgacem and A Dufresne. Cassava bagasse cellulose nanofibrils reinforced thermoplastic cassava starch. *Carbohyd. Polym.* 2009; **78**, 422-31.

[58] Y Lu, L Weng and X Cao. Morphological, thermal and mechanical properties of ramie crystallites-reinforced plasticized starch biocomposites. *Carbohyd. Polym.* 2006; **63**, 198-204.

[59] JS Alves, KC Reis, EGT Menezes, FV Pereira and J Pereira. Effect of cellulose nanocrystals and gelatin in corn starch plasticized films. *Carbohyd. Polym.* 2015; **115**, 215-22.

[60] K González, A Retegi, A González, A Eceiza and N Gabilondo. Starch and cellulose nanocrystals together into thermoplastic starch bionanocomposites. *Carbohyd. Polym.* 2015; **117**, 83-90.

[61] J George, R Kumar, VA Sajeevkumar, KV Ramana, R Rajamanickam, V Abhishek, S Nadanasabapathy and Siddaramaiah. Hybrid HPMC nanocomposites containing bacterial cellulose nanocrystals and silver nanoparticles. *Carbohyd. Polym.* 2014; **105**, 285-92.

[62] H Ma, B Zhou, HS Li, YQ Li and SY Ou. Green composite films composed of nanocrystalline cellulose and cellulose matrix regenerated from functionalized ionic liquid solution. *Carbohyd. Polym.* 2011; **84**, 383-9.

[63] J Bras, ML Hassan, C Bruzesse, EA Hassan, NA El-Wakil and A Dufresne. Mechanical, barrier, and biodegradability properties of bagasse cellulose whiskers reinforced natural rubber nanocomposites. *Ind. Crop. Prod.* 2010; **32**, 627-33.

[64] PM Visakh, S Thomas, K Oksman and AP Mathew. Crosslinked natural rubber nanocomposites reinforced with cellulose whiskers isolated form bamboo waste: Processing and mechanical/thermal properties. *Compos. Appl. Sci. Manuf.* 2012; **43**, 735-41.

[65] TM Santos, MSMS Filho, CA Caceres, MF Rosa, JPS Morais, AMB Pinto and HMC Azeredo. Fish gelatin films as affected by cellulose whiskers and sonication. *Food Hydrocoll.* 2014; **41**, 113-8.

[66] G Mondragon, C Peña-Rodriguez, A González, A Eceiza and A Arbelaiz. Bionanocomposites based on gelatin matrix and nanocellulose. *Eur. Polym. J.* 2015; **62**, 1-9.

[67] JP Reddy and JW Rhim. Characterization of bionanocomposite films prepared with agar and paper-mulberry pulp nanocellulose. *Carbohyd. Polym.* 2014; **110**, 480-8.

[68] M Atef, M Rezaei and R Behrooz. Characterization of physical, mechanical, and antibacterial properties of agar-cellulose bionanocomposite films incorporated with savory essential oil. *Food Hydrocoll.* 2015; **45**, 150-7.

[69] WH Gao, KF Chen, RD Yang, F Yang and WJ Han. Properties of bacterial cellulose and its influence on the physical properties of paper. *Bioresources* 2011; **6**, 144-53.

[70] S Gea, FG Torres, OP Troncoso, CT Reynolds, F Vilasecca, M Iguchi and T Peijs. Biocomposites based on bacterial cellulose and apple and radish pulp. *Int. Polym. Proc. XXII* 2007; **5**, 497-501.

[71] B Surma-Ślusarska, D Danielewicz and S Presler. Properties of composites of unbeaten birch and pine sulphate pulps with bacterial cellulose. *Fibre Text East Eur.* 2008; **16**, 127-9.

[72] Indriyati, R Yudianti and M Karina. Development of nanocomposites from bacterial cellulose and poly(vinyl alcohol) using casting-drying method. *Proc. Chem.* 2012; **4**, 73-9.

