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Review

Production of nanocrystalline cellulose from lignocellulosic biomass: Technology and applications

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ABSTRACT

The use of renewables materials for industrial applications is becoming impellent due to the increasing demand of alternatives to scarce and unrenewable petroleum supplies. In this regard, nanocrystalline cellulose, NCC, derived from cellulose, the most abundant biopolymer, is one of the most promising materials. NCC has unique features, interesting for the development of new materials: the abundance of the source cellulose, its renewability and environmentally benign nature, its mechanical properties and its nano-scaled dimensions open a wide range of possible properties to be discovered. One of the most promising uses of NCC is in polymer matrix nanocomposites, because it can provide a significant reinforcement. This review provides an overview on this emerging nanomaterial, focusing on extraction procedures, especially from lignocellulosic biomass, and on technological developments and applications of NCC-based materials. Challenges and future opportunities of NCC-based materials will be are discussed as well as obstacles remaining for their large use.

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Abbreviations

Polymers

PAA	poly(acrylic) acid
PAH	poly-(allylamine hydrochloride)
PCL	polycaprolactone
PDDA	poly-(dimethyldiallylammonium chloride)
PEO	polyethyleneoxide
PHA	poly(hydroxyalkanoates)
PHO	poly(hydroxyoctanoate)
PLA	poly(lactic acid)
PMMA	poly(methylmethacrylate)
PP	polypropylene
PS	plasticized starch
PU	polyurethane
PVC	poly(vinyl chloride)
PVOH	poly(vinyl alcohol)

Others

AFM	atomic force microscopy
BNC	bacterial nanocellulose
c-NCC	carboxylated nanocrystalline cellulose
CTABr	cetyltrimethylammonium bromide
DDLS	depolarized dynamic light scattering
DMTA	dynamic mechanical thermal analysis
DLS	dynamic light scattering
DP	degree of polymerization
DSC	differential scanning calorimetry
E	Young's module
LbL	layer by layer
MCC	microcrystalline cellulose
MFC	microfibrillated cellulose
NCC	nanocrystalline cellulose
NMR	nuclear magnetic resonance
OECD	Organisation for Economic Co-operation and Development
SANS	small angle neutron scattering
SEM	scanning electron microscopy
s-NCC	surfactant modified cellulose nanocrystals
TEM	transmission electron microscopy
TEMPO	2,2,6,6-tetramethylpiperidine-1-oxyl
T_g	glass–rubber transition temperature
T_m	melting point
ε_B	elongation at break
σ	tensile strength

1. Introduction

There is a general interest in the sustainable production of chemicals and/or materials from biomass, which may play a major role in producing systems traditionally produced from petroleum. Biodegradable plastics and biocompatible composites generated from renewable biomass feedstock are regarded as promising materials that could replace petrochemical based polymers, reduce global dependence on fossil fuel sources and provide simplified end-of-life disposal. Most of the low-value biomass is termed lignocellulosic, referring to its main constituent biopolymers: cellulose, hemicelluloses and lignin. In particular, cellulose is the most abundant renewable polymer resource available today, and it is considered an almost inexhaustible source of raw material for the increasing demand for environmentally friendly and biocompatible products.

For millennia, cellulose has been used in the form of wood and plant fibres as an energy source, for building materials, paper, textiles and clothing. The use of natural cellulose based materials continues today as verified by the huge number of industries in forest product, paper, textiles, etc. These uses have been considered by some authors (Moon, Martini, Nairn, Simonsen, & Younblood, 2011) as *first generation* uses of cellulose, take advantage of its hierarchical structure. An important field of cellulose application is in composite materials as reinforcement of engineering polymer systems (Biagiotti, Puglia, & Kenny, 2004a). However, certain drawbacks such as incompatibility with the hydrophobic polymer matrix, the tendency to form aggregates during processing and water-swellable nature of cellulose, especially in its amorphous regions (Hubbe, Rojas, Lucia, & Sain, 2008), greatly reduce the potential of natural fibres to be used as reinforcements in polymers. Moreover, properties of cellulosic fibres are strongly influenced by many factors, which differ from different parts of a plant as well as from different plants (Siquera, Bras, & Dufresne, 2010). Their mechanical properties also depend on the cellulose type.

New properties and functions, including uniformity and durability, are required for the next (*second*) *generation* of cellulose based products and their engineering applications. Such features can be displayed by cellulose elementary "building blocks", known as nanocrystalline cellulose, NCC. This is the base reinforcement unit that strengthen all subsequent structures in plant, trees, etc. NCC can be a useful material on which to base a new polymer composite industry: in fact, it contains only a small number of defects and therefore its axial Young's modulus is extraordinary, and close to the one derived from theoretical chemistry and potentially stronger than Kevlar, and within the range of other reinforcement materials, as shown in Table 1. The experimental strength is also very high, as shown in Table 1. NCC has also properties such as low density, high aspect ratio, high surface area, and modifiable surface properties due to reactive —OH side groups. Moreover, biodegradability in aqueous environment has recently been evaluated according to OECD standard for various nanoparticles: cellulose nanoparticles were found to degrade faster than its macroscopic counterpart, whereas other important and widely used nanoparticles such as fullerenes and carbon nanotubes did not biodegrade at all (Kümmerer, Menz, Schubert, & Thielmens, 2011).

Advantages in the use of NCC are related not only to their useful, unsurpassed, physical and chemical properties, or to their

Table 1
Mechanical properties of various materials.

Materials	σ, MPa	E, GPa	Density, g/cm^3	References
Crystalline cellulose	7500–7700	110–220	1.6	Moon et al. (2011)
302 stainless steel	1280	210	7.8	Hamad (2006)
Aluminium	330	71	2.7	http://biovisiontech.ca/technology.html; Ashby (1989)
Softwood Kraft pulp	700	20	1.5	Hamad (2006)
Kevlar KM2 fibre	3880	88	1.4	Cheng, Chen, and Weerasooriya (2004)

biodegradability, renewability, sustainability, abundance, high biocompatibility. In fact its dimensions, in the nanometer scale, open a wide range of possible properties to be discovered. At the nanometer level, some material properties are affected by the laws of atomic physics rather than behaving as traditional bulk materials do. In fact, their extremely small features size is of the same scale as the critical size for some physical phenomena, such as light. Some authors have proposed that nanotechnology will change our lives in profound ways, allowing engineers to come up with more efficient ways of meeting human needs. The excitement has also caught the attention of forest products technologists, and it is believed that nanotechnology has the potential to change completely the forest product and the biomass "industry" through improvements of the products and designing new applications of biomass derived materials with different properties (Duran, Lemes, Duran, Freer, & Baeza, 2011; Hamad, 2006; Hubbe et al., 2008; Hubbe, 2006; Lucia & Rojas, 2007; Peng, Dhar, Liu, & Tam, 2011).

NCC has garnered in the material community a tremendous level of attention that does not appear to be relenting, as shown by the increasing number of scientific contributions (papers and patents) in the field. There have also been several reviews and books (Lucia & Rojas, 2009; Oksman & Sain, 2006; Roam, 2009), describing various aspects of nanocrystalline cellulose, including processing (Dufresne, 2010; Duran, Lemes, & Seabra, 2012; Eichhorn et al., 2010; Eichhorn, 2011; Frone, Panaitescu, & Donescu, 2011; Hubbe et al., 2008; Siquera, Bras, et al., 2010; Visakh & Thomas, 2010), chemical modification of surfaces (Dufresne, 2008; Habibi, Lucia, & Rojas, 2010; Hubbe et al., 2008; Klemm, Heublein, Fink, & Bohn, 2005; Klemm et al., 2011; Peng et al., 2011), NCC-containing nanocomposites (Dufresne, 2008, 2010; Duran et al., 2012; Eichhorn et al., 2010; Habibi et al., 2010; Hubbe et al., 2008; Klemm et al., 2005, 2011; Ramires & Dufresne, 2011; Siquera, Bras, et al., 2010) and self-assembly of suspensions (Eichhorn, 2011; Habibi et al., 2010; Hamad, 2006; Holt, Stoyanov, Pelan, & Paunov, 2010).

