Carbohydrate Polymers 87 (2012) 963–979

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

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

Review

Green composites from sustainable cellulose nanofibrils: A review

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ARTICLE INFO

Article history:
Received 20 July 2011
Received in revised form 23 August 2011
Accepted 24 August 2011
Available online 31 August 2011

Keywords:
Cellulose
Green composites
Cellulose nanocomposites
Cellulose nanofibrils

ABSTRACT

Green composites are materials having ecofriendly attributes that are technically and economically feasible while minimizing the generation of pollution. In this context it refers to the combination of fully degradable fibers mostly cellulosic materials and natural resins to develop green composite materials. In the past decade, overdependence on petroleum products (synthetic polymers, resins, etc.) has consistently increased and on account of this, the researchers are now focusing more on green materials specially cellulosics. Cellulosic fibers in micro and nano scale are attractive to replace man-made fibers as reinforcement to make environmentally friendly green products. In this study, we will discuss the processing, extraction, properties, chronological events and applications of cellulose and cellulosic-based nanocomposite materials. Cellulosic nanocomposites are currently considered one of the most promising areas of scientific and technological development in the field of plant products. The aim of this review is to demonstrate the current state of development in the field of cellulose nanofibril based green composites research and application through examples.

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doi:10.1016/j.carbpol.2011.08.078

1. Introduction

Sustainability, industrial ecology, eco-efficiency, and green chemistry are guiding the development of the next generation of materials, products, and processes. Biodegradable plastics and bio-based polymer products based on annually renewable agricultural and biomass feedstock can form the basis for a portfolio of sustainable, eco-efficient products that can compete and capture markets currently dominated by products based exclusively on petroleum feedstock (La Mantia & Morreale, 2011; Mohanty, Misra, & Drzal, 2002).

In recent years, there is increasing interest in the development of biodegradable and/or plant derived composite materials, which we sometimes refer to as “green” composites (Jiang & Hinrichsen, 1999; Luo & Netravali, 1999a, 1999b; Takagi, 2005; Takagi & Asano, 2008; Takagi & Ichihara, 2004) because of strong global demand for creating a resource circulating society. In the case of the “green” composites, various kinds of natural fibers are being added to biodegradable resins such as poly-lactic acid (PLA) and modified starch to reinforce plant derived, polymeric matrix materials and improve their mechanical properties.

Natural fibers, on the other hand, such as wool and cotton, come from renewable animal or plant sources but they usually lack the high-performance characteristics of many synthetic fibers (Abdul Khalil, Hanida, Kang, & Nik Fuaad, 2007; Abdul Khalil, Kumar, Asri, Nik Fuaad, & Ahmad, 2007). Natural fibers or lignocellulosic materials are classified according to what part of the plant they come from. Five different fiber classifications include: (1) bast or stem fibers, which are the fibrous bundles in the inner bark of the plant stem running the length of the stem; (2) leaf fibers, which run the length of leaves; (3) seed-hair fibers; (4) core, pith or stick fibers, which form the low density, spongy inner part of the stem of certain plants; and (5) all other plant fibers not included above (Abdul Khalil, Ismail, Ahmad, Ariffin, & Hassan, 2001). Examples of bast or stem fibers include jute, flax, hemp, kenaf, ramie, roselle, and urena. Leaf fibers include banana, sisal, henequen, abaca, pineapple, cantala, caroa, mauritius, and phormium. Seed-hair fibers include coir, cotton, kapok, and milk weed floss. Core fibers represent the center or pith fibers of such plants as kenaf and jute and can represent over 85% of the dry weight of these plants. The remaining fibers include roots, leaf segments, flower heads, seed hulls and short stem fiber (Abdul Khalil, Hanida, et al., 2007; Abdul Khalil, Kumar, et al., 2007).

A broad classification (non-wood and wood fibers) of natural fibers is represented schematically in Fig. 1. The new field of bio-based nanomaterials promises to deliver environmentally friendly, high-performance bio-fiber materials that can replace some of the synthetic materials. Cellulose, which is the ubiquitous organic compound, is a structural component of the cell walls of many plants. Its industrial use is mainly for making paper and cardboard but recently it has also attracted significant interest as a source of biofuel production. The researchers with nanotechnological bent of mind are interested in it because highly crystalline cellulose nanofibers, abundantly present in natural plant bodies, have unique properties and sizes different from synthetic nanofibers. These scientists believe that cellulose nanofibers have a high potential to be used as transparent and extremely strong films in many different areas. This could lead to environmentally compatible and high-performance packaging components. “Because of the presence of numerous hydrogen bonds between cellulose microfibrils in plant cell walls, it has been impossible to convert native cellulose fibers into aqueous dispersions of individual cellulose microfibrils

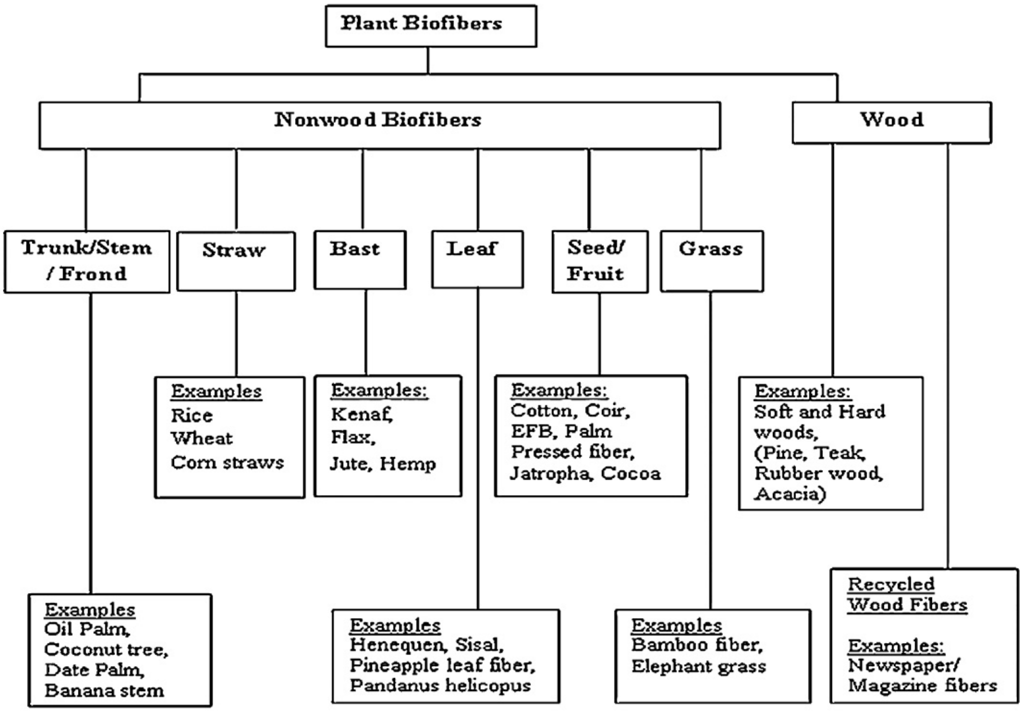

Fig. 1. Schematic representation of reinforcing biofibers classification.

Table 1
Chemical composition of some typical cellulose-containing materials.

Type of biofibre	Composition (%)				
	Source	Cellulose	Hemicellulose	Lignin	Extract
Wood	Hardwood	43–47	25–35	16–24	2–8
	Softwood	40–44	25–29	25–31	1–5
Non-wood	Bagasse	40	30	20	10
	Coir	32–43	10–20	43–49	4
	Corn cobs	45	35	15	5
	Corn stalks	35	25	35	5
	Cotton	95	2	1	0.4
	EFB	50	30	17	3
	Flax (retted)	71	21	2	6
	Flax (unretted)	63	12	3	13
	Hemp	70	22	6	2
	Henequen	78	4–8	13	4
	Istle	73	4–8	17	2
	Jute	71	14	13	2
	Kenaf	36	21	18	2
	Ramie	76	17	1	6
	Sisal	73	14	11	2
	Sunn	80	10	6	3
	Wheat straw	30	50	15	5

Adapted from Mohanty et al. (2002).

without significant decreases in microfibril length and without impairing their structural potential.

From the current research study, cellulose is the most common organic polymer, representing about 1.5×10^{12} tons of the total annual biomass production, and is considered an almost inexhaustible source of raw material for the increasing demand for environmentally friendly and biocompatible products (Klemm, Heublein, Fink, & Bohn, 2005).

The primary occurrence of cellulose is the existing lignocellulosic material in forests, with wood as the most important source. Other cellulose-containing materials include agriculture residues, water plants, grasses, and other plant substances. Besides cellulose, they contain hemicelluloses, lignin, and a comparably small amount of extractives. Commercial cellulose production concentrates on harvested sources such as wood or on naturally highly pure sources such as cotton (Table 1).

The morphology and orientation of cellulose in cell walls of straws have been reported. Yu, Liu, Shen, Jiang, and Huang (2005) reported the morphology and orientation of cellulose in the vessels of vascular bundles of wheat straw. In the vascular bundles, cellulose acts as the framework, and cellulose chains are high in orientation. In the thickening part of the vessels, cellulose exists in the form of cellulose crystalline lamellae but not cellulose microfibrils. The crystalline lamellae are perpendicular to the tangential direction of annular rings and incline clockwise with an angle of about 30 40° to the tangential direction of the spiral line in the spiral vessels. They also proposed a model of the arrangement of cellulose chains in the vascular bundles, as shown in Fig. 2. Cellulose is a linear homopolymer composed of D-glucopyranose units linked by β-1,4-lycosidic bonds ($C_{6n}H_{10n+2}O_{5n+1}$ (n = degree of polymerization of glucose)). As the main component of cell wall, cellulose is predominantly located in the secondary wall. In the primary cell wall, cellulose consists of roughly 6000 glucose units.