[73] A Stoica-Guzun, M Stroescu, I Jipa, L Dobre and T Zaharescu. Effect of ɤ irradiation on poly(vinyl alcohol) and bacterial cellulose composites used as packaging materials. *Radiat. Phys. Chem.* 2013; **84**, 200-4.

[74] CJ Grande, FG Torres, CM Gomez, OP Troncoso, J Canet-Ferrer and J Martínez-Pastor. Development of self-assembled bacterial cellulose-starch nanocomposites. *Mater. Sci. Eng. C* 2009; **9**, 1098-104.

[75] N Soykeabkaew, N Laosat, A Ngaokla, N Yodsuwan and T Tunkasiri. Reinforcing potential of micro- and nano-sized fibers in the starch-based biocomposites. *Compos. Sci. Tech.* 2012; **72**, 845-52.

[76] F Quero, M Nogi, H Yano, K Abdulsalami, SM Holmes, BH Sakakini and SJ Eichhorn. Optimization of the mechanical performance of bacterial cellulose/poly(L-lactic) acid composites. *ACS Appl. Mater. Int.* 2009; **2**, 321-30.

[77] Y Kim, R Jung, HS Kim and HJ Jin. Transparent nanocomposites prepared by incorporation microbial nanofibrils into poly(L-lactic acid). *Curr. Appl. Phys.* 2009; **9**, S69-S71.

[78] KY Lee, P Bharadia, JJ Blaker and A Bismarck. Short sisal fibre reinforced bacterial cellulose polylactide nanocomposites using hairy sisal fibres as reinforcement. *Compos. Appl. Sci. Manuf.* 2012; **43**, 2065-74.

[79] DR Ruka, GP Simon and KM Dean. *In situ* modifications to bacterial cellulose with the water insoluble polymer poly-3-hydroxybutyrate. *Carbohyd. Polym.* 2013; **92**, 1717-23.

[80] S Gea, CT Reynolds, N Roohpur, N Soykeabkaew, B Wirjosentono, E Bilotti and T Peijs. Biodegradable composites based on poly(ε-caprolactone) and bacterial cellulose as a reinforcing agent. *J. Biobased Mater. Bioenerg.* 2010; **4**, 384-90.

[81] N Soykeabkaew, C Sian, S Gea, T Nishino and T Peijs. All-cellulose nanocomposites by surface selective dissolution of bacterial cellulose. *Cellulose* 2009; **16**, 435-44.

[82] RD Pavaloiu, A Stoica-Guzun, M Stroescu, SI Jinga and T Dobre. Composite films of poly(vinyl alcohol)-chitosan-bacterial cellulose for drug controlled release. *Int. J. Biol. Macromol.* 2014; **68**, 117-24.

[83] CF Souza, N Lucyszyn, MA Woehl, IC Riegel-Vidotti, R Borsali and MR Sierakowski. *Carbohyd. Polym.* 2013; **93**, 144-53.

[84] OA Saibuatong and M Phisalaphong. Novo aloe vera-baterial cellulose composite film from biosynthesis. *Carbohyd. Polym.* 2010; **79**, 455-60.

[85] Y Li, S Qing, J Zhou and G Yang. Evaluation of bacterial cellulose/hyaluronan nanocomposite biomaterials. *Carbohyd. Polym.* 2014; **103**, 496-501.

[86] P Qu, Y Gao, GF Wu and LP Zhang. Nanocomposites of poly(lactic acid) reinforced with cellulose nanofibrils. *Bioresources* 2010; **5**, 1811-23.

[87] KY Lee, M Tang, CK Williams and A Bismarck. Carbohydrate derived copoly(lactide) as the compatibilizer for bacterial cellulose reinforced polylactide nanocomposites. *Compos. Sci. Tech.* 2012; **72**, 2546-50.

[88] E Espino-Pérez, J Bras, V Ducruet, A Guinault, A Dufresne and S Domenek. Influence of chemical surface modification of cellulose nanowhiskers on thermal, mechanical, and barrier properties of poly(lactide) based bionanocomposites. *Eur. Polym. J.* 2013; **49**, 3144-54.