This current review follows these earlier ones and, where appropriate, specific topics already adequately covered in previous reviews are summarized and/or referenced out to the corresponding review paper. This review provides an overview on this emerging nanomaterial, focusing on developments of extraction procedures, especially from lignocellulosic biomass, and on developments of applications of NCC-based materials. To the best of our knowledge, there are no reviews specifically focused on the extraction procedures, because of existing literature methods to produce NCC are described before analysing the main topic/s of the paper. Herein we not only described current research on extraction of NCC with inclusion of methods especially developed for the use of biomass as starting material, but we also provided a critical and analytical examination of the drawbacks of various methodologies used so far, taking advantage of our expertise in the field of new reaction media/catalysts for "greener" conditions in preparative chemistry (Aramini, Brinchi, Germani, & Savelli, 2000; Brinchi, Chiavini, Goracci, Di Profio, & Germani, 2009; Brinchi, Di Profio, Germani, Savelli, & Bunton, 1998; De Santi, Cardellini, Brinchi, & Germani, 2012; Gentili et al., 2009). This examination is aimed at developing ideas to improve both the cost and the whole sustainability of NCC production. As regards applications of NCC, as already mentioned, a wide number of reviews and books have been written on several topics. Herein we tried to give only a general idea of the main fields of applications (summarizing and/or referencing out to the corresponding review papers) and we analyzed in particular topics related to our experience and direct research work (Biagiotti et al., 2004a; Biagiotti, Puglia, & Kenny, 2004b) focusing the attention on fully bio-based nanocomposites, such as those based on starch and PLA, and describing developments in improved thermal stability and modulate barrier properties of NCC based bio-nanocomposites. Finally, we critically analyzed the literature available to provide the reader with a detailed and updated list of challenges in the use of NCC nanocomposites that we hope may be of help in directing future work. This contribution is, in fact, aimed at stimulating increased interest in the field, which provides the chemical, biological, physical, and engineering communities a plethora of opportunities for technological improvements and new developments.

2. Structure and morphology of cellulose

Cellulose is one of the most important natural polymers produced in the biosphere, and it is considered the most abundant renewable polymer on Earth. His annual production is estimated to be over 7.5×10^{10} tons (Habibi et al., 2010). Cellulose is widely distributed in higher plants; wood, consisting of up to 50% cellulose, is the most important raw material source for cellulose. Furthermore, it is also distributed in annual crops, and even in several marine animals (for example, tunicates), and to a lesser degree in algae, fungi, bacteria, invertebrates, and even amoeba (Klemm et al., 2011). Regardless of its source, cellulose consists of a linear homopolysaccharide composed of β-D-glucopyranose units linked together by β-1-4-linkages. The repeat unit is a dimer of glucose, known as cellobiose. Each monomer has three hydroxyl groups, and it is therefore obvious that these hydroxyl groups and their ability to form hydrogen bonds play a major role in directing the crystalline packing and also governing the physical properties of cellulose (Maya Jacob & Sabu, 2008). The number of glucose units or the degree of polymerization (DP) is up to 20,000, but its value can vary among a wide range, and the value is around 10,000 in wood (Maya Jacob & Sabu, 2008). In nature, cellulose does not occur as an isolated individual molecule, but it is found as assemblies of individual cellulose chain-forming fibres. The morphological hierarchy is defined by elementary fibrils, which pack into larger units called microfibrils, which are in turn assembled into fibres (Fengel & Wegener, 1989; Habibi et al., 2010). Within the cellulose fibrils there are regions where the cellulose chains are arranged in a highly ordered structure – crystallites – and regions that are disordered – amorphous-like – (Moon et al., 2011). It is these crystalline regions that are extracted, resulting in NCC. In the crystalline regions the inter- and intra-molecular interactions networks and the molecular orientations can vary, giving rise to cellulose polymorphs or allomorphs. Six interchangeable polymorphs have been identified, I, II, III_I, III_{II}, IV_I, IV_{II}. A more detailed description of cellulose crystallites is provided, among others, in reviews by Moon et al. (2011), and that one by Habibi et al. (2010).

Table 2
Cellulose and lignin contents in several types of biomass.

Type of biomass	Cellulose, wt.%	Lignin, wt.%
Coir fibres[a]	43	45
Corn stover[b]	33	14
Corn cob[b]	70	20
Cotton stalk[b]	65	18
Flax fibres[a]	60–81	2–3
Hemp fibres[a]	70–78	3.7–5
Kenaf fibres[a]	36	18
Pineapple leaf fibres[c]	79–83	3–4
Pine-sawdust[b]	60	30
Ramie[d]	76	1
Rice-husk[b]	55	35
Rice-straw[b]	62	18
Sisal fibres[a]	43–88	4–12
Sugarcane bagasse[a]	40	20
Sunn[d]	80	6
Wheat straw[d]	30	15
Wood[e]	40–60	10–35

[a] From Ref. Biagiotti et al. (2004b).
[b] From Ref. Gani & Narus (2007).
[c] From Ref. Cherian et al. (2010).
[d] From Ref. Mohanty, Misra, and Drzal (2002).
[e] From Ref. Hamelinck, van Hooijdonk, and Faaij (2005).

In higher plants, cellulose plays an essential role like reinforce element in the cell wall, generally together with lignin and hemicelluloses. These three polymers are closely associated making up lignocellulosic biomass. Actually, the lignocellulosic structure can be regarded as a bio-nanocomposite, which results from a unique interplay between nano-scale domains of cellulose, hemicelluloses and lignin (Hon & Shiraishi, 2001). The relative content of cellulose and lignin in lignocellulosic biomass varies among species; examples are shown in Table 2. From a technological point of view, lignin content evaluation in the biomass is important to optimize the chemical and mechanical pretreatment parameters necessary to produce a pure cellulose pulp. Indeed lignin is the hardest chemical component to take away from lignocellulosic biomass.

3. Nanocrystalline cellulose

3.1. Micro- and nano-cellulose particles

There is a wide range of cellulose particle types that are being studied for various commercial applications. The diversity of cellulose particle types depend on cellulose source and extraction processes. The nomenclature has not been standardized and some misunderstanding and ambiguities are present in the literature (Klemm et al., 2011; Moon et al., 2011; Siquera, Bras, et al., 2010). A detailed cellulose particles classification is reported in the review by Moon et al. (2011). Here we would like to focus attention on cellulose particles with dimensions in the nanometer scale, but we have to mention microcrystalline cellulose, MCC, that is a commercially available material used for applications in pharmaceutical and food industry and also as starting material to prepare NCC in laboratories. Its dimensions are in the range of 10–50 μm.

The word “nanocellulose” generally refers to cellulosic materials with one dimension in the nanometer range. On the basis of their dimensions, functions, and preparation methods, which in turn depend mainly on the cellulosic source and on the processing conditions, nanocelluloses may be classified in three main subcategories. Herein we follow the nomenclature used by Klemm et al. (2011) and we use the terms nanocrystalline cellulose, NCC, and microfibrillated cellulose, MFC, as indicated in Table 3. Another type of nanocelluloses is the bacterial nanocellulose, BNC, synthesized with a bottom-up method from glucose by a family of bacteria, referred to as *Gluconoacetobacter xylinius* (Klemm et al., 2011); it is not reported in Table 3 because we focus our attention on nanocellulose produced with top-down method from wood or agricultural/forest crops or residues.

The name MFC is widely used in scientific and commercial literature – it is commercially available (Klemm et al., 2011). MFC is generally produced by delamination of wood pulp by mechanical pressure before and/or after chemical or enzymatic treatment (Klemm et al., 2011). The microfibrils, long and flexible, are around 20 nm wide, and several micrometres in length; they consist of alternating crystalline and amorphous domains. One of the main drawbacks to the MFC production has been the very high energy consumption amounting to over 25,000 kWh per ton (Klemm et al., 2011), but more recently there has been a focus on energy-efficient production methods (Lindström, Ankerfors, & Henriksson, 2007; Pääkkö et al., 2007). We will no longer consider MFC because we focus our attention on NCC. Anyway it is important to note the differences between MFC and NCC of comparable dimensions (NCC from tunicates, algae and bacteria). In fact, NCC exhibits elongated crystalline rodlike shapes, and has very limited flexibility – as compared to MFC – because does not contain amorphous regions.

3.2. Nanocrystalline cellulose

NCC is formed by rigid rod-like particles with widths and lengths of 5–70 nm and between 100 nm and several micrometres respectively. The particles are 100% cellulose and highly crystalline, between 54 and 88% (Moon et al., 2011). The aspect ratio, defined as the length to diameter ratio, spans a broad range. The variety of dimensions, morphologies, degree of crystallinity depends on the source of cellulosic material and conditions under which preparation is carried out (Habibi et al., 2010) as well as on the experimental technique used, as shown in Table 4. Moreover, as the cleaving of cellulose chains occurred randomly during the acid hydrolysis process, the dimensions of NCC are not uniform. It was reported that NCC derived from tunicate and bacterial cellulose is generally larger in dimensions compared to those obtained from wood and cotton (see Table 4). This is because tunicate and bacterial cellulose are highly crystalline hence there are lower fractions of amorphous domains that need to be cleaved resulting in the production of larger nanocrystals. NCC from wood is 3–5 nm in width and 100–200 nm in length, and that from wheat straw – an interesting residual lignocellulosic biomass – seems similar.