The study of cellulosic nanofibres as a reinforcing phase in nanocomposites started two decades ago (Dufresne, 2010; Eichhorn et al., 2010). Since then a huge amount of literature has been devoted to cellulose nanofibres, and it is becoming an increasingly topical subject. Different descriptors of these nanofibres are often referred to in the literature. These include "nanowhiskers" (or just simply "whiskers"), "nanocrystals" or even "monocrystals". These crystallites have also often been referred to in literature as "microfibrils", "microcrystals" or "microcrystallites", despite their nanoscale dimensions. The term "whiskers" is used to designate elongated crystalline rod-like nanoparticles, whereas the designation "nanofibrils" should be used to designate long flexible nanoparticles consisting of alternating crystalline and amorphous strings.

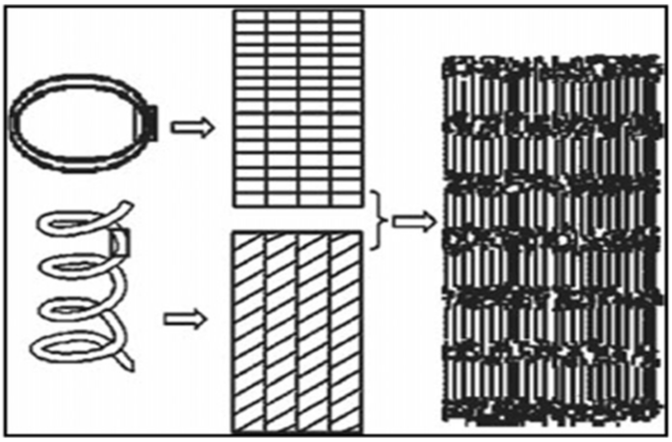

Fig. 2. A schematic model of cellulose molecules in the annular and spiral vessels.

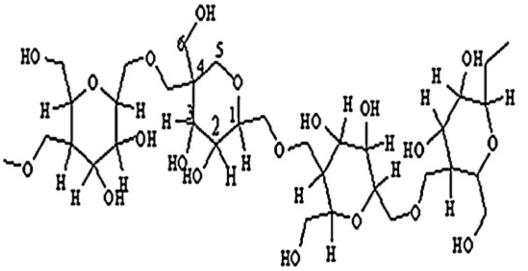

Fig. 3. Cellulosic units joined by glycosidic linkages.

Cellulose fibers exhibit a unique structural hierarchy derived from their biological origin. They are composed of nanofiber assemblies with a diameter that range from 2 to 20 nm, and a length of more than a few micrometers. These sources of nanometer-sized single fibers of cellulose, has been reviewed in Table 2.

Fig. 3 shows the molecular structure of cellulose as a carbohydrate polymer generated from repeating β-D-glucopyranose molecules that are covalently linked through acetal functions

Table 2
Various sources of nanocellulosic fibers.

Various sources (nanocellulosic fibers)	References
Wood	Abe, Iwamoto, and Yano (2007), Chen et al. (2011)
Cotton	de Morais Teixeira et al. (2010)
Potato tuber cells	Dufresne et al. (2000)
Cladodes and spines from *Opuntia ficus*-indica	Malainine et al. (2003)
Prickly pear fruits of *Opuntia ficus*-indica	Habibi, Heux, Mahrouz, and Vignon (2008)
Lemon and maize	Rondeau-Mouro et al. (2003)
Soybean	Wang and Sain (2007a)
Wheat straw and soy hulls	Alemdar and Sain (2008)
Hemp	Wang and Sain (2007b)
Coconut husk	Rosa et al. (2010)
Branch-barks of mulberry	Li et al. (2009)
Pineapple leaf	Cherian et al. (2010)
Banana rachis	Zuluaga et al. (2009)
Sisal	Moran, Alvarez, Cyras, and Vazquez (2008)
Pea hull	Chen, Liu, Chang, Cao, and Anderson (2009)
Sugar beet	Dinand, Chanzy, and Vignon (1999), Dufresne, Cavaille, and Vignon (1997)
Oil palm empty fruit bunch	Fahma, Iwamoto, Hori, Iwata, and Takemura (2010)

between the equatorial OH group of C4 and the C1 carbon atom (β-1,4-glucan), which is, in principle, the manner in which cellulose is biogenetically formed.

In essence, the principle reason to utilise cellulose nanofibres in composite materials is because one can potentially exploit the high stiffness of the cellulose crystal for reinforcement. This can be done by breaking down the hierarchical structure of the plant into individualized nanofibres of high crystallinity, therefore reducing the amount of amorphous material present. Since plant fibers are hierarchically fibrous it is possible to do this, yielding a fibrous form of the material (nanowhiskers, nanofibrils), which due to their aspect ratio (length/diameter) and therefore reinforcing capabilities are potentially suitable for composite materials. A high aspect ratio to the fibers is desirable as this enables a critical length for stress transfer from the matrix to the reinforcing phase.

The aim of this paper is to demonstrate the current state of development in the field of cellulose nanofibrils and cellulose based green composite research and application through examples. It should be also pointed out that cellulose as a natural product belongs to the polymers, which hold an impressive future potential for fundamental knowledge as well as for large-scale production in a wide range of applications.

2. Cellulose

Cellulose is defined as a macromolecule, a nonbranched chain of variable length of 1–4-linked β-d-anhydroglucopyranose units. In contrast, cellulose pulp represents purified cellulosic materials, and still contains other carbohydrates. These definitions are not trivial, since Zugenmaier (2008), who coined the term "cellulose" for sufficiently purified plant tissues, used the term "cellulose" for what is nowadays called pulp. Other researchers continued to use the term "cellulose" in Payen's original definition (Purves, 1946). Payen found 43.6–45% carbon, 6.0–6.5% hydrogen and the remainder was oxygen (theoretical C 44.4%, H 6.2%) for the extraction of the fibrous wrap and wood of all young plant cells but for also seeds, cotton linters as well as a few mosses and lichens. The purified residue represented dextrorotatory, gummy materials. These observations convinced Payen that the purified materials contained one uniform chemical species, which was a carbohydrate, based on glucose residues similar to starch: "In fact, wood contains a substance isomeric with starch, which we call cellulose and a material filling the cells, the real ligneous substance." His idea was that cellulose was a more highly aggregated isomer than starch and when opponents disputed the uniformity of cellulose, he replied that chemical treatment might modify its state of aggregation. In contrast (Fremy, 1859), who investigated enzymatic conversions, insisted that the differences in the properties of cellulose and starch are due to isomeric states of these substances (Zugenmaier, 2008).

Payen's opinion that cellulose was constituted invariably of glucose residues was based on inadequate data and experimental methods for discriminating monosaccharides at that time. Acid hydrolyzates of many materials consisting of celluloses were later found to contain substantial amounts of galactose, arabinose, mannose or xylose as well as glucose. The endosperm of ivory nut, which Payen had thought consisted of especially pure cellulose, yielded almost exclusively mannose (Purves, 1946). Later, the less resistant carbohydrates, other than glucose, were given the generic name of hemicelluloses. Cotton was then considered as a standard because it consisted almost entirely of glucose residues. The term "cellulose" following Payen and further Zugenmaier (2008), who used drastic extraction reagents, was reserved for the portion of the cell wall resembling cotton cellulose in its physical and chemical properties (Zugenmaier, 2008).

Other sources of cellulose include various algae (*Valonia*, *Oocystis apiculata*), tunicates and even bacteria (*Gluconacetobacter xylinus*). Depending on the source of cellulose, its structure can vary considerably.

2.1. Structure of cellulose

Cellulose is composed of polymer chains consisting of unbranched β (1,4) linked D glucopyranosyl units (anhydroglucose unit, AGU). The length of these β (1,4) glucan chains depends on the source of cellulose. For lignocellulosics, a degree of polymerization (DP) of up to 10,000 was found. However, such large chains of insoluble molecules are difficult to measure, due to enzymatic or mechanical degradation during analysis (Klemm et al., 2005; O'Sullivan, 1997). Three hydroxyl groups, placed at the positions C2 and C3 (secondary hydroxyl groups) and C6 (primary hydroxyl groups) can form intra- and intermolecular hydrogen bonds. These hydrogen bonds allow the creation of highly ordered, three-dimensional crystal structures. In vascular plants the glucan chains are synthesized in transmembrane protein complexes, called cellulose synthase complex (CSC) or terminal complex (TC). The TC consists of a globule in the center and six hexagonally arranged particles that form a rosette which has a diameter of around 25 nm. Freeze-fractured samples of plant cell walls proved the existence of the rosette in the plasmatic face of the plasma membrane.

In current opinion, each of the six lobes of this rosette consists of six enzymes, the cellulose synthases. The synthases each polymerize a single glucan chain, using uridine diphosphate glucose (UDP-glucose) as a substrate. The individual chains then assemble and crystallize to a single cellulose microfibril (MF) with a diameter of 3.5 nm (for wood), by implication consisting of 36 glucan chains (Diotallevi & Mulder, 2007). However, the actual number of active catalytic subunits, defining the number of glucan chains per microfibril has never been experimentally demonstrated and is still subject of research (Besseuille & Bulone, 2008). In this context it has to be mentioned that the term "microfibril" is a historical term and defines the smallest entity that can be isolated from the cell wall structure. It does not reflect the real nano size of these fibrils which is in the range of 3–30 nm, depending on the source of the cellulose. The diameter, length and aspect ratio of various types Nanofibers have been tabulated in Table 3.

A second form of terminal complexes was observed in different algae and in the bacterium *G. xylinus*, showing linear arrays of

Table 3
Nanocellulose dimensions.