[89] Z Song, H Xiao and Y Zhao. Hydrophobic-modified nano-cellulose fiber/PLA biodegradable composites for lowering water vapor transmission rate (WVTR) of paper. *Carbohyd. Polym.* 2014; **111**, 442-8.

[90] S Gårdebjer, A Bergstrand and A Larsson. A mechanistic approach to explain the relation between increased dispersion of surface modified cellulose nanocrystals and final porosity in biodegradable films. *Eur. Polym. J.* 2014; **57**, 160-8.

[91] C Tan, J Peng, W Lin, Y Xing, K Xu, J Wu and M Chen. Role of surface modification and mechanical orientation on property enhancement of cellulose nanocrystals/polymer nanocomposites. *Eur. Polym. J.* 2015; **62**, 186-97.

[92] A Abdulkhani, J Hosseinzadeh, A Ashori, S Dadashi and Z Takzare. Preparation and characterization of modified cellulose nanofibers reinforced polylactic acid nanocomposite. *Polym. Test.* 2014; **35**, 73-9.

[93] T Mukherjee, M Sani, N Kao, RK Gupta, N Quazi and S Bhattacharya. Improved dispersion of cellulose microcrystals in polylactic acid (PLA) based composites applying surface acetylation. *Chem. Eng. Sci.* 2013; **101**, 655-62.

[94] P Purnama and SH Kim. Bio-based composite of stereocomplex polylactide and cellulose nanowhiskers. *Polym. Degrad. Stabil.* 2014; **109**, 430-5.

[95] AN Frone, S Berlioz, JF Chailan and DM Panaitescu. Morphology and thermal properties of PLA-cellulose nanofibers composites. *Carbohyd. Polym.* 2013; **91**, 377-84.

[96] JM Raquez, Y Murena, AL Goffin, Y Habibi, B Ruelle, F Debuyl and P Dubois. Surface-modification of cellulose nanowhiskers and their use as nanoreinforcers into polylactide: A sustainably-integrated approach. *Compos. Sci. Tech.* 2012; **72**, 544-9.

[97] JP Mesquita, CL Donnici, IF Teixeira and FV Pereira. Bio-based nanocomposites obtained through covalent linkage between chitosan and cellulose nanocrystals. *Carbohyd. Polym.* 2012; **90**, 210-7.

[98] E Fortunati, M Peltzer, I Armentano, L Torre, A Jiménez and JM Kenny. Effects of modified cellulose nanocrystals on the barrier and migration properties of PLA nano-biocomposites. *Carbohyd. Polym.* 2012; **90**, 948-56.

[99] E Fortunati, S Rinaldi, M Peltzer, N Bloise, L Visai, I Armentano, A Jiménez, L Latterini and JM Kenny. Nano-biocomposite films with modified cellulose nanocrystals and synthesized silver nanoparticles. *Carbohyd. Polym.* 2014; **101**, 1122-33.

[100] E Fortunati, F Luzi, D Puglia, R Petrucci, JM Kenny and L Torre. Processing of PLA nanocomposites with cellulose nanocrystals extracted from Posidonia oceanica waste: Innovative reuse of coastal plant. *Ind. Crops Prod.* 2015; **67**, 439-47.

[101] MP Arrieta, E Fortunati, F Dominici, E Rayón, J López and JM Kenny. Multifunctional PLA-PHB/cellulose nanocrystal films: Processing, structural and thermal properties. *Carbohyd. Polym.* 2014; **107**, 16-24.

[102] MP Arrieta, E Fortunati, F Dominici, E Rayón, J López and JM Kenny. PLA-PHB/cellulose based films: Mechanical, barrier and disintegration properties. *Polym. Degrad. Stabil.* 2014; **107**, 139-49.

[103] MP Arrieta, E Fortunati, F Dominici, J López and JM Kenny. Bionanocomposite films based on plasticized PLA-PHB/cellulose nanocrystal blends. *Carbohyd. Polym.* 2015; **121**, 265-75.