The precise morphological characteristics of NCC are usually studied by microscopy (transmission electron microscopy, TEM; scanning electron microscopy, SEM; atomic force microscopy, AFM) or light scattering techniques, including small angle neutron scattering (SANS) and polarized or depolarized dynamic light scattering (DLS and DDLS respectively). The most conventional and common one is TEM, which can directly provide high-resolution images, but this technique typically shows aggregation of the particles, mainly due to the drying step for the preparation of the specimen. To overcome this problems and other artefacts (overestimation of dimensions) of this technique, Elazzouzi-Hafraoui et al. (2008), recently reported the use of TEM in cryogenic mode. AFM has been widely used to provide valuable and rapid indication of surface topography of NCC under ambient conditions, at scale length down to Ångström level (Hanley et al., 1992; Kvien et al., 2005). However, this technique has the drawback of tip-broadening resulting in overestimation of crystallite dimensions (Holt et al., 2010; Kvien et al., 2005). Light scattering techniques have recently been brought forward as an important tool in determining NCC dimensions, through the development of models. Braun et al. (2008), used low angle laser light scattering at reduced particle concentration and obtained values of NCC from cotton linter of 13 nm wide and 272 nm long. DLS measurements of NCC suspensions (de Souza Lima et al.,

Table 3
Types of nanocelluloses.[a]

Type of nanocellulose	Synonyms	Typical source	Average size
Nanocrystalline cellulose, NCC	Cellulose nanocrystals, crystallites, whiskers, rod like cellulose microcrystals	Wood, cotton, hemp, flax, wheat straw, rice straw, mulberry bark, ramie, MCC, Avicel, tunicin, algae, bacteria	Diameter: 5–70 nm Length: 100–250 nm (from plant); 100 nm–several micrometres (from cellulose of tunicates, algae, bacteria)
Microfibrillated cellulose, MFC	Microfibrillated cellulose, nanofibrils, microfibrils, nanofibrillated cellulose	Wood, sugar beet, potato tuber, hemp, flax	Diameter: 5–60 nm Length: several micrometres

[a] Adapted from Ref. Klemm et al. (2011).

2003) led to calculate values for the rod dimensions similar to those of dried samples in TEM (see Table 4).

4. Extraction of nanocrystalline cellulose

NCC has been isolated from a variety of cellulosic sources, including plants, animals (tunicates), bacteria and algae and in principle could be extracted from almost any cellulosic material. In practise, researchers have shown clear preferences. Commonly studied source materials have included wood, plants, and some kind of relatively pure cellulose such as MCC or bleached Kraft pulp. Wood, owing to its natural abundance, is a key source of cellulose because of its widespread availability and high content of cellulose. Actually, for most studies related to initial basic research or to nanocomposite, NCC has been prepared from commercially available MCC or from filter paper, or related products, because of their purity and ready availability in laboratories (Klemm et al., 2011). Moreover, tunicate has been a favoured source of NCC because of its length and high crystallinity (Terech et al., 1999), although its widespread use is restricted by the high cost of harvesting and limited availability.

The isolation of NCC from cellulose source materials occurs in two stages, as shown in Fig. 1. The first one is a pre-treatment of the source material. For wood and plants it involves the complete or partial removal of matrix materials – hemicelluloses, lignin, etc. – and isolation of the cellulosic fibres. The second one is a controlled chemical treatment – generally hydrolysis – to remove the amorphous regions of the cellulose polymer.

4.1. Pre-treatment of lignocellulosic biomass

For wood and plant source materials, the pre-treatments are similar and consist of techniques that are usually used in pulp and paper industry. In practice, lignin impedes separation of wood into its component fibres, so delignification is a necessary preparation step to produce NCC. Excellent descriptions of pulping and bleaching processes are available, for instance in the review by Siquera, Bras, et al. (2010), and the book by Smook (1992). Here we may briefly say that the processes mainly consist of a chemical treatment (pulping) of biomass previously chipped to depolymerize and eventually solubilize lignin and hemicelluloses, and a subsequent bleaching with oxidizing agents such as oxygen or $NaClO_2$.

The steam explosion process is another efficient pre-treatment method for converting lignocellulosic biomass with the final aim of separating nanofibers (Cherian et al., 2010; Naik et al., 2010). Steam explosion pre-treatment technologies have been an active area of research for the past two decades, especially because the resulting feedstock is much more amenable to enzymatic hydrolysis (Hayes, 2009). In this process the biomass sample is first milled and then subjected to high pressure steam for short time (20 s to 20 min) at a temperature 200–270 °C and a pressure of 14–16 bar. The pressure in digester is then dropped quickly by opening the steam and the material is exposed to normal atmospheric pressure to cause explosion which break down lignocellulosic structure. Steam explosion causes the hemicelluloses and lignin from the wood to be decomposed and converted into low molecular weight fraction which can be recovered by extraction. Therefore most of water soluble fraction of hemicelluloses can be removed by water extraction. At the same time, a part of the low molecular weight fraction of lignin is also extracted. Other chemical treatments are necessary to remove all lignin content. All these steps allow elimination of lignin and hemicelluloses, while leaving cellulose moieties intact if optimal conditions are respected. The effectiveness of the steam explosion is dependent on the biomass feedstock and, for instance, the process is less effective for softwood than for hardwood (Hamelinck et al., 2005).

4.2. Hydrolysis

Rånby (1951), is considered the pioneer in the production of colloidal suspensions of cellulose crystals by controlled sulphuric acid hydrolysis of cellulose fibres. The method of choice for the isolation of NCC from cellulose is still based on controlled sulphuric acid hydrolysis, owing to the stability of the resulting suspensions (Beck-Candanedo et al., 2005; Elazzouzi-Hafraoui et al., 2008; Favier, Chanzy, & Cavaille, 1995). During hydrolysis amorphous domains are preferentially hydrolyzed, whereas crystalline regions

Table 4
Examples of length (L) and diameter (d) of NCC from various sources obtained via different techniques.

Source	L, nm	d, nm	Technique	References
Bacterial	100–1000	10–50	TEM	Araki, Wada, and Kuga (2001)
Tunicate	1160	16	DLS	de Souza Lima, Wong, Paillett, Borsali, and Pecora (2003)
	100–some 1000	15–30	TEM	Kimura et al. (2005)
Valonia	>1000	10–20	TEM	Revol (1982)
MCC	ca. 500	10	AFM	Pranger and Tannenbaum (2008)
Cotton	255	15	DLS	de Souza Lima et al. (2003)
	100–150	5–10	TEM	Araki et al. (2001)
Cotton linter	25–320	6–70	TEM	Elazzouzi-Hafraoui et al. (2008)
	300–500	15	AFM	Li et al. (2009)
Softwood	100–150	4–5	AFM	Beck-Candanedo, Roman, and Gray (2005)
Hardwood	140–150	4–5	AFM	Beck-Candanedo et al. (2005)
Wheat straw	150–300	ca. 5	TEM	Dufresne, Cavaille, and Helbert (1997)
Rice straw	117 ± 39	8–14	TEM	Ping and Hsieh (2012a)

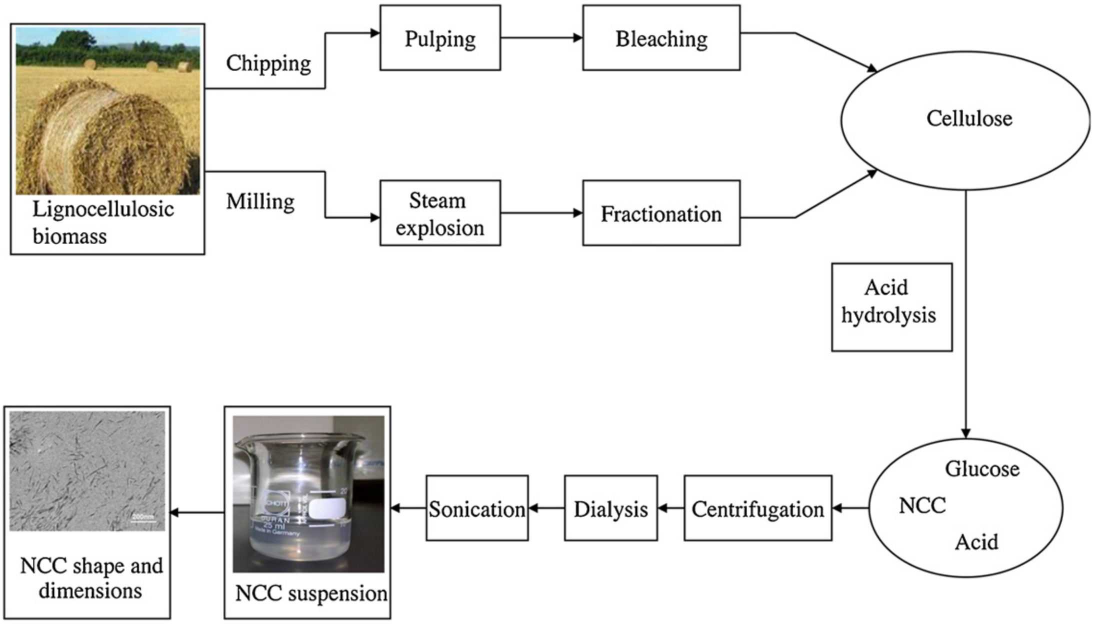

Fig. 1. Scheme of main steps needed to prepare NCC from lignocellulosic biomass.

have higher resistance to acid attack (Habibi et al., 2010). Typical procedures currently employed consist of several steps, as shown in scheme in Fig. 1. It must be said that the very limited commercial availability of NCC is mainly due to the time consuming production process and the low yield.