Cellulose structure	Diameter (nm)	Length (nm)	Aspect ratio (*L*/*d*)
Microfibril	2–10	>10,000	>1000
Microfibrillated cellulose (MFC)	10–40	>1000	100–150
Cellulose whisker	2–20	100–600	10–100
Microcrystalline cellulose (MCC)	>1000	>1000	~1

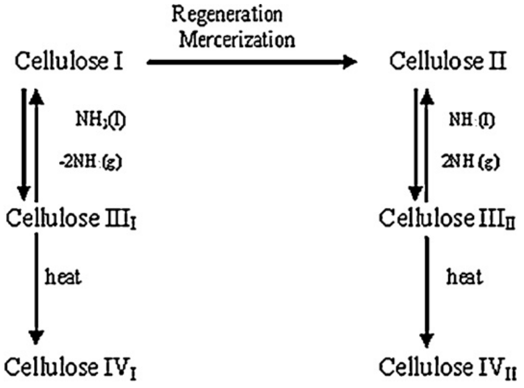

Fig. 4. Interconversion of the polymorphs of cellulose (With permission from Ref. O'Sullivan, 1997, copyright Springer).

synthesizing enzymes of varying number, depending on the organism (Delmer, 1987). The biosynthesis of the glucan chains is closely linked to the assembly and crystallization of the glucan chains into highly ordered (crystalline) domains within a microfibril. Native cellulose (cellulose I) occurs in two different crystalline forms (suballomorphs) designated I_α and I_β, coexisting in variable portions depending on the origin of the cellulose. While cellulose I_α consists of triclinic unit cells, the I_β allomorph (which is predominant in higher plants) exhibits a monoclinic type of unit cells. Cellulose II (another allomorph) has been rarely found in nature (e.g. in the marine algae *Halicystis*) but it can be produced artificially from cellulose I by regeneration or mercerization. The regeneration process involves dissolution of the cellulose in a specific solvent (e.g. N-methylmorpholine-N-oxide), while in the mercerization process the cellulose is only swollen in aqueous sodium hydroxide. In both processes, a final re-crystallization step leads to the final cellulose II, which is thermodynamically more stable than the cellulose I allomorph. Interestingly, there has been strong evidence that cellulose II consists of antiparallel chains, opposed to the parallel arrangement of the glucan chains in cellulose I (Besseuille & Bulone, 2008). However, this is still subject of intense discussion. Apart from these structures, there are further allomorphs of cellulose known, namely cellulose III and cellulose IV (Fig. 4) (Klemm et al., 2005; O'Sullivan, 1997).

As illustrated above, the glucan chains of several cellulose synthases assemble and merge into a single microfibril, giving rise to a highly ordered structure. However, these microfibrils are not perfectly crystalline; they also show para-crystalline (amorphous) domains of low order and defects. The generally accepted model is the fringed-fibrillar model, proposing that the single glucan chains pass through an irregular pattern of amorphous and crystalline domains (Fig. 5) (Klemm et al., 2005). During hydrolysis in acidic environment, the glucan chains are preferably cut in the amorphous domains. The resulting microfibril fragments are called whiskers due to their typical slender, rod-like shape.

The single microfibrils then pack to larger bundles (fibril bundles, fibril agglomerates), hold together by the matrix substances (hemicelluloses, lignin and pectin). As the skeletal component in all plants, cellulose is organized in a cellular hierarchical structure. The cell walls of plants are divided by a middle lamella from each other, followed by the primary cell wall layer. The secondary cell wall layer is divided in S1 and S2, with the latter containing the main quantity of cellulose (Fig. 6) (Klemm et al., 2005).

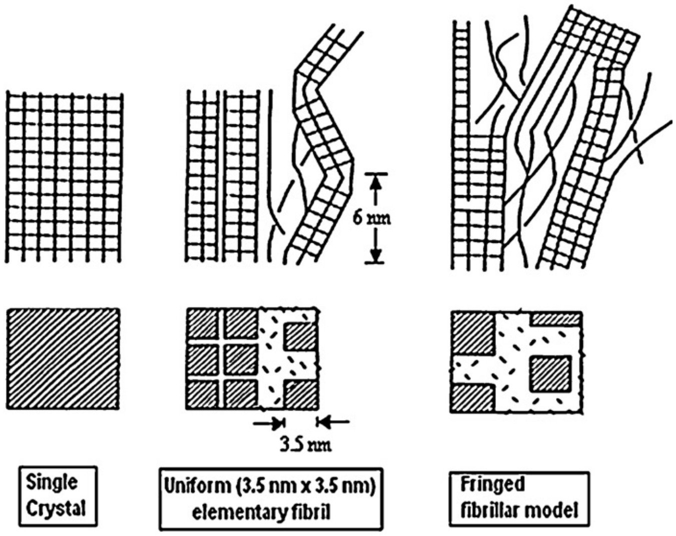

Fig. 5. Various models of the supramolecular structure of cellulose microfibrils (Klemm et al., 2005).

The cellulose microfibrils organized in the cell walls have characteristic orientations (microfibril angles), which differ depending on the cell wall layer and according to the plant type. This orientation of the microfibrils is probably directed by microtubules, which have often been found in a parallel orientation to the microfibrils. It is supposed that during the biosynthesis of the glucan chains the TC is driven backwards by the force generated from the rigid microfibrils and that this movement is guided by restriction of lateral movement within channels of oriented microtubules (Delmer, 1987).

The orientation of the microfibrils has a strong effect on the mechanical properties of the fibers of various plant types. For instance, low microfibril angles like in S2 (with microfibril orientation almost parallel to the fiber axis) give rise to a large modulus of elasticity, while large angles lead to higher elongation at break (Klemm et al., 2005). As a consequence of its fibrillar structure and the large amounts of hydrogen bonds, cellulose has a high tensile strength. It is therefore the structural element of a plant that bears the load in tensile mode (Sjöström, 1993).

2.2. Nanofibrillated cellulose

The first successful isolation of cellulose microfibrils was reported in 1983 (Herrick, Casebier, Hamilton, & Sandberg, 1983; Turbak, Snyder, & Sandberg, 1983). Using a Gaulin laboratory homogenizer, dilute slurries of cut cellulose fibers from softwood pulp were subjected to high shear forces to yield individualized cellulose microfibrils. The resulting gels showed a clear increase in viscosity after several passes through the homogenizer. After carbon dioxide critical point drying of mechanically disintegrated cellulose fibers, scanning electron microscope (SEM) images revealed a network of isolated microfibrils and fibril aggregates (Fig. 7).

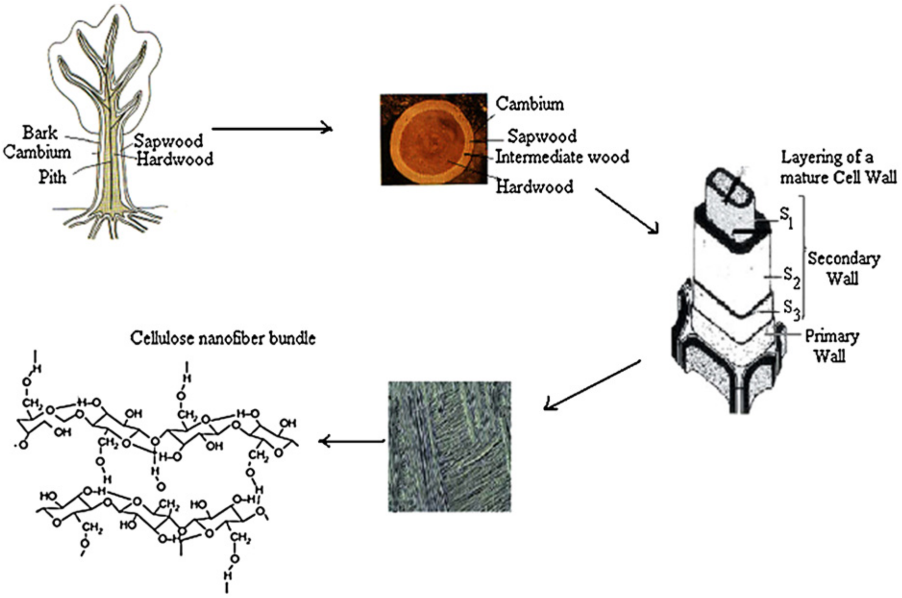

Fig. 6. Microstructure of wood fiber cell wall: *P* primary cell wall layer, *S*1, *S*2, and *S*3 are the inner, middle and outer layers of the secondary wall, respectively.

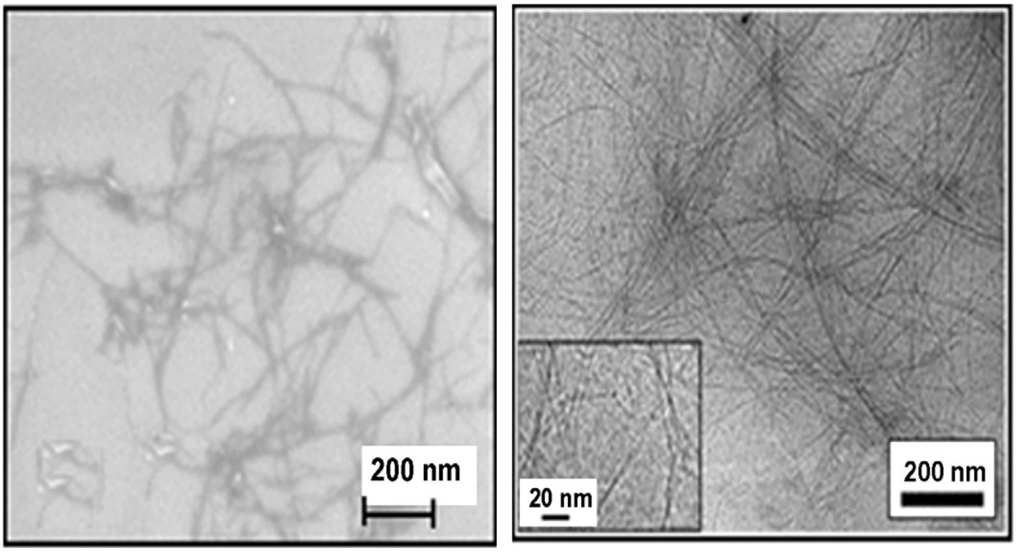

Fig. 7. Scanning electron microscope (SEM) images revealing a network of isolated microfibrils and fibril aggregates.

As mentioned before, the term microfibril is misleading as it does not reflect the real dimensions of the fibril. Furthermore, it is not possible to obtain a perfectly homogeneous sample of single cellulose microfibrils. Therefore, mechanical disintegration of pulps usually aims at the isolation of cellulose fibril aggregates having diameters below 100 nm. In this work, such cellulose portions are termed nanofibrillated cellulose. Some of the first nanocomposites containing NFC were prepared in 1983 (Boldizar, Klason, Kubat, Naslund, & Saha, 1987). Softwood pulp was hydrolyzed in 2.5 M hydrochloric acid (HCl) at 105 °C and afterwards pumped through a slit homogenizer. By varying the hydrolysis time and the number of passes through the homogenizer several NFC gels were prepared.

2.3. Nano cellulose whiskers

One of the first reports on nanocomposites containing cellulose whiskers was presented in 1995 (Favier, Chanzy, & Cavaillé, 1995). Mantles of tunicates (a worm-like sea animal) were cut in small fragments and bleached, followed by a disintegration process using a blender and a Gaulin laboratory homogenizer. The resulting suspension was then hydrolyzed with 55% (w/w) sulphuric acid (H_2SO_4). SEM images revealed rod-like, highly crystalline cellulose whiskers with diameters and lengths in the nano scale (Fig. 8).

The reinforcing effect of cellulose whiskers was compared to the effect of NFC in poly (styrene-co-butyl acrylate) latex. It was shown that both fillers led to an increase in tensile modulus and tensile strength. However, the incorporation of NFC resulted in significantly higher values, due to the entanglements between the fibrils leading to a rigid network of NFC. In addition, DMA analysis showed a higher thermal stability (higher storage modulus) in the rubbery state of the polymer latex when reinforced with NFC, compared to whiskers (Azizi Samir, Alloin, Paillet, & Dufresne, 2004).

Nanocomposites containing cellulose whiskers and poly (lactic acid) (PLA) were prepared by extrusion. The whiskers were prepared by swelling microcrystalline cellulose in N,Ndimethylacetamide/lithium chloride (DMAc/LiCl), followed

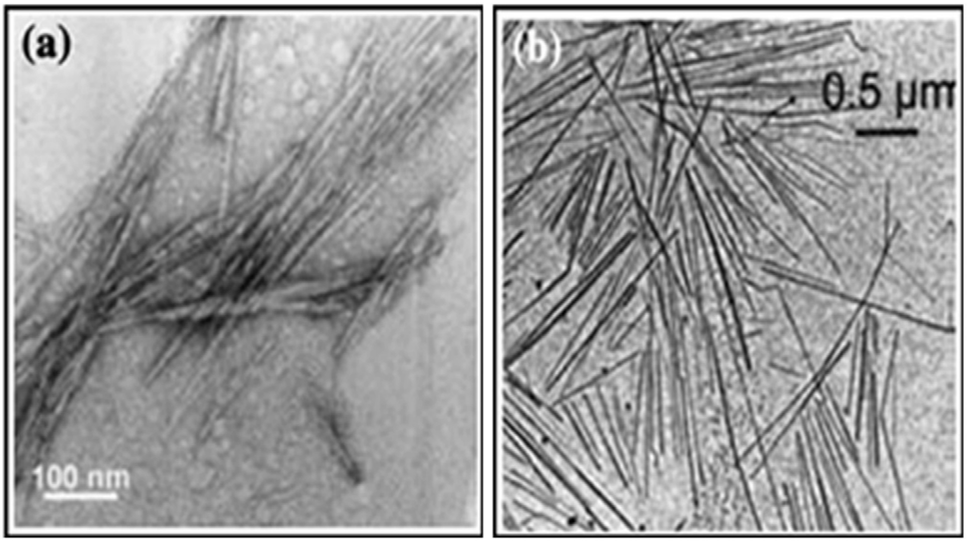

Fig. 8. Transmission electron microscope images of cellulose whiskers, obtained from (a) acid hydrolysis of microcrystalline cellulose and (b) tunicat.

by ultrasonication of the suspension. To avoid the problem of aggregation of the whiskers during drying, the suspension was fed directly into the polymer melt during the extrusion process. The vapor generated by feeding the whisker suspension was removed by several venting systems. However, the suspension enhanced thermal degradation of the whiskers. The addition of poly (ethylene glycol) (PEG) improved the dispersion of the whiskers in PLA. However, the nanocomposites did not show improvements in mechanical properties compared to neat PLA. This was mainly attributed to the combination of the used additives (DMAc/LiCl and PEG) (Oksman, Mathew, Bondeson, & Kvien, 2006).

Another approach to prepare nanocomposites containing cellulose whiskers and PLA comprised the use of a surfactant on the whiskers. The surfactant treated whiskers were freeze-dried and dispersed in chloroform under ultrasonication. Thin films were cast from the mixtures in silicon molds. SEM images showed an increase in the dispersion of the surfactant modified whiskers within the PLA compared to the dispersion of conventional whiskers. In addition, DMA analysis showed an interaction between the PLA matrix and the surfactant modified whiskers due to a shift of the glass temperature ($\tan\theta$ peak) of 22 K (Petersson, Kvien, & Oksman, 2007).

In recent years, the number of works on the preparation of nanocomposites containing cellulose whiskers has clearly increased. A more detailed overview on this topic can be obtained from several reviews (Hubbe, Rojas, Lucia, & Sain, 2008; Siró & Plackett, 2010).

3. Extraction methods of nanofibrils

Several processes have been used to extract highly purified nanofibers from cellulosic materials as shown in Table 4. All these methods lead to different types of nanofibrillar materials, depending on the cellulose raw material and its pretreatment, and more importantly, depending on the disintegration process itself.

3.1. Pulping processes

Pulp consists of cellulose fibers, usually acquired from wood. The liberation of these fibers from the wood matrix can be done in two ways, either mechanically or chemically. Mechanical methods are energy consuming; however, they make use of almost the whole wood material. In chemical pulping, only approximately half of the wood becomes pulp, the other half is dissolved. However, modern chemical pulping mills efficiently recover the chemicals and burn the remaining residues. The combustion heat covers the whole energy consumption of the pulp mill (Alriols, Tejado, Blanco, Mondragon, & Labidi, 2009; Ek, Gellerstedt, & Henriksson, 2009).

3.1.1. Mechanical pulping

Ground wood pulp is produced by pressing round wood logs against a rotating cylinder made of sandstone, scraping the fibers off. Another type of mechanical pulp is refiner pulp, obtained by feeding wood chips into the center of rotating, refining discs in the presence of water spray. The disks are grooved, the closer the wood material gets to the edge of the disk, the finer the pulp (Ek et al., 2009).

Apart from fibers released from the wood matrix, mechanical pulp also contains fines. These are smaller particles, such as broken fibers, giving the mechanical pulp its specific optical characteristics (Ek et al., 2009; Sjöström, 1993).

3.1.2. Homogenization

The fibrillation of pulp fiber to obtain nano-orderunit web-like network structure, called microfibrillated cellulose, is obtained through a mechanical treatment of pulp fibers, consisting of refining and high pressure homogenizing processes. The refining process used is common in the paper industry, and is accomplished via a piece of equipment called a refiner. In a disk refiner, the dilute fiber suspension to be treated is forced through a gap between the rotor and stator disks, which have surfaces fitted with bars and grooves, against which the fibers are subjected to repeated cyclic stresses. This mechanical treatment brings about irreversible changes in the fibers, increasing their bonding potential by modification of their morphology and size. In the homogenization process, dilute slurries of cellulose fibers previously treated by refining are pumped at high pressure and fed through a spring high pressure loaded valve assembly. As this valve opens and closes in rapid succession, the fibers are subjected to a large pressure drop with shearing and impact forces. This combination of forces promotes a high degree of microfibrillation of the cellulose fibers, resulting in microfibrillated cellulose (Herrick, Hamilton, & Sandberg, 1982).

The refining process is carried out prior to homogenization due to the fact that refining produces external fibrillation of fibers by

Table 4
Various processes of extracting highly purified nanofibers.

Extraction processes and methods	References
Mechanical treatments, e.g. cryocrushing	Chakraborty, Sain, and Kortschot (2005), Chakraborty, Sain, and Kortschot (2006)
Grinding	Abe et al. (2007), Abe, Nakatsubo, and Yano (2009) Abe and Yano (2009), Abe and Yano (2010), Nogi, Iwamoto, Nakagaito, and Yano (2009)
High pressure homogenizing	Herrick et al. (1983), Nakagaito and Yano (2004, 2005, 2008a, 2008b), Turbak et al. (1983)
Chemical treatments, e.g. acid hydrolysis	Araki, Wada, Kuga, and Okano (2000), Elazzouzi-Hafraoui et al. (2007), Liu, Liu, Yao, and Wu (2010)
Biological treatments, e.g. enzyme-assisted hydrolysis	Hayashi, Kondo, and Ishihara (2005), Henriksson, Henriksson, Berglund, and Lindstrom (2007), Paakko et al. (2007)
TEMPO-mediated oxidation on the surface of microfibrils and a subsequent mild mechanical treatment	Iwamoto et al. (2010), Saito et al. (2009), Saito, Kimura, Nishiyama, and Isogai (2007), Saito, Nishiyama, Putaux, Vignon, and Isogai (2006)
Synthetic and electrospinning methods	Frenot, Henriksson, and Walkenstrom (2007), Kim, Kim, Kang, Marquez, and Joo (2006), Ma, Kotaki, and Ramakrishna (2005)
Ultrasonic technique	Cheng, Wang, and Han (2010), Cheng, Wang, and Rials (2009), Cheng, Wang, Rials, and Lee (2007), Wang and Cheng (2009), Zhao, Feng, and Gao (2007)

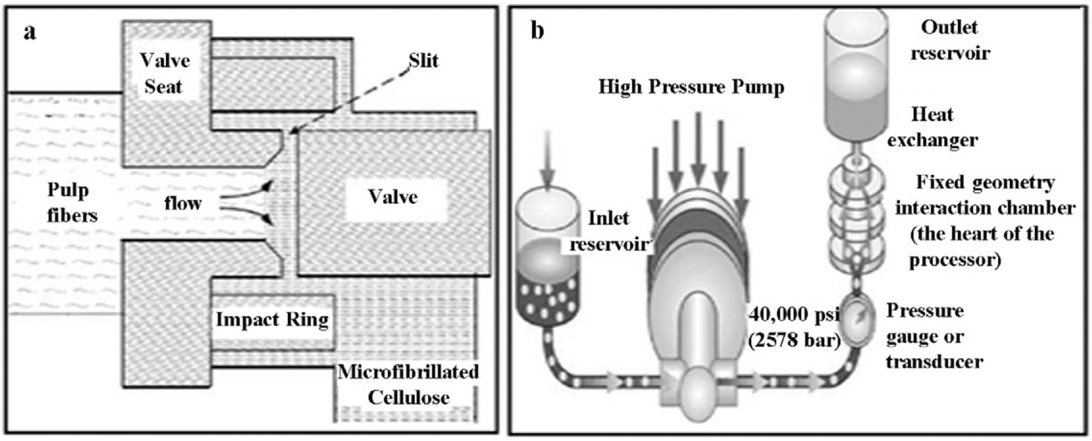

Fig. 9. Schematic representations of (a) the homogenizer and (b) the microfluidizer.

gradually peeling off the external cell wall layers (*P* and *S*1 layers) and exposing the *S*2 layer and also causes internal fibrillation that loosens the fiber wall, preparing the pulp fibers for subsequent homogenization treatment (Wagberg, 2005). Nakagaito and Yano (2004) studied how the degree of fibrillation of pulp fibers affects the mechanical properties of high strength cellulose composites. It was found that fibrillation solely of the surface of the fibers is not effective in improving composite strength, though there is a distinct point in the fibrillation stage at which an abrupt increase in the mechanical properties of composites occurs. In the range between 16 and 30 passes through refiner treatments, pulp fibers underwent a degree of fibrillation that resulted in a stepwise increment of mechanical properties, most strikingly in bending strength. This increase was attributed to the complete fibrillation of the bulk of the fibers. For additional high pressure homogenization-treated pulps, composite strength increased linearly against water retention values, which characterize the cellulose's exposed surface area, and reached maximum value at 14 passes through the homogenizer (Fig. 9).