Typical procedures for the production of NCC consist of the following steps:

(1) Strong acid hydrolysis of pure cellulosic material under strictly controlled conditions of temperature, time, agitation, and with control of other conditions such as nature and concentration of the acid and the acid to cellulose ratio;
(2) Dilution with water to stop reaction and repeated washing with successive centrifugation;
(3) Extensive dialysis against distilled water to fully remove free acid molecules;
(4) Mechanical treatment, usually sonication, to disperse the nanocrystals as a uniform stable suspension;
(5) Eventual concentration and drying of the suspension to yield solid NCC.

Perhaps one of the most detailed reports on sulphuric acid hydrolysis of cellulose was provided by Dong et al. (1998): it includes investigation on the effects of temperature, reaction time, and sonication on the properties of resulting nanocrystals. In particular they showed how as the reaction time increased from 10 to 240 min at 45 °C the surface charge of crystallite generally increased while the length of the crystallites decreased and approximately levelled off.

4.3. Challenges in the production of NCC

Extraction is central to further developing and processing NCC into functional, high-value added materials, and, as such, attempts to face the drawbacks in the conventional methodology, to reduce the cost and enlarge the production are continuously reported in the literature. In particular the reduction in the cost of NCC production is often addressed, because it could increase the number of markets appropriate for NCC applications. Some problems and attempts to face them are discussed in the following sections.

4.3.1. Use of residual biomass to produce NCC

At present, the research is focusing on the possible use of forest or agricultural residues as NCC sources for their abundance at low economical and energetic cost, and for the simplified waste disposal. In the different climatic zones worldwide, various local sources are used for attempts of valorization in this sense and, in same cases, technologies must be adapted to use certain sources. For instance NCC has been prepared from pineapple leaf fibres (Cherian et al., 2010), swede root (Bruce et al., 2005), grass (Pandey et al., 2008, 2009, 2012), wheat straw (Dufresne et al., 1997; Helbert et al., 1996), rice straw (Ping & Hsieh, 2012a), coconut fibres and branch-bark of mulberry (Duran et al., 2011) and recently also from chardonnay grape skins (Ping & Hsieh, 2012b).

Since plant-based cellulose nanofibres have the potential to be extracted into fibres thinner than bacterial cellulose, many researchers have been extensively studying the extraction of nanofibres from wood and other plant fibres. However, because of the complicated multilayered structure of plant fibres and the interfibrillar hydrogen bonds, the fibrils obtained by common methods (high pressure homogenizer, a grinder, cryocrushing) are aggregated nanofibres with a wide distribution in width. Abraham et al. (2011), have recently developed a simple and low cost process to obtain an aqueous stable colloid suspension of cellulose nanofibrils from various lignocellulosic fibres. They considered three different start fibres: banana (pseudo stem), jute (stem) and pineapple leaf fibre. The authors concluded that pineapple leaf fibre is the best one for the preparation of nanocellulose; however, jute fibre is cheaply and abundantly available and the raw jute fibre has about 60–70% cellulose content. Hence for the cost effective production of nanocellulose, jute fibre is the potential candidate.

Finally, okra natural fibre extracted from its bast, was used as the source material to produce cellulose micro- and nano-fibres, with a view to obtaining cellulose structures with a high crystallinity and thermal stability, by means a pre-treatment with alkali, followed by sulphuric acid extraction. The hydrolysis parameters applied, though building on previous investigations of extraction starting from microcrystalline material, proved also sufficiently suitable for hydrolysis from a macrofibre, such as okra, while the results from morphological, thermal and mechanical analyses showed some potential for okra fibres, and in general for bast herbaceous fibres, for their application in the form of NCC in nanocomposite systems (Fortunati, Puglia, et al., 2012).

4.3.2. *Integration of NCC and cellulose biofuels productions*

Currently both production of nanocelluloses and cellulose biofuels are not economical, so the inclusion of the production in the biorefinery would increase the number of jobs and the profitability of the venture (Duran et al., 2011). In a recent paper Zhu et al. (2011), demonstrate a novel concept to integrate these productions: enzymatic fractionation was used to separate glucose stream for biofuel production and recalcitrant cellulosic solid fraction. This last one was used by these authors to produce MFC. On the other hand, Oksman et al. (2011), separated NCC from a bio-residue of bioethanol production from lignocellulosic biomass. The bio-residue used, called usually "lignin", resulted to contain high percentage of cellulose (ca. 50%), and NCC with more than 73% crystallinity was obtained from it with relatively good yield. Moreover, Mandal and Chakrabarty (2011), have recently considered the possibility to extract cellulose nanocrystals from sugarcane bagasse. Sugarcane bagasse is a residue produced in large quantities every year by the sugar and alcohol industries, as well as by the bioethanol production facilities.

4.3.3. *Standardization of the NCC produced*

Reliable recipe for production with uniform size, aspect ratio, surface chemistry is necessary, because it would provide more control in NCC suspensions, and in the design and processing of NCC-based composites. To date, additional final steps such as filtration (Elazzouzi-Hafraoui et al., 2008), differential centrifugation (Bai et al., 2009), or ultracentrifugation (de Souza Lima & Borsali, 2002) have been reported in order to reduce the polydispersity of the crystallites. An interesting investigation carried out by Beck-Candanedo et al. (2005), reported that shorter nanoparticles with narrow polydispersity were produced at longer hydrolysis times, using sulfuric acid. It is necessary, however, to develop means to produce NCC with controlled size, aspect ratio, controlled surface chemistry; such control will allow for repeatable, optimized materials. A recent attempt in this area is the work of Hamad and Hu (2010), about structure–process–yield interrelations in the sulfuric acid NCC extraction from bleached softwood Kraft pulp. Their results systematically show that sulfation plays a significant role in determining the yield of extracted NCC, and in imparting NCC characteristics in terms of crystallinity and degree of polymerization (Hamad & Hu, 2010).

4.3.4. *Increase of NCC yield from sulfuric acid hydrolysis*

Efforts in increasing the yield in NCC extraction have important impact on final cost. Bondeson et al. (2006), investigated optimizing the hydrolysis conditions by an experimental factorial design matrix and demonstrated that NCC is obtained with a yield of 30% (based on initial weight) with sulphuric acid 63.5% (w/w) for 2 h. More recently Hamad and Hu (2010), carried out a systematic investigation of the structure–process–yield interrelations in the NCC extraction from a commercial softwood Kraft pulp. NCC with high crystallinity (>80%) was obtained using 64% sulphuric acid, with yields between 21 and 38%. The highest yield was obtained using a temperature of 65 °C when shortening the reaction time down to 5 min.

4.3.5. *Valorization of waste liquor of acid hydrolysis*

In order to decrease the general cost and to face environmental concern of concentrated strong acid solutions, valorization of the waste liquor stream needs to be addressed. It contains sugars, in monomeric and oligomeric forms, and residual sulphuric acid. A recent patent by Jemaa, Paleologou, and Zhang (2011), claims the efficient use of membrane nanofiltration to achieve separation of the acid and sugars in the waste liquor stream, and the use of a second membrane filtration to separate monomeric from oligomeric sugars.

4.3.6. *Use of other acids and/or other processes*

The use of a concentrated strong acid, especially sulphuric, has a number of important drawbacks such as hazard, corrosivity (corrosion resistant reactors have to be used), environmental incompatibility. Concentrated sulphuric acid is, however, generally used, but the use of phosphoric, hydrobromic and hydrochloric acids has been reported (Habibi et al., 2010). During the sulphuric acid hydrolysis there is a certain degree of grafting of sulphate group onto the surface of NCC (Revol et al., 1992); these groups impart a negative surface charge to NCC which stabilizes the aqueous suspension against flocculation, but they also compromise the thermostability of nanocrystals (Roman & Winter, 2004). However, if NCC was prepared by hydrolysis in hydrochloric acid, their aqueous suspensions tend to flocculate (Araki et al., 1998).