3.1.3. *Chemical pulping*

The mainly followed strategy to isolate fibers from the wood compartment is to remove the matrix substance lignin. Delignification is done by degrading the lignin molecules, bringing them into solution and removing them by washing. However, there are no chemicals being entirely selective toward lignin. Therefore, also a certain amount of the carbohydrates (cellulose and hemicellulose) is lost in this process. In addition, complete removal of lignin is not possible without severely damaging the carbohydrates. After delignification, some lignin is therefore remaining in the pulp and this amount is determined by the pulp's kappa number. Of all pulp produced worldwide, almost three quarters are chemical pulp, of which the major part is produced by the kraft process (Ek et al., 2009; Sjöström, 1993).

The kraft process (or sulphate process) is the dominant chemical pulping method worldwide. The cooking chemicals used are sodium hydroxide (NaOH) and sodium sulphide (Na_2S), with OH– and HS– as the active anions in the cooking process. The hydrogen sulphide is the main delignifying agent and the hydroxide keeps the lignin fragments in solution. Optionally, only sodium hydroxide can be used as cooking chemical and this process is called soda cooking (Ek et al., 2009; Sjöström, 1993). The sulphite process involves dissolving lignin with sulphurous acid (H_2SO_3) and hydrogen sulphite ions ($HSO_3{}^-$) as active anions in the cooking process. More recently developed pulping methods include the use of organic solvents as ethanol, methanol and peracetic acid (CH_3CO_3H) for delignification (Ek et al., 2009; Sjöström, 1993).

As a final step, the pulp can be bleached, to obtain a whiter product with lower amounts of impurities and improved ageing resistance (yellowing and brittleness resistance). These effects are mainly connected to lignin in chemical pulp. In several stages, different chemicals are used for bleaching, e.g. hydrogen peroxide (H_2O_2), chlorine dioxide (ClO_2), ozone (O_3) or peracetic acid (Ek et al., 2009; Sjöström, 1993).

Comparing the kraft process and the sulfite process, there are numerous differences between the final pulps obtained. Sulfite pulps are more readily bleached and are obtained in higher yields. They are also more readily refined and require less power for refinement. On the other hand, paper from Kraft pulps is generally stronger compared to paper from sulfite pulp, even though the degree of polymerization is lower in Kraft pulp cellulose (Young, 1994).

3.1.4. Acid hydrolysis

Suspensions of nanocrystalline cellulose were prepared. Hydrolysis was carried out with sulphuric acid with constant stirring. Immediately following the acid hydrolysis, the suspension was diluted 10-fold with deionized water to quench the reaction. The suspension centrifuges at 6000 rpm for 10 min to concentrate the cellulose and to remove excess aqueous acid. The resultant precipitate should be rinsed, recentrifuged, and dialyzed against water for 5 days until constant neutral pH (Cranston & Gray, 2006).

3.1.5. Steam explosion

Several methods are used to extract highly purified microfibrils from the plant cell wall. They are generally based on successive chemical and mechanical treatments. The steam explosion treatment is currently still being extensively studied as a promising pretreatment method. Lignocellulosic biomass materials can be fractionated into biopolymer constituents by steam explosion technology.

Treating various biomass resources by steam explosion has been studied by many researchers (Chornet & Overend, 1989; Donaldson, Wong, & Mackie, 1988; Excoffier, Toussaint, & Vignon, 1991; Kokta, 1991; Tanahashi, 1990; Tanahashi et al., 1982). The steam explosion process was first introduced by Mason in 1927 to defibrate wood into fiber for board production (Vignon, Garcia-Jaldon, & Dupeyre, 1995). The treatment of lignocellulosic resources with high pressure steam, for short periods of time, followed by sudden decompression (explosion) represents a simple treatment for biomass that achieves fiberization or “mulching” by a combination of chemical and mechanical action. During the steam explosion process, the raw material is exposed to pressurized steam followed by rapid reduction in pressure resulting in substantial break down of the lignocellulosic structure, hydrolysis of the hemicellulose fraction, depolymerization of the lignin components and defibrillization (Cristobal et al., 2008; Cristobal, Encarnacion, Ignacio, Maria, & Eulogio, 2006; Deep et al., 2011). Marchessault mentions that the steam explosion is an auto hydrolysis process (Marchessault, 1991). Effects of this process on biomass are:

i. Cleavage of some accessible glycosidic links.
ii. Cleavage of β-ether linkages of lignin.
iii. Cleavage of lignin–carbohydrate complex bonds.
iv. Minor chemical modification of lignin and carbohydrates.

Both the aspect ratio and percentage yield of nanocellulose obtained by this technique has been found to be very high as compared to other conventional methods.

3.1.6. High-intensity ultrasonication

This process consists of combination of chemical pretreatment and high-intensity ultrasonication (Fig. 10). In the chemical pretreatment stage, the wood fibers are being purified to prepare the cellulose fibers according to general methods (Abe & Yano, 2009; Abe & Yano, 2010). First, lignin is removed from the samples using acidified sodium chlorite solution at 75 °C for an hour; this process is then repeated five times until the product became white. Next, the samples are treated in 3 wt% potassium hydroxide at 80 °C for 2 h and then in 6 wt% potassium hydroxide at 80 °C for 2 h in order to leach hemicellulose, residual starch, and pectin. After a series of chemical treatments, the samples are filtered and rinsed with distilled water until the residues gets neutralized. To avoid generating strong hydrogen bonding among nanofibers after matrix removal, the samples are kept in a water-swollen state during the whole chemical process.

After chemical pretreatment, the purified cellulose fibers are soaked in distilled water (concentration: ~0.5% in mass). About 120 ml of solution containing chemical-purified cellulose fibers are then placed in a common ultrasonic generator of 20–25 kHz in frequency equipped with a cylindrical titanium alloy probe tip of 1.5 cm in diameter. The subsequent ultrasonication is conducted for 30 min to isolate the nanofibers. To investigate the effect of ultrasonic intensity on the nanofibrillation of the chemical-purified cellulose fibers, the output power of the ultrasonication is conducted at different power viz. 400, 800, 1000, and 1200 W, respectively. The ultrasonic treatment is carried out in an ice/water bath, and the ice is maintained throughout the entire ultrasonication time.

4. Modification of microfibrillated cellulose

Due to the hydrophilic nature of cellulose, MFC cannot be uniformly dispersed in most non-polar polymer media. Consequently, MFC modification is of interest in order to improve compatibility with a wider variety of matrices. Although many methods have been proposed for cellulose surface modification (John & Anandjiwala, 2008; John, Francis, Varughese, & Thomas, 2008), including corona or plasma discharges (Bataille, Ricard, & Sapieha, 1989), surface derivatization (Hafren, Zou, & Cordova, 2006), graft copolymerization (Gruber & Granzow, 1996) or application of surfactant (Bonini et al., 2002; Heux, Chauve, & Bonini, 2000), reports on surface modification of nanocellulosic fibers, in particular MFC, are limited in number. Some approaches aiming to hydrophobize nanocellulosic materials are briefly discussed in the following.

4.1. Acetylation

In research by Kim, Nishiyama, and Kuga (2002), cellulose was partially acetylated to modify its physical properties while preserving the microfibrillar morphology. In this case, the degree of acetyl substitution had a crucial influence on material properties. Ifuku et al. (2007) found that acetylation improved the transparency and reduced the hygroscopicity of cellulose/acrylic resin composite materials. However, the composites had an optimum degree of substitution (DS) and excessive acetylation reduced their properties. Acetylation has also been reported to improve the thermal degradation resistance of cellulosic fibers (Nogi et al., 2006). No studies reporting acetylation of MFC surfaces have been published so far.

4.2. Silylation

Gousse, Chanzy, Cerrada, and Fleury (2004) utilized isopropyl dimethylchlorosilane for surface silylation of cellulose microfibrils resulting from the homogenization of parenchymal cell walls. These authors claimed that microfibrils retained their morphology under mild silylation conditions and could be dispersed in a non-flocculating manner into organic solvents. Andresen, Johansson, Tanem, and Stenius (2006) hydrophobized MFC via partial surface silylation using the same silylation agent and reported that when silylation conditions were too harsh, partial solubilization of MFC and loss of nanostructure could occur. Films prepared from the modified cellulose by solution casting showed a very high water contact angle (117–146^{o}). It is probable that in addition to decreased surface energy, higher surface roughness as a result of modification could contribute to increased hydrophobicity. It has also been reported that hydrophobized MFC could be used for the stabilization of water-in-oil type emulsions (Andresen & Stenius, 2007).

4.3. Application of coupling agents

Lu, Askeland, and Drzal (2008) successfully modified MFC by applying three different coupling agents, 3-aminopropyltriethoxysilane, 3-glycidoxypropyltrimethoxysilane,

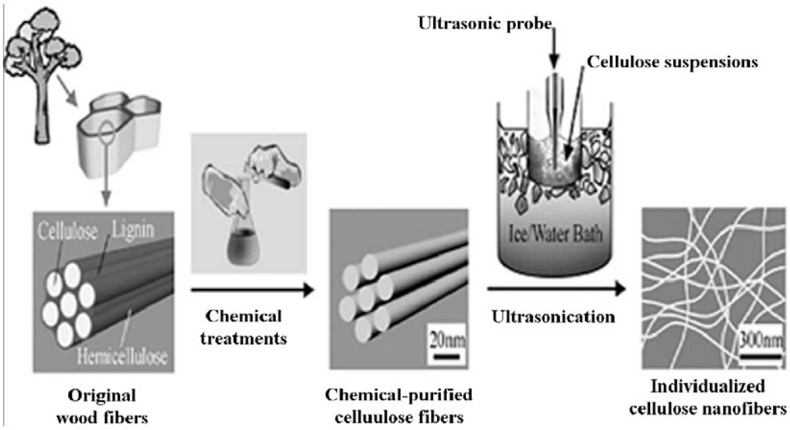

Fig. 10. Procedure for individualizing cellulose nanofibers (Chen et al., 2011).

and a titanate coupling agent (Lica 38), in order to enhance the adhesion between microfibrils and epoxy resin polymer matrix. The surface modification changed the character of MFC from hydrophilic to hydrophobic while the crystalline structure of the cellulose microfibrils remained intact. Among the tested coupling agents, the titanate gave the most hydrophobic surface, possibly due to the lower polarity of the titanate modifier alkyl chain. Unlike silane coupling, titanate coupling is thought to occur via alcoholysis, surface chelation or coordination exchange. When there are hydroxyl groups present on the surface of the substrate, the monoalkoxy- and neoalkoxy-type titanium-derived coupling agents react with the hydroxyl groups to form a monomolecular layer.

4.4. Grafting

Stenstad, Andresen, Tanem, and Stenius (2008) reported three methods for modification of MFC by heterogeneous reactions in both water and organic solvents. Epoxy functionality was introduced onto the MFC surface by oxidation with cerium (IV) followed by grafting with glycidyl methacrylate. Reactive epoxy groups could serve as a starting point for further functionalization with ligands which typically do not react with the surface hydroxyls present in native MFC. A major advantage of this technique is that the reaction is conducted in aqueous media, thereby avoiding the use of organic solvents and laborious solvent exchange procedures. By this method, cellulose nanofibers with a surface layer of moderate hydrophobicity can be prepared. In the same research, a far more hydrophobic MFC surface was obtained by grafting of hexamethylene diisocyanate, followed by reaction with amines. Succinic and maleic acid groups can be introduced directly onto the MFC surface as a monolayer by a reaction between the corresponding anhydrides and the surface hydroxyl groups of the MFC (Stenstad et al., 2008). Siqueira, Bras, and Dufresne (2009) applied noctadecyl isocyanate ($C_{18}H_{37}NCO$) as the grafting agent in order to improve MFC compatibility with polycaprolactone.

The potential use of chemically coated hemp nanofibers as reinforcing agents for biocomposites was explored by Wang and Sain (2007b). The cellulose nanofibers were treated using five different chemicals: ethylene acrylic acid, styrene maleic anhydride, guanidine hydrochloride, and Kelcoloids_HVF and LVF stabilizers (propylene glycol alginate). Bio-nanocomposites were prepared from PLA and PHB as matrices. Nanofibers were only partially dispersed in the polymers and therefore mechanical properties were lower than those predicted by theoretical calculations.

Although the purpose of nanocellulose modification is usually to enhance compatibility with non-polar polymers, thus to improve mechanical properties, chemical modification may also add extra functionality to nanocellulosic materials. For example, positively charged amine-functionalized MFC is reported to be antimicrobially active in biomedical applications (Thomas, Heine, Wollseifen, Cimpeanu, & Möller, 2005). Andresen and Stenius (2007) also added extra functionality to microfibrillated cellulose film by covalently grafting the cellulose with octadecyldimethyl (3-trimethoxysilylpropyl) ammonium chloride (ODDMAC). The surface-modified MFC films showed antibacterial activity against both Gram-positive and Gram-negative bacteria, even at very low concentrations of antimicrobial agent on the surface, killing more than 99% of *Escherichia coli* and *S. aureus* when the atomic concentration of ODDMAC nitrogen on the film surface was 0.14% or higher.

5. Cellulose nanocomposites

Nanocomposites in general are two-phase materials in which one of the phases has at least one dimension in the nanometer range (1–100 nm). The advantages of nanocomposite materials when compared with conventional composites are their superior thermal, mechanical and barrier properties at low reinforcement levels (e.g. B5 wt%), as well as their better recyclability, transparency and low weight (Oksman et al., 2006; Sorrentino & Vittoria, 2007). Biodegradable polymers, in particular, may require improvement in terms of brittleness, low thermal stability and poor barrier properties (Sorrentino & Vittoria, 2007). A number of researchers have therefore explored the concept of fully bio-derived nanocomposites as a route to development of bioplastics or bioresins with better properties (Oksman et al., 2006; Petersson et al., 2007; Plackett, Andersen, Pedersen, & Nielsen, 2003). Biopolymer- based nanocomposites have also been the subject of recent reviews (Akbari & Moghadam, 2007; Pandey et al., 2005; Rhim, 2007; Rhim & Ng, 2007).

5.1. Poly-lactic acid based nanocellulosic composites

Polylactide or poly (lactic acid), otherwise known as PLA, is biodegradable thermoplastic polyester that is manufactured by biotechnological processes from renewable resources (e.g. corn). Although other sources of biomass can be used, corn has the advantage of providing the required high-purity lactic acid. The use of alternative starting materials (e.g. woody biomass) is being pursued in order to reduce process costs; however, the number of steps involved in deriving pure lactic acid from such raw materials means that their use remains much less cost effective at present.

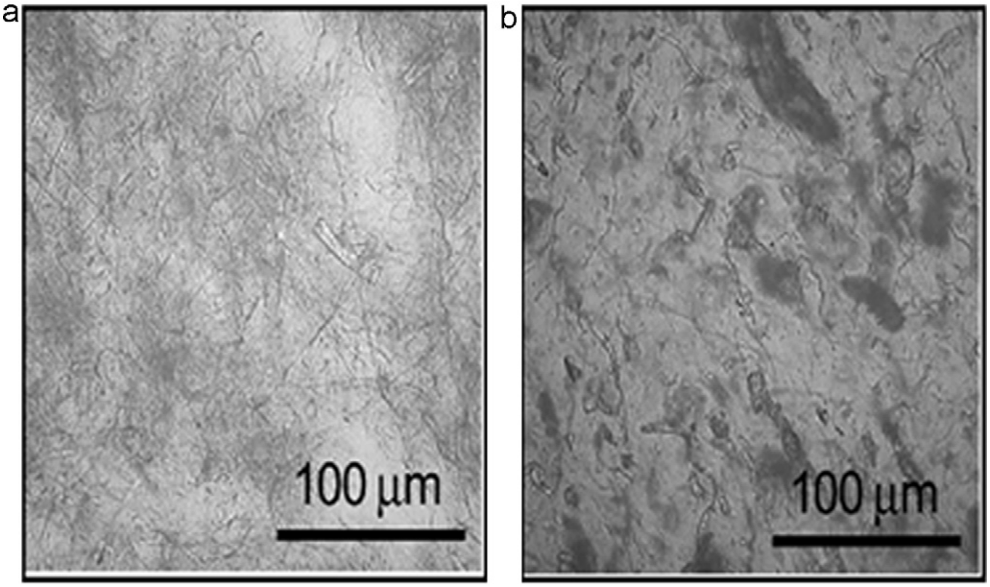

Fig. 11. Microscopy images of composites prepared by (a) the solvent method and (b) direct mixing method.

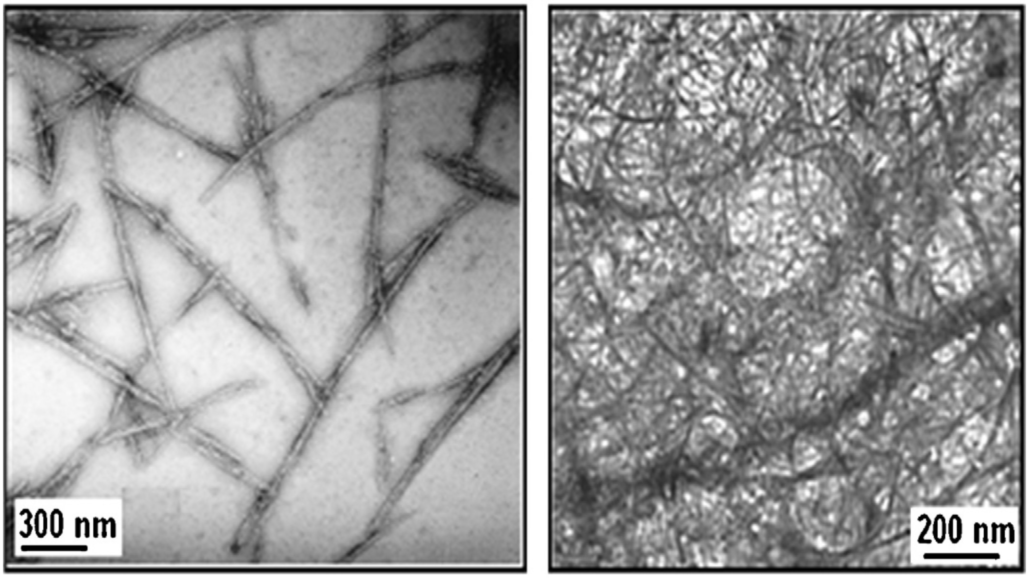

Fig. 12. Transmission electron micrograph of cellulose nano-crystals in poly-hydroxybutyrate.