4.3.6.1. Use of ultrasonic treatment. Ultrasonication has been proposed as assistance for acid hydrolysis. Recently novel spherical NCC nanocrystals were prepared by a post-treatment with sulphuric acid of NCC generated by hydrolysis in HCl under ultrasonic treatment: this method allowed a surface charge density control (Wang et al., 2007). Moreover, the production of nanocrystalline cellulose has been obtained using sono-chemical assisted hydrolysis in water or maleic acid (an organic not strong acid) although reported yields are low: 2–5% in water and 10% in aqueous maleic acid, based on dry weight of the starting material (Filson & Dawson-Andoh, 2009).

4.3.6.2. Oxidation. Surface carboxylated NCC (c-NCC) has been obtained by oxidation. 2,2,6,6-Tetramethylpiperidine-1-oxyl (TEMPO)–NaBr–NaClO system was used, with ultrasonic treatment, to oxidize cotton linter pulp (Qin et al., 2011). During the oxidation some of the amorphous regions were gradually hydrolyzed and a stable and well dispersed aqueous suspension was therefore obtained in one step. Anyway, yields are not reported in this contribution, and it must be taken into account that TEMPO is relatively expensive and toxic. Another simple and versatile one-step procedure to produce highly crystalline c-NCC has recently been proposed by Leung et al. (2011). It consisted in a oxidation at 60 °C with ammonium persulfate; the reaction time was substrate-dependent. The c-NCC samples from different cellulosic sources showed a similar mean particle length and length polydispersity. Yields were relatively high, and the method is amenable to scale-up. This approach could be considered as a chemical nanoscissor effective in processing raw cellulosic materials, in contrast with acid hydrolysis which requires pre-treatment steps for the isolation of cellulose.

4.3.6.3. Use of ionic liquids. Ionic liquids have been suggested as systems to dissolve cellulose, and then, due to changed conditions, to reprecipite the material in a wide range of morphologies (Kilpelainen et al., 2007). Ionic liquids, IL, which are salts of low melting point and relatively low viscosity, are innovative media labelled to be "green", used for various applications, including selectivity in chemical acid-catalyzed processes, taking advantage of their tunable properties (Biondini et al., 2006, 2010; Welton, 1999). They have been recently used as both solubilizing agents and catalysts to carry out cellulose hydrolysis: MCC was hydrolyzed in 1-butyl-3-methylimidazolium hydrogen sulfate to yield NCC of high crystallinity, with possible reuse of the IL; however, this NCC showed low thermal stability (Man et al., 2011). We may suggest that new reaction media such as Deep Eutectic Solvents can be even more useful. They have recently appeared in the horizon as a new generation of ionic solvents of low cost, referred to as "advanced IL", simply prepared mixing an hydrogen bond donor molecule with halide salts (Abbott et al., 2003, 2011). Their usefulness for NCC extraction is related to the even broader tunability, easy of preparation for non chemists, and effective promotion of acid-catalyzed processes (De Santi et al., 2012).

4.3.6.4. Enzymatic hydrolysis. There is limited literature on the use of enzymatic hydrolysis for nanocellulose production, and it is mainly focused on preparation of MFC (Duran et al., 2011; Pääkkö et al., 2007). As far as we know, there is an exception: in a quite detailed paper, Siqueira, Tapin-Lingua, Bras, da Silva Perez, and Dufresne (2010), investigated various combinations of mechanical shearing, acid and enzymatic hydrolysis in order to produce nanoparticles from sisal pulp. They showed that NCC could be obtained by enzymatic hydrolysis, and that, depending on the treatment and on their sequence, MFC coexist with NCC in the obtained suspensions.

4.3.7. Drying

Drying of the final aqueous suspensions has rarely been reported for problems related with it, but it seems to be a necessary step in order to mitigate transportation costs. In most cases NCC is processed as aqueous suspension because its hydrophilic nature and propensity to agglomerate during drying (Gardner et al., 2008). In fact, during drying, forces resulting from the removal of water and high temperature may drive the molecular contact of NCC and cause agglomeration. There is a well perceived need to develop robust processes to dry NCC which will maintain nanoscale dimensions for material applications (where a dry form is necessary) and to mitigate the higher transportation costs of aqueous suspensions. Furthermore not only drying but also understanding the drying process is necessary for the use of NCC in developing industrial applications in polymer nanocomposites. The well established method of oven drying causes increase in dimensions to hundreds of microns or even to millimetres, so the nanoscale dimensions are lost (Peng et al., 2012; Voronova et al., 2012). Quite recently a paper reports a comparative investigation between different methods such as freeze drying, supercritical drying and spray drying (Peng et al., 2012). Results show that freeze drying and supercritical drying create highly networked structures of agglomerates with multi-scalar dimensions including nanoscale. The spray drying is proposed by the authors as a technically suitable manufacturing process to dry NCC suspensions: the particle sizes range from nano to micron scale and are controllable, the cost is low and the method is scalable.

4.3.8. Scale-up

For industrial use of NCC at least one main question needs to be addressed: the scaling-up from laboratory size quantities to pilot plants quantities. As far as we know, the following pilot plant facilities are in the design stage for NCC processing: FPInnovation (http://fpinnovation.ca), Domtar (http://domtar.com/index.asp), BioVisionTechnology Inc. (http://biovisiontech.ca/technology.html) USDA-Forest Service Forest Production (http://www.flp.fs.fed.us/research/focus/nano_intro.shtml).

5. Applications of NCC

Major studies over the last decades have shown that NCC can be used as filler in nanocomposites to improve mechanical and barrier properties: several reviews have been written on these topics (Dufresne, 2008, 2010; Duran et al., 2012; Eichhorn et al., 2010; Habibi et al., 2010; Hamad, 2006; Hubbe et al., 2008; Klemm et al., 2005, 2011; Oksman & Sain, 2006; Siquera, Bras, et al., 2010; Visakh & Thomas, 2010). Incorporation of NCC into a wide range of polymeric matrices was attempted, including synthetic and natural ones (such as starch or PLA). Some examples are shown in Table 5,

Table 5
Examples of polymeric matrices used for nanocomposites with NCC as filler. Polymers with asterisk (*) are natural or natural-like biopolymers.

Polymer	References
Poly(lactic acid), PLA*	Kvien, Tanem, and Oksman (2005), Pandey et al. (2012), Fortunati, Puglia, et al. (2012), Fortunati, Armentano, Zhou, Puglia, et al. (2012), Fortunati, Peltzer, et al. (2012), Fortunati, Armentano, Zhou, Iannoni, et al. (2012), Roohani et al. (2008), Bondeson and Oksman (2007), Hamad and Miao (2011), Xiang, Joo, and Frey (2009).
Regenerated cellulose*	Qi, Cai, Zhang, and Kuga (2009), Ma, Zhou, Li, Li, and Ou (2011).
Cellulose*	Magalhaes, Cao, Ramires, and Lucia (2011).
Cellulose acetate butyrate	Petersson, Mathew, and Oksman (2009), Grunnert and Winter (2002).
Starch-based polymers*	Anglès and Dufresne (2000, 2001), Cao, Chen, Chang, Stumborg, et al. (2008), Cao, Chen, Chang, Muir, et al. (2008), Lu, Weng, and Cao (2005).
Xylan*	Saxena and Raguskas (2009), Saxena, Elder, Kenvin, and Ragauskas (2010), Saxena, Elder, Kenvin, Ragauskas, and Arthur (2011).
Soy protein*	Wang, Cao, and Zhang (2006).
Chitosan*	Li et al. (2009), Azeredo et al. (2010), de Mesquita, Donnici, and Pereira (2010).
Poly(hydroxyalkanoate), PHA*	de Mesquita et al. (2010), Dufresne, Kellerhals, and Witholt (1999)
Poly(hydroxyoctanoate), PHO*	Dubief, Samain, and Dufresne (1999)
Poly(ethylene-co-vinyl acetate), EVA	Chauve, Heux, Arouini, and Mazeau (2005)
Poly-(dimethyldiallylammonium chloride), PDDA	Podsiadlo et al. (2005)
Poly-(allylmethylamine hydrochloride), PAH	Jean, Dubreuil, Heux, and Cousin (2008)
Poly(methylmethacrylate), PMMA	Dong et al. (2012), Liu, Liu, Yao, and Wu (2010)
Polysulfone	Li et al. (2011)
Poly(acrylic) acid, PAA	Lu and Hsieh (2009)
Poly(styrene-co-butyl acrylate)	Favier, Chanzy, et al. (1995), Helbert, Cavaille, and Dufresne (1996), Oksman, Mathew, Bondeson, and Kvien (2006)
Poly(oxyethylene), PEO	Horvath, Lindström, and Laine (2006), Zhou, Chu, Wu, and Wu (2011)
Polypropylene, PP	Ljungberg et al. (2005), Ljungberg, Heux, and Cavaille (2006)
Polyvinyl chloride, PVC	Chazeau, Cavaille, Canova, et al. (1999), Chazeau, Cavaille, and Terech (1999), Chazeau, Cavaille, and Perez (2000).
Poly(vinylalcohol), PVOH	Dufresne, Dupeyre, and Vignon (2000), Peresin, Habibi, Zoppe, Pawlak, and Rojas (2010), Paralikar, Simonsen, and Lombard (2008), Li, Yue, and Liu (2012)
Polystyrene	Rojas, Montero, and Habibi (2009)
Polyurethane, PU	Auad et al. (2012), Marcovich, Auad, Bellesi, Nutt, and Aranguren (2006), Pei, Malho, Ruokolainen, Zhou, and Berglund (2011).
Polycaprolactone, PCL	Zoppe, Peresin, Habibi, Venditti, and Rojas (2009), Habibi et al. (2008), Habibi and Dufresne (2008)