Iwatake, Nogi, and Yano (2008), has reported the reinforcement of polylactic acid (PLA) using microfibrillated cellulose (MFC, mechanically fibrillated pulp, mostly consisting of nanofibers). The study was carried out to know the potential of reinforcement by a nanofiber network, with the goal of making sustainable 'green-composites'. MFC has been premixed with PLA using organic solvent and the mixture was kneaded to attain uniform dispersion of MFC in PLA. The production procedure to attain uniform dispersion of MFC in a PLA compound was assessed, and then mechanical and thermo-mechanical properties of the sheets after hot-pressing of the compounds were studied. Needle-leaf Bleached Kraft Pulp (NBKP) and refiner-treated NBKP were also used to study the effects of filler morphology. The MFC increased Young's modulus and tensile strength of PLA by 40% and 25%, respectively, without a reduction of yield strain at a fiber content of 10 wt%. On the other hand, NBKP reduced the yield strain by 30% and reduced the strength by 15% at a fiber content of 5 wt%.

The uniformly dispersed MFC reinforcement as shown in Fig. 11 increased the Young's modulus and tensile strength of PLA by 40% and 25%, respectively, without a reduction of yield strain at a fiber content of 10 wt%. Furthermore, the storage modulus of the composites was kept constant above glass transition temperature of matrix polymer. MFC is a promising reinforcement of PLA composites.

5.2. *Poly-hydroxy butyrate based nanocellulosic composites*

The simplest of the family of polyhydroxyalkanoate (PHA) biopolymers is poly-*R*-3-hydroxybutyrate or PHB. This polymer was first discovered in 1925 by Lemoigne and was initially described as a lipid inclusion in the bacterium *Bacillus megaterium* (Gilmore, Fuller, & Lenz, 1990). Later research has demonstrated that PHB is a high molecular weight polymer used in carbon and energy storage by a variety of microorganisms (Luzier, 1992).

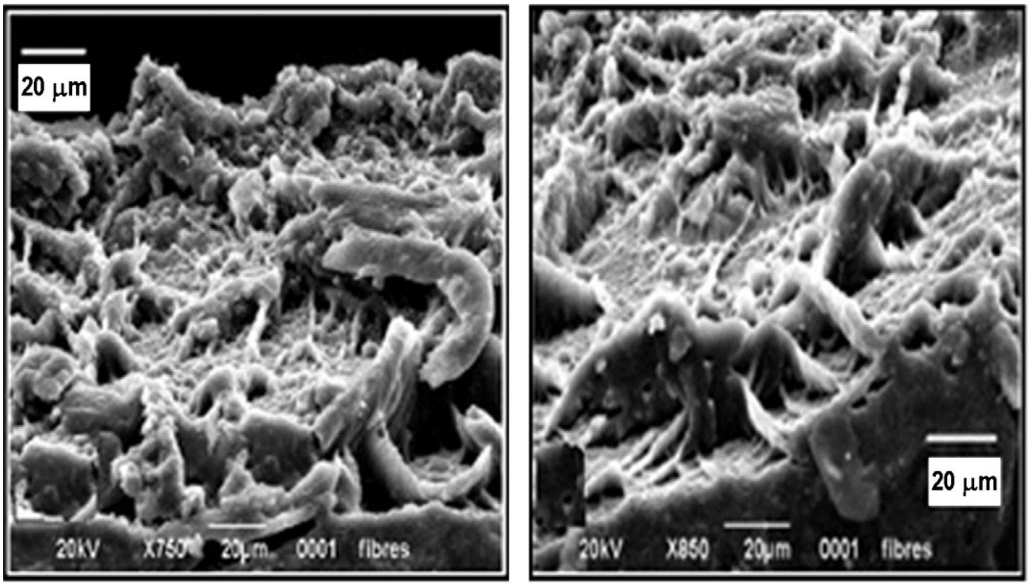

Fig. 13. SEM images of starch cellulose nanofibril nanocomposites with 10% cellulose nanofibrils.

PHAs have received much research attention in recent years with a large number of publications ranging in topic from biosynthesis, microstructure, thermal and mechanical properties through to studies on biodegradation (Hankermeyer & Tjeerdema, 1999). Much of the research has been driven by the availability of PHAs from renewable resources and the similarity of PHA physical properties to those of conventional plastics (Evans & Sikdar, 1990; Plackett & Vázquez, 2004; Williams & Peoples, 1996). Grunert and Winter (2002) prepared nanocrystals by acid hydrolysis of cellulose microfibrils. These were topochemically trimethylsilylated, in an attempt to reduce their hydrophilicity. Composites were made by dispersing either native or silylated crystals in cellulose acetate butyrate matrixes and solution casting of the dispersions. Particles were characterized by transmission electron microscopy as shown in Fig. 12. The unmodified cellulose crystals exhibited better reinforcement characteristics than the trimethylsilated crystals.

One restriction on the use of cellulose crystals as reinforcement is their incompatibility with a typically more hydrophobic thermoplastic matrix. To overcome this problem, cellulose nanocrystals from bacterial cellulose were topochemically trimethylsilylated. Both native and surface trimethylsilylated nanocrystals were employed as the particulate phase in nanocomposites with a cellulose acetate butyrate matrix.

5.3. *Starch based nanocellulosic composites*

Starch from a variety of crops such as corn, wheat, rice and a potato is a source of biodegradable plastics which are readily available at low cost when compared with most synthetic plastics (Ma, Chang, & Yu, 2008). Starch is comprised of amylose, a linear polymer with molecular weight between 103 and 106 and amylopectin, a branched polymer with a-(1–6)-linked branch points (Dufresne & Vignon, 1998). In the glassy state starch tends to be brittle and is very sensitive to moisture. In order to extrude or mold an object from starch, it is often converted into a thermoplastic starch (TPS) (Dufresne, Dupeyre, & Vignon, 2000). TPS is obtained after disruption and plasticization of native starch by applying thermomechanical energy in a continuous extrusion process (Averous, 2004; Thomas, Pothan, & Cherian, 2009).

Water and glycols are commonly used plasticizers, although urea (Huang, Yu, & Ma, 2004; Ma, Chang, & Yu, 2008; Ma, Chang, Yu, & Wang, 2008) and formamide (Ma & Yu, 2004a, 2004b; Wang, Yu, Chang, & Ma, 2008) have also been explored. Both native starch and TPS can suffer from poor mechanical properties and high water uptake compared to conventional polymers, moreover these properties may change after processing (Averous, 2004; Ma, Chang, & Yu, 2008). Two main approaches have been applied to overcome these problems- blending or chemical modification. Starch can be blended with biodegradable polymers such as PHB (Lai, Don, & Huang, 2006; Thire, Ribeiro, & Andrade, 2006), PLA (Hao, Geng, Xu, Lu, & Yu, 2008; Jang, Shin, Lee, & Narayan, 2007; Ning, Jiugao, & Xiaofei, 2008), PCL (Kim, Kim, & Kim, 2007; Rosa, Volponi, & Guedes, 2006; Sarazin, Li, Orts, & Favis, 2008; Wang, Rodriguez-Perez, Reis, & Mano, 2005) and chitosan (Durango et al., 2006; Nakamatsu, Torres, Troncoso, Yuan, & Boccaccini, 2006; Xu, Kim, Hanna, & Nag, 2005). Fabrication of composites based on organic or inorganic reinforcement is another possible solution to improve the performance of starch films. Application of fillers such as clays (Cyras, Manfredi, Ton-That, & Vázquez, 2008; Lee, Heitmann, & Pawlak, 2007; Lee, Xu, & Hanna, 2007; Yoon & Deng, 2006), natural fibers (Alvarez, Terenzi, Kenny, & Vázquez, 2004; Duanmu, Gamstedt, & Rosling, 2007; Ma, Yu, & Kennedy, 2005; Romhany, Karger-Kocsis, & Czigany, 2003) cellulose whiskers (Cao, Chen, Chang, Muir, & Falk, 2008; Mathew, Thielemans, & Dufresne, 2008), or microcrystalline cellulose (Kadokawa, Murakami, Takegawa, & Kaneko, 2009; Kumar & Singh, 2008; Ma, Chang, & Yu, 2008) are reported. MFC and BC have also been reported as promising candidates for starch reinforcement (Grande et al., 2008; Mondragón, Arroyo, & Romero-García, 2008; Sreekala, Goda, & Devi, 2008) and some of these applications are discussed here.

Dufresne et al. (2000) and Dufresne and Vignon (1998) aimed to improve the thermomechanical properties and to reduce the water sensitivity of potato starch-based nanocomposites, while preserving the biodegradability of the material through addition of MFC. The cellulose filler and glycerol plasticizer content were varied between 0–50 wt% and 0–30 wt%, respectively. MFC significantly reinforced the starch matrix, regardless of the plasticizer content, and the increase in tensile modulus as a function of filler content was almost linear. The tensile modulus was found to be 7 GPa at 50 wt% cellulose content compared to 2 GPa for unreinforced samples (0% MFC). However, it was noted that when the samples were conditioned at high relative humidity (75% RH), the reinforcing effect of the cellulose filler was strongly diminished. Since starch

Table 5
Chronological order of events in the exploration of cellulose and its related applications.

Year	Progress	References
1832	Synthesis of 'Cellulose nitrate'	Braconnot, H. (1833). Ann, 1, 242, 245
1839	Payen isolates cellulose as the principal constituent of wood	Zugenmaier (2008)
1845	Invention of Cellulose esters	Schonbein, C. F. (1847). Philos. Mag., 31, 7
1983	Isolated microfibrillated cellulose by mechanical homogenization from hardwood	Herrick et al. (1983)
1998	Developed solidified liquid crystals for optical applications like in security paper	Revol, J. F., Godbout, L., & Gray, D. (1998). PPR 1331 report
2004	Prepared cellulose whiskers reinforced nanocomposites from an organic medium suspension	Azizi Samir et al. (2004)
2004	Studied cellulose microfibril-based nanocomposites for semistructural applications	Nakagaito and Yano (2004)
2004	Reinforcing agents for low-thickness polymer electrolytes for lithium batteries application	My Ahmed Said Azizi Samir, Fannie Alloin, Wladimir Gorecki, Jean-Yves Sanchez, & Alain Dufresne. (2004). J. Phys. Chem. B 108, 10845–10852
2005	Optically transparent cellulose nanocomposites	Yano, H., Sugiyama, J., Nakagaito, A. N., Nogi, M., Matsuura, T., Hikita, M., & Handa, K. (2005). Adv Mater 17:153
2006	Sisal cellulose whiskers reinforced polyvinyl acetate nanocomposites	Nancy Lis Garcia de Rodriguez, Wim Thielemans, & Alain Dufresne. (2006). Cellulose 13, 261–270
2007	Biofoams based on amylopectin-rich potato starch and cellulose nanofibres from wood pulp	Svagan, A. J., Samir, M., & Berglund, L. A. (2007). Biomacromolecules 8, 2556
2008	Biocomposites of cellulose reinforced starch: improvement of properties by photo-induced cross linking	Pratheep Kumar, A., & Raj Pal Singh. (2008). Bioresource Technology 99, 8803–8809
2008	Robust aerogels were prepared by freeze drying of cellulose nanofibre water suspensions	Paakko, M., Vapaavuori, J., Silvennoinen, R., Kosonen, H., Ankerfors, M., Lindstrom, T., Berglund, L. A., & Ikkala, O. (2008). Soft Matter 4, 2492
2008	Nanopaper from cellulose nanofibril suspensions	Henriksson, M., Berglund, L. A., Isaksson, P., Lindstrom, T., & Nishino, T. (2008). Biomacromolecules 9, 1579
2008	Reinforcing adhesives using cellulose nanofibres	Gardner, D. J., Oporto, G. S., Mills, Ryan, Samir, My Ahmed Said Aziz. (2008). 22 (5/6), 545–567(23)
2009	Cellulose microfibrils from banana rachis: effect of alkaline treatments on structural and morphological features	Zuluaga et al. (2009)
2010	Cellulose nanowhiskers from coconut husk fibers: effect of preparation conditions on their thermal and morphological behavior	Rosa et al. (2010)
2010	Isolation of nanocellulose from pineapple leaf fibers by steam explosion	Bibin Mathew Cherian, Alcides Lopes Leao, Sivoney Ferreira de Souza, Thomas, S., Pothan, L. A. & Kottaisamy, M. (2010). Carbohydrate Polymers, 81(3), 720–725

is more hydrophilic than cellulose, in moist conditions it absorbs most of the water and is then plasticized. The cellulosic network is surrounded by a soft phase and the interactions between the filler and the matrix are strongly reduced.

Besides improving mechanical properties of starch, addition of MFC to the matrix resulted in a decrease of both water uptake at equilibrium and the water diffusion coefficient. A different approach to achieve starch-nanocellulose composites has been presented by Grande et al. (2008). In their study, starch was added to the culture medium of cellulose-producing bacteria (Acetobacter sp.) in order to introduce the granules into the forming network of cellulose. The application of such a bottom-up technique allowed the preservation of the natural ordered structure of cellulose nanofibers. Fig. 13 shows SEM picture of starch cellulose nanocomposites with 10% cellulose nanofibrils. From the image, it is clear that the nanofibers are well dispersed and covered by the matrix. Fiber bundles can be observed embedded in the polymer matrix.

The BC-starch mats were hot pressed to obtain nanocomposite sheets. Atomic force microscopy and environmental scanning electron microscopy (ESEM) revealed that starch acted as a matrix which filled the voids in the BC network. The gelatinized starch formed a homogenous layer on BC fibers and a typical brittle fracture surface of the composites was observed. Using MFC, a molded product with a bending strength of 250 MPa was obtained by Yano and Nakahara (2004) without the use of binders. When 2 wt% oxidized tapioca starch was added, the yield strain doubled and the bending strength reached 310 MPa.

Recently, nanocomposites from wheat straw nanofibers and thermoplastic starch from modified potato starch was prepared by the solution casting method (Alemdar & Sain, 2008). Thermal and mechanical performance of the composites was compared with the pure thermoplastic starch using thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA) and tensile testing. The tensile strength and modulus were significantly enhanced in the nanocomposite films, which could be explained by the uniform dispersion of nanofibers in the polymer matrix. The modulus of the TPS increased from 111 to 271 MPa with maximum (10 wt%) nanofiber filling. In addition, the glass transition (Tg) of the nanocomposites was shifted to higher temperatures with respect to the pure TPS. Mondragón et al. (2008) applied glyceryl monostearate (GMS) as surfactant in TPS-MFC nanocomposites prepared by solution casting. As expected, cellulose nanofibers derived from husks and corncobs increased the Young‘s modulus and tensile strength of TPS films due to the strong interactions between the starch matrix and the high aspect ratio nanofibers. It was also noticed that mechanical properties could be further improved by the application of GMS surfactant.

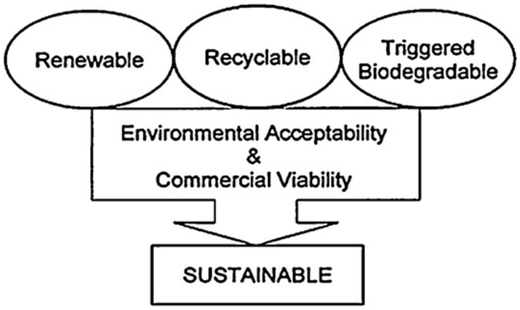

Fig. 14. Concept of “sustainable” bio-based product.

6. Sustainability

More and more, sustainable development is becoming a priority of businesses and governments alike. We frequently hear about the effects of global warming and the depletion of fossil reserves, and it would seem to be only a matter of time before we are forced to look at renewable resources to fulfill our need for materials in a sustainable fashion. The concept of sustainability can be schematically shown in Fig. 14.

Science and technology continue to move toward renewable raw materials and more environmentally friendly and sustainable resources and processes. Cellulose as cellulose nanofibrils, derivatives and polysaccharides as a whole is of growing importance in the development and application of polymer materials. This progression has triggered a distinct renaissance of cellulose research and application all over the world over the past 10 years. In this context, it has been essential to increase the current knowledge of organic and polymer chemistries as well as in the chemistry of low-molecular-weight carbohydrates and other polysaccharides in the basic and application-oriented work in the field of cellulose. Moreover, it has been important to intensify the interdisciplinary interactions between wood industry, chemical engineering, biology, physics, pharmacy, and the medicine.

All signs and symptoms seem to indicate that the impressive rate of development in the field of cellulose will continue or will even accelerate. The establishment of centers of excellence, new pilot, process, and production plants, the expansion of large-scale technical products, a close cooperation of fundamental and applied research, as well as an effective international cooperation of scientists and facilities are distinct evidence of this fact. New insight into the processes of wood pulping and overall wood processing, into the production of cellulose from other plants as well as into the analysis of cellulose products will help to ensures that the quality, variety of products, and ecological acceptance of the starting materials will grow, along with the consistent ecological orientation of industrial cellulose chemistry.

7. Chronological events and applications

Recent advances in the field of engineering, biomaterials and their medical applications indicate the significance and potential of various nanocellulose in the development of novel classes of medical devices and applications in healthcare and veterinary medicine. Despite significant improvement in properties, disposal and recycling problems, combined environmental and societal concerns make continued use of petroleum based nanocomposites unattractive. As a consequence, natural fiber-reinforced thermoset and thermoplastic composites have been intensively studied in the last years since they present a positive environmental impact and interesting characteristics.

The chronological order of events that took place in the exploration of cellulose and its related applications in various fields is shown in Table 5.

8. Conclusions

Green materials are the wave of the future. It has been shown that cellulose nanofibres have an exciting potential as reinforcements in nanocomposites. They also, due to their size and the ability to chemically modify their surface, have great potential for a wide variety of applications; foams, adhesives, hierarchical materials and electronic display materials. A number of methods have been reviewed that enable cellulose nanofibres to be extracted from either plants or animal sources. It has to be remembered that in order to do this, some disruption of structure may occur, and so efforts to reduce damage during extraction are of paramount importance. It is also worth noting that mechanical means of fiber separation do require large amounts of energy, and so efforts to reduce this, either by enzymatic or chemical methods, will become increasingly important. The potential mechanical properties of cellulose nanofibres compete well with other engineering materials, and we have seen that this could be useful in high-end technological applications. We have seen how dispersion is also a critical step in the production of cellulose nanocomposites. Layer-by-layer deposition offers a facile route to overcoming this, with remarkable percolation of whiskers interacting with each other, and with the surrounding matrix, in a way that greatly enhances the mechanical properties of the resultant material. Cellulose nanowhiskers have a high surface area to volume ratio. This means that the surface plays a dominant role in not only the mechanical efficiency of stress transfer in a nanocomposite, but also the ability to modify the surface chemistry.

Although there have been many promising achievements at laboratory or pilot scale, there are several challenges to solve in order to be able to produce cellulose-based nanocomposites at the industrial scale. A major obstacle which needs to be overcome for successful commercialization of MFC is the high energy consumption connected to the mechanical disintegration of the fibers into nanofibers, often involving several passes through the disintegration device. However, by combining the mechanical treatment with certain pre-treatments researchers have shown that it should be possible to decrease energy consumption significantly.

In order to achieve improved mechanical properties in polymer nanocomposites, good filler-matrix interaction is essential. Due to compatibility problems of nanocellulosic materials and hydrophobic matrices, it can be anticipated that nanocomposites based on hydrophilic matrix polymers will be easier to commercialize. The improvement of compatibility with apolar materials, on the other hand, requires chemical modification of nanocelluloses. Although a number of studies have been aimed at chemical modification of nanocellulose (e.g. MFC), there is as yet no industrially practical way to produce cellulose nanocomposites based on hydrophobic biopolymers. Consequently, more research targeting novel, environmentally friendly methods of modification, as well as an understanding of the mechanism of reactions occurring at the cellulose nanofiber polymer matrix interface, is now required.

Acknowledgements

The authors would like to express gratitude for the assistance by Universiti Sains Malaysia (USM) and Ministry of Higher Education (MOHE) for extending their support in the form of “Perdana Exchange Fellowship Program”. Research University (RU) grant (1001/PTEKIND/814133) and Malaysian Palm Oil Board (MPOB) Graduate Students Assistantship Scheme (GSAS) is gratefully acknowledged for their support.

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