Table 6
Mechanical properties of PS (plasticized starch) and PS/NCC nanocomposites obtained from tensile test.[a]

Samples	σ, MPa	E, MPa	ε_B, %
PS	3.9 ± 0.3	31.9 ± 5.1	68.2 ± 3.1
PS/NCC (5%)	6.4 ± 0.2	82.6 ± 5.3	44.3 ± 5.2
PS/NCC (10%)	7.6 ± 0.3	180.4 ± 13.2	35.9 ± 4.3
PS/NCC (15%)	8.2 ± 0.4	255.3 ± 12.1	26.8 ± 5.5
PS/NCC (20%)	8.9 ± 0.3	311.9 ± 20.5	14.1 ± 4.2
PS/NCC (25%)	10.5 ± 0.5	447.5 ± 14.3	9.4 ± 1.6
PS/NCC (30%)	11.9 ± 0.8	498.2 ± 23.4	7.2 ± 1.8

[a] Data from Ref. Cao, Chen, Chang, Muir, et al. (2008).

but the list, though long, is clearly not exhaustive of the vast number of research results available Attention is increasingly devoted to fully-biobased and biodegradable systems, and “green composites” is the term used to indicate composites with both polymeric matrix and filler being bio-based (Abdul Khalil et al., 2012).

Actually, as more researchers from various scientific fields become interested in NCC, other possible uses have been proposed and explored, such as foams, aerogels (Eichhorn et al., 2010), building block for permselective membranes (Thielemans et al., 2009), improvements in adhesive materials (Eichhorn et al., 2010) or adhesive by itself (Jiang, Berry, Bouchard, & Audet, 2011), use in lithium battery products as a mechanical reinforcing agent for low-thickness polymer electrolytes (Samir, Alloin, Sanchez, & Dufresne; 2004; Samir, Alloin, Mateos, Sanchez, & Dufresne, 2004; Samir, Alloin, & Dufresne, 2006; Schroers et al., 2004), use in biomolecular NMR (Fleming et al., 2000). A broad range of applications of NCC exist, even if a high number of unknowns remain to be discovered. Examples of applications related to the improvement and engineering of certain materials properties follow. They are not exhaustive of the continuously increasing number of applications reported in the literature.

5.1. Improvement of nanocomposite mechanical properties

The enhancement in mechanical properties of nanocomposites by addition of NCC represents a strong opportunity for industrial sector. The first publication related to the use of NCC as reinforcing fillers in poly(styrene-co-butyl acrylate) based nanocomposites was reported by the Favier, Chanzy, et al. (1995), in France. A list of papers relative to investigations in this field would be quite long, and excellent reviews cover this aspect (Dufresne, 2008, 2010; Duran et al., 2012; Eichhorn et al., 2010; Habibi et al., 2010; Hamad, 2006; Hubbe et al., 2008; Klemm et al., 2005, 2011; Oksman & Sain, 2006; Siquera, Bras, et al., 2010; Visakh & Thomas, 2010). Herein we would like to focus attention on fully bio-based nanocomposites such as those based on starch. Although this biopolymer has great potential to replace plastics, material based only on starch often lack the required strength (Kvien et al., 2007). Starch-based polymers can be reinforced by the addition of a percentage of NCC as filler, as observed for instance by Anglès and Dufresne (2000, 2001), Cao, Chen, Chang, Stumborg, and Huneault (2008), Cao, Chen, Chang, Muir, and Falk (2008) and other scientists (Kvien et al., 2007; Lu et al., 2005). Examples of the observed increase in tensile strength (σ), Young’s modulus (E) and elongation to break (ε_B) are reported in Table 6.

5.2. Cellulose effects on nanocomposite thermal properties

Thermal properties of NCC and its composites are both limiting and enabling with regard to potential applications, and some issues have been reviewed (Dufresne, 2008; Habibi et al., 2010; Hubbe et al., 2008; Moon et al., 2011; Siquera, Bras, et al., 2010). In fact, thermal degradation of cellulose materials or the reduction of mechanical properties at high temperatures are among the major issues that limit NCC application (Hubbe et al., 2008; Moon et al., 2011), but in some cases thermal properties improved with addition of NCC. The improvement of glass–rubber transition temperatures, T_g, melting point, T_m, and thermal stability has been investigated by several authors through differential scanning calorimetry (DSC). Siquera, Bras, et al. (2010), highlighted the efforts in the evaluation of changes in transition temperatures of NCC enhanced polymers; for these parameters several authors did not observe relevant variations, and this is surprising due to the high specific area of the nanofiller.

On the other hand, DMTA, dynamic mechanical thermal analysis, showed how the introduction of NCC in composites improves the response of the mechanical properties as compared to the neat matrix polymer (Moon et al., 2011). The T_g of the composite is unchanged from that of the neat polymer, but at temperatures above T_g the composite has higher storage and loss moduli, and the stabilization effect increased with increasing NCC concentration within the matrix (Helbert et al., 1996). Quite recently, Auad et al. (2012) observed an improvement of the thermal performances of shape memory segmented polyurethanes (SPUs) by the addition of nanocellulose. A small amount of nanocrystals added by suspension casting markedly improved the stiffness of a commercial shape memory PU (polyurethane) without deterioration in the shape memory properties.

The important industrial problem of slow crystallization of some different thermoplastic matrix as poly(lactic acid) (PLA) was recently investigated by different authors and, in some cases, addressed by the use of cellulose nanocrystals as biobased nucleating agents (Colom et al., 2003; Pei et al., 2010; Wu et al., 2007). The nonisothermal cold crystallization behaviour of poly(lactic acid) (PLA) based high performance nanocomposites reinforced with nanocrystalline cellulose and silver nanoparticles was recently investigated (Fortunati, Armentano, Zhou, Puglia, et al., 2012). Pristine (NCC) and surfactant modified cellulose nanocrystals (s-NCC) and silver nanoparticles were used in the production of binary and ternary systems by solvent casting process. The presence of surfactant on the nanocrystal surface favoured the dispersion of NCC in the PLA matrix, while the nonisothermal crystallization studies, underlined the effect of cellulose nanocrystal content and modification on the crystallization process.

5.3. Barrier properties of NCC nanocomposites

The topic of barrier properties by nanosystems is of high interest as related to many applications, including, for instance, toxic metal separation from wastes (Lehn, 1995; Spreti et al., 2006) and biomethane upgrading (Cotana & Giraldi, 2010; Uchytil et al., 2011). A special field is packaging; in this sector, the increasing demand for safe and minimally processed materials makes attractive fully biobased nanocomposites (Davis & Song, 2006). In fact, packaging is the largest single market for plastic materials consumption and it is also one of the main sources of problems for waste disposal. In particular, food packaging materials require both mechanical strength and barrier for such molecules as gases (mainly oxygen), moisture migration, flavour and aroma control. Barrier property investigations of NCC-improved materials have mainly focused on water vapour transmission and oxygen permeability.

For instance, NCC was incorporated by Saxena and Raguskas (2009) into xylan/sorbitol films to prepare biodegradable barrier membranes. Addition of an amount of 10% NCC exhibited a 74% reduction in water transmission properties, as shown in Table 7. These films exhibited also a significantly reduced oxygen permeability with respect to films prepared solely from xylan and sorbitol, and with respect to the often used barrier plastic ethylene vinyl alcohol (Saxena et al., 2010). The authors believed that the

Table 7
Oxygen transmission rates for xylan/NCC films.[a]

Samples	Specific oxygen transmission rate, cm^3/m^2 day
Control (xylan)	354.950
Xylan + 5% NCC	1.442
Xylan + 10% NCC	1.364
Xylan + 25% NCC	1.038
Xylan + 50% NCC	0.139
Ethylene vinyl alcohol	3–5

[a] Data from Ref. Saxena and Raguskas (2009).

high degree of crystallinity of NCC and its rigid hydrogen-bonded network were responsible of formation of an integrated matrix (as described by the percolation theory) which gives improvement of barrier properties. The possibility to increase the barrier properties of PLA film producing PLA nano-biocomposite systems reinforced with un-modified and surfactant modified cellulose nanocrystals by solvent casting method were recently demonstrated (Fortunati, Peltzer, et al., 2012). Reductions of 34% in water vapour permeability were obtained for films with 1 wt.% of modified crystals and good oxygen barrier properties were obtained for all nano-biocomposites underlining the success of the solvent casting procedure and the reinforcement effect of cellulose. Moreover, the possibility to combine different reinforcement phases in a polymer matrix was recently considered in order to obtain multifunctional systems with increased mechanical and thermal properties providing also an antimicrobial response. Fortunati, Armentano, Zhou, Iannoni, et al. (2012), have recently published a paper showing a "smart" packaging material, based on innovative nanocomposites films prepared by the addition of cellulose nanocrystals, with silver nanoparticles, in a matrix of polylactic acid, PLA. This film could generate an antibacterial effect against *Staphylococcus aereus* and *Escherichia coli* other than improvement of mechanical properties. The antibacterial activity of the new multifunctional PLA nanocomposite is more evident on films containing Ag, and this confirms previous report showing that silver ions interfere with respiratory chain causing a decrease in bacterial viability (Rai et al., 2009).

5.4. Optical properties

Liquid crystallinity of NCC coupled to birefrangence of suspensions (firstly observed by Marchessault et al., 1959) leads to interesting optical phenomena, which were the focus of some reviews. Revol, Godbout, and Gray (1997) have taken advantage of these properties: they obtained solid iridescent cellulosic films with unique and tunable optical properties by controlling evaporation of suspending water on a flat surface. The perceived colour of the film depends on the pitch of cholesteric order and the angle of incidence of the light. Proposed applications of the films include their use in security paper (Revol et al., 1997) such as banknotes, ID cards and passports, as well as in optically variable coating or inks whose colour depends on the viewing angle. New methods to achieve control of the film colours are continued to be searched: for instance the use of ultrasounds have recently been investigated (Beck, Bouchard, & Berry, 2010).

5.5. Biomedical applications

Considering its safety and efficacy, NCC has attracted increasing attention in biomedical applications. Toxicity tests conducted so far indicate that NCC is non-toxic to cell (Roman et al., 2010), and does not give serious environmental concerns (Kovacs et al., 2010; Kümmerer et al., 2011). Recently NCC has demonstrated utility for fluorescence bioassay and bioimaging applications (Dong & Roman, 2007; Filpponen et al., 2011; Mahmoud et al., 2010). For instance, NCC has been labelled with the fluorescent moiety fluorescin-5′-isothiocyanate to be used as indicator in nanomedicine (Dong & Roman, 2007). A novel nanocomposite consisting of NCC and gold nanoparticles has been investigated as a matrix for enzyme/protein immobilization (Denisov et al., 2010; Mahmoud et al., 2009). Moreover, NCC has recently been investigated as drug delivery excipient for both hydrophilic ionazable water soluble antibiotics and hydrophobic anticancer drugs (Jackson et al., 2011). This study showed how it was necessary to coat NCC with cationic surfactant cetyltrimethylammonium bromide (CTABr) to bind significant quantities of the hydrophobic anticancer agents, and then these drugs were released in a controlled manner over a period of several days.

As regards biomedical application of nanocellulose, confusion must be avoided between some (few) applications of NCC and the major use of another type of nanocellulose, BNC. In fact many papers and patents have been published on the use of BNC for medical devices such as wound dressing, implants, including cardio-vascular graft (Klemm et al., 2011).

5.6. Templating with NCC

Since the 90s the synthesis of mesoporous materials through template approach has attracted significant attention, in both fundamental and applied fields, and NCC has attractive properties in this context (Peng et al., 2011). Porous titania with anatase structure was prepared using NCC as a template (Shin & Exarhos, 2007) and a NCC-inducing route was proposed for the synthesis of shape-controlled nanoparticles to lead to novel cubic-shaped TiO_2 nanoparticles (Zhou et al., 2007). Recently various types of mesoporous silica films (Shopsowitz et al., 2010), and mesoporous organosilica films (Shopsowitz et al., 2012) with chiral organization were produced by calcinating the NCC/silica composite systems; these films have colours that arise from the chiral nematic pore structure. Colours of films can be varied through control of the reaction conditions. These discoveries can lead to various possible application such as tunable reflective filters, support for asymmetric catalysis (MacLachlan, Shopsowitz, Hamad, & Qi, 2011). Some metal nanoparticles have also been synthesized on NCC surface via a reduction method; for instance Ni nanoparticles (Shin et al., 2007), Ag with antimicrobial properties (Drogat et al., 2011) Au-Ag alloy nanoparticles (Shin et al., 2008). These reducing processes could be recognized as "green" processes. Recently Ag, Au, Cu, Pt nanoparticles were synthesized on NCC with the use of cationic surfactants CTABr, which resulted critical to achieve control over the nanoparticle dimensions (Padalkar et al., 2010; Stanciu, Padalkar, & Moon, 2011); similarly semiconductors nanoparticles of CdS, ZnS, PbS were prepared using NCC templates and CTABr (Padalkar et al., 2011).

6. Challenges in the use of NCC nanocomposites

As already outlined previously, there is a variety of challenges in the production of NCC, especially regarding the cost and the quality of NCC extracted. Other challenges for NCC having the potential to expand its use in new composite materials will be here mentioned.

6.1. Properties prediction

One key point is the limited ability to predict properties. In fact the impact of the nanoscale filler surface on the morphology, dynamic, and properties of the surrounding polymer chains is not easily predicted from classical models (Siquera, Bras, et al., 2010). Research efforts in this context have been recently reviewed by Moon et al. (2011). These authors outlined that there is a need for the development of standardized measurement methods and reporting for NCC structure and properties, and a need for the development of tools for NCC characterization within the polymer matrix (very challenging issue), for instance finely dispersed or aggregated. A recent contribution in this context is provided by Postek et al. (2011), who discussed some instrumentation, metrology and standardization issues associated with the ramping up for production and use of NCC.

All this is necessary to develop models for the design of improved materials. In fact, the approach is the search for relations between variations of properties at various length scales and the final macroscopic properties of composites, in a processing-structure–property perspective. A contribution in this area is, for instance, the recent attempt of Bras et al. (2011), to correlate the stiffness of sheets of NCC and nanoparticle dimensions. Most of the drawbacks and/or challenges in the use of NCC have their central issue in the difficulty to understand/control/predict macroscopic properties.

6.2. *Water sorption*

Tendency of cellulose to absorb moisture is problematic, and this has been cited by many authors as a barrier to many potential applications (Hubbe et al., 2008; Moon et al., 2011). Although nanocrystals have lower susceptibility than cellulose to moisture absorption (Klemm et al., 2011), in some cases it was observed that NCC-reinforced nanocomposite weakened by water absorption or in high humidity environment (Peresin, Habibi, Vesterinen, et al., 2010). In fact, it can cause filler-matrix adhesion to decrease. However, for matrix materials that readily absorb water, such as starch based polymers, addition of NCC can lead to water sorption and water diffusion decrease, as compared to the neat polymer matrix material (Dufresne et al., 2000; Moon et al., 2011). It is clearly necessary to understand and control nanoscale water–cellulose interaction, for modification of the final product properties.

6.3. *Thermal stability*

As already mentioned, thermal stability of cellulose materials is among the major issues that limit NCC applications. The onset of thermal degradation of NCC, which typically occurs at 200–300 °C, (Moon et al., 2011) provides an upper limit to applications and processing especially for thermoplastics because their processing often exceeds 200 °C. In fact, the investigation of thermal behaviour of nanocomposites is mostly carried out in the literature to evaluate the operational ranges of work of NCC enhanced polymers referring to conventional ones. This issue has already been treated in previous reviews (Hubbe et al., 2008; Moon et al., 2011; Siquera, Bras, et al., 2010). Here we would like to mention investigations aimed at understanding/improving thermal degradation behaviour of NCC as related to its structure. In fact the presence of acid sulphate groups was found to decrease the thermal stability, and usually the higher acid sulphate group content in NCC leads to a lower temperature of thermal degradation (Roman & Winter, 2004). Methods adopted to improve thermal stability of NCC involve the diminishing of acid sulphate groups content by desulphation and neutralization by alkaline solutions: this last one showed efficiency (Wang et al., 2007). Novel spherical nanocrystals prepared by hydrolysis of MCC with mixed acids (H_2SO_4 and HCl) demonstrated lower sulphate content and also better thermal stability (Wang et al., 2007).

6.4. *Preparation of nanocomposites*

Processing techniques have an important impact on the resulting composite performances. Other than the cost, main problems include:

- dispersion of NCC in non polar medium, in order to use NCC for composites also with hydrophobic matrices
- scale-up
- uniformity of the dispersion of nanoparticles within the polymeric matrix and simultaneous development of satisfactory adhesion between the two phases.
- problem of damage to the NCC during the composite processing.

Due to the polar surface of NCC and to the difficulty to disperse it in non polar medium, the majority of reported nanocomposites have been prepared by mixing water-compatible materials (Anglès & Dufresne, 2000, 2001; Lu et al., 2005; Oksman et al., 2006; Roohani et al., 2008). Several reviews focus on the topic of NCC-reinforced nanocomposite preparation (Dufresne, 2008, 2010; Duran et al., 2012; Eichhorn et al., 2010; Habibi et al., 2010; Hubbe et al., 2008; Klemm et al., 2005, 2011; Oksman & Sain, 2006; Ramires & Dufresne, 2011; Siquera, Bras, et al., 2010). Herein we would like to focus attention on methods investigated to overcome some of the mentioned problems. Some examples are briefly outlined below.

Strategies to enlarge the range of polymer matrices consist in using emulsions of non polar polymer and in modification of NCC surface. Emulsions were used by Favier, Canova, et al. (1995), in his pioneering work, and subsequently by several others with, foe instance, poly(hydroxyoctanoate), PHO (Dubief et al., 1999), or poly(vinyl chloride), PVC (Chazeau, Cavaille, Canova, Dendievel, & Boutherin, 1999; Chazeau, Cavaille, & Terech, 1999; Chazeau et al., 2000). Surface modification of NCC improves NCC dispersability in a wide range of organic solvents, and detailed reviews do exist about surface modifications (Peng et al., 2011; Dufresne, 2010; Habibi et al., 2010; Holt et al., 2010). Two strategies are possible: use of suspensions of surfactant-coated NCC (Bonini et al., 2002; Hubbe et al., 2008) and covalent chemical modification of the surface (for instance oxidation, cationization, esterification) (Habibi et al., 2010; Hubbe et al., 2008). Among chemical modifications, grafting of long alkyl chain seems useful: it can lead to preserve the mechanical properties of the material (Dufresne, 2010; Habibi et al., 2010). Actually, some authors believe that long chain surface chemical modification can represent a new promising way of processing nanocomposite materials (Dufresne, 2010; Peng et al., 2011), but the problem associated with it is the rather high cost (Hubbe et al., 2008). Electrospinning has also emerged as an alternative processing method (Habibi et al., 2010; Peng et al., 2011). Electrospun NCC in water-soluble polymers by using water as solvent was reported (Chazeau et al., 2000), but there are also methods to electrospin polymer solutions containing NCC in organic media: surfactant-coating (Rojas et al., 2009) or polymer grafting (Zoppe et al., 2009) were used to disperse NCC. However, as for the casting-evaporation technique, the dispersion of NCC can be challenging (Habibi et al., 2010).

Methods of scaling up from the laboratory scale work to a larger scale production of nanocomposites are necessary. Processing of NCC nanocomposites by extrusion methods is believed to open possibilities in this sense (Dufresne, 2010; Oksman et al., 2006). It was carried out by pumping the suspension of nanocrystals into the polymer melt during the extrusion process. Attempts to promote the dispersion of NCC within the matrix using poly(vinyl alcohol), PVOH, was reported (Bondeson & Oksman, 2007). The main challenge of this technique lies in the poor dispersion and agglomeration of NCC inside the polymeric matrix, which limits mechanical properties of prepared composites. Another drawback of this technique is the possibility of NCC damage, which can result from the high temperature required or from the shear stress employed (Hubbe et al., 2008).

With regard to the main problem of obtaining high uniformity of NCC dispersion within the matrix, the new template approach by Capadona et al. (2008, 2009), allowed to obtain well-dispersed polymer/NCC composites. The procedure consists of several steps (i) a non solvent is added to a dispersion of NCC in the absence of any polymer, (ii) solvent exchange promotes the self assembly of a gel of NCC, (iii) the gelled NCC scaffold is interpenetrated with a polymer by immersion in a polymer solution, before the nanocomposite is (iv) dried and (v) compacted. Another useful method in this context seems the layer by layer assembly (LbL) of anionic NCC with a variety of cationic polyelectrolytes. The feasibility of LbL assembly of NCC was first demonstrated with the polycation poly-(dimethyldiallylammonium chloride), PDDA, by Podsiadlo et al. (2005): he reported the characterization of the nanocomposite formed by NCC and PDDA with LbL and observed high uniformity and dense packing of NCC. In fact the monitoring of the assembly could be easily followed by UV–Vis absorbance after each deposition, and ellipsometry could give indication of the thickness of each individual bilayer. The feasibility of LbL assembly of NCC was therefater demonstrated for poly-(allylamine hydrochloride), PAH, (Jean et al., 2008) also using strong magnetic fields (Cranston & Gray, 2006), and for a biopolymer such as chitosan (de Mesquita et al., 2010). This method is considered (Peng et al., 2011) one of the most promising tools to provide immobilization of NCC inside the polymer matrix as well as to obtain high loading of the material.

6.5. Durability

This is a key issue for applications destined for long-term use. As mentioned by Hubbe et al. (2008) it is hard to guarantee to the end-user, at a practical level, that a specific item purchased today will last as long as a similar item made of standard materials such as wood, plastics, metal.

6.6. Safety concern

Another important drawback relates to the impact of nanoparticles on human health, because there are safety concerns about nanomaterials in general, as their size allows them to penetrate into cells and eventually remain in the system (Hoet et al., 2006). Several researches are working on this subject. The polemic is important and is manly due to some previous health problems (asbestosis) but also because the term nanoparticle is not clearly defined (Siquera, Bras, et al., 2010). Studied conducted so far on NCC seem to indicate absence of toxicity, as previously mentioned.

Moreover, production of innovative “green materials” derived from natural sources is currently one of the main points of interest in the industrial areas of food packaging and in this contest the use of cellulose nanocrystals has been proposed as the load-bearing constituent in developing new and inexpensive bio-materials due to their high aspect ratio, good mechanical properties and fully degradable and renewable character (Sturcova et al., 2005). The European Commission (Commission Regulation. (2011). Commission Regulation (EU) No. 10/2011) regulates the use of plastic materials and articles when come into contact with food. Anyway, further testing is necessary especially regarding evaluation on the environmental fate (Alvarez & Cervantes, 2011), potential NCC uptake and exposure studies, so that a detailed risk assessment can be determined.

7. Concluding remarks

In this review we showed some of the opportunities coming from the use of NCC, an outstanding renewable material that can be extracted from lignocellulosic biomass. Main challenges in the field are related to an efficient NCC separation from the natural resource. Despite the abundant availability of raw materials, NCC is not commercially available because the production is time consuming and the yield is low. Resuming the current situation for the preparation of NCC, major areas of active research include:

- Development of processes to use residual biomass as NCC source;
- Integration of NCC and cellulosic biofuel production;
- Standardization of NCC types, especially in terms of dimensions and surface properties;
- Improvement of separation technologies, through optimization of the acid hydrolysis or through implementation of new processes aimed at saving time and at obtaining higher yields, and at using safer reaction conditions;
- Valorization of waste liquors, with subsequent reduction of costs and simplified waste disposal;
- Development of processes to dry NCC which will maintain nanoscale dimensions: this can mitigate transportation costs;
- Scale-up of the process to provide large quantity of NCC for application development.

With regard to applications of NCC we reported and discussed only selected examples, not exhaustive of the continuously increasing number of applications in various fields reported in the literature. The list of nanocomposites reported in Table 5 is also non exhaustive of the increasing number of systems under investigation.

Moreover, a summary of key challenges for a wide use of NCC in applications includes:

- Properties prediction;
- Problems with water sorption an thermal stability;
- Preparation of nanocomposite. Major problems are related with the use of hydrophobic polymeric matrices, the uniformity of the dispersion of NCC within the polymeric matrix, the cost, and the scaling-up;
- Durability;
- Safety concerns.

Concluding, we may say that these challenges and drawbacks become the strong driving force for discovering more efficient processes and technologies to produce both NCC and nanocomposites, and for inventing new applications.

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