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Nanocellulose Patents Trends: A Comprehensive Review on Patents on Cellulose Nanocrystals, Microfibrillated and Bacterial Cellulose

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Abstract: Cellulose nanoparticles (i.e. cellulose elements having at least one dimension in the 1-100nm range) have received increasing attention during the last decade. This is not only evident in academic articles, but it is also manifested by the increasing number of nanocellulose patents that are published every year. In the current review, nanocellulose patents are reviewed using specific software which provides valuable information on the annual number of patents that have been published throughout the years, main patent owners, most prolific inventors, and patents on the field that have received more citations. Patent statistics on rod-like cellulose nanoparticles extracted from plants by acid hydrolysis (nanocrystals), mechanical treatment leading to microfibrillated cellulose (MFC), and microbially produced nanofibrils (bacterial cellulose, BC) are analyzed in detail. The aim of the current review is to provide researchers with patent information which may help them in visualizing the evolution of nanocellulose technology, both as a whole and also divided among the different nanosized particles that are currently the subject of outstanding scientific attention. Then, patents are not only analyzed by their content, but also by global statistics which will reveal the moment at which different cellulose nanoparticles technologies achieved a breakthrough, the relative interest received by different nanocellulose particles throughout the years, the companies that have been most interested in this technology, the most prolific inventors, and the patents that have had more influence in further developments. It is expected that the results showing the explosion that nanocellulose technology is experiencing in current days will still bring more research on the topic and contribute to the expansion of nanocellulosics applications.

Keywords: Patent trends, nanocellulose, cellulose nanocrystals, microfibrillated cellulose, bacterial cellulose.

1. INTRODUCTION

Cellulose is a linear polysaccharide consisting of a chain of β(1→4) linked D-glucose units. Cellulose is the major component of wood and most natural fibers such as cotton, flax, hemp, jute, ramie and sisal. This natural polymer represents about a third of the plant tissues and can regenerate through photosynthesis. Cellulose is also produced by a family of sea animals called tunicates (sea squirts), by several species of algae, and by some species of bacteria, amoebae and fungi. Although as raw material cellulose fibers and many of their derivatives have been known and used for more than a hundred and fifty years, in the last decade cellulose has received a revived interest based in the understanding that macrofibers are built up by smaller and mechanical stronger entities which can be extracted under proper conditions. During biosynthesis of cellulose chains, van der Waals forces and hydrogen bonding between hydroxyl groups and oxygen of adjacent molecules promote parallel stacking of multiple cellulose chains forming elementary fibrils that further aggregate into larger microfibrils [1]. Depending on their origin, the microfibrils diameters may vary, but in general they are within 2-20nm and several microns in length. Microfibrils contain crystalline and amorphous zones. In fact, each microfibril can be considered as a string of cellulose crystals linked along the microfibril axis by disordered amorphous domains, e.g., twists and kinks [2-5].

Extraction of nano-scale cellulosic elements from lignocellulosic fibers is one of the most studied topics in the literature today. This is due to a number of desirable characteristics of nanocellulosics which include renewability, abundance and low cost of the raw material (cellulose), as well as a large surface-to-volume ratio, high strength and stiffness, very low coefficient of thermal expansion, low weight, low density, high aspect ratio and biodegradability. Applications of nanocellulosics include reinforcement of composite materials, tissue engineering scaffolds, moistening masks for cosmetic applications, filtration media, thickening agents, rheology modifiers, adsorbents, paper reinforcement, etc.

Even if a variety of methods have been described and patented, extraction of cellulose nanoparticles (i.e. elements having at least on dimension in the 1-100nm range) from wood and natural fibers has traditionally been performed mainly by two routes: acid hydrolysis and mechanical treatment. Strong acid hydrolysis promotes transversal cleavage of non-crystalline fractions of cellulose microfibrils, leading

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to the so-called *cellulose nanocrystals* or *whiskers* which are rod-like particles with diameters in the rage of 2-20nm and 100-600nm in length [6]. Nanocrystals are characterized by high crystallinity and their aqueous suspensions display a colloidal behavior. Cellulose nanowhiskers may find application as reinforcing components in different polymer matrices [7-8]; in the synthesis of polymers with liquid crystalline behavior for electronic applications [9]; in the immobilization of enzymes for the preparation of active biocatalysts [10], in medical imaging to locate tumors or bacterial cells [11]; in the delivery of drugs [12], etc.

On the other hand, strong mechanical treatment that imposes high shear forces to cellulose fibers, allows the extraction of microfibrils and microfibril aggregates with high aspect ratio which form highly entangled networks. This kind of nanocellulose is called *microfibrillated cellulose* (MFC), and it was first produced in 1977 from a 3% slurry of chopped pulp fibers at the ITT Rayonier Eastern Research Division (ERD) Lab in Whippany, N.J., USA [13]. Authors used a homogenizer called Manton Gaulin-type Milk Homogenizer which produced high shear and impact, by means of high pressure (up to 8000 psi) and temperature close to 80°C [14, 15]. Although widely used the mechanical process developed for the production of MFC has an important drawback which is the high energy input involved (several passes through high pressure homogenizers which get frequently blocked). In the last years, enzymatic and chemical pretreatments have been proposed to reduce the energy input of the process [16-18]. In reference to MFC uses and potential applications, MFC has been mainly used as reinforcing phase in polymer nanocomposites [19, 20], in the production of papers with increased strength [21], in the food and cosmetic industries as thickener, flavor carries, and suspension stabilizer.

Finally, in recent years another route for the production of micro/nanofibers of cellulose has received great attention. This is the microbial synthesis of cellulose in which specific bacteria synthesize cellulose microfibrils as a primary metabolite. Cellulose molecules are synthesized in the interior of the bacterial cell and spun out to form nanofibrils of *ca*. 2-4nm in diameter which then aggregate in the form of ribbon-shaped microfibrils of *ca*. 80 x 4 nm [22]. The overlapping and intertwisted cellulose ribbons form a non-woven mat with very high water content. The Young's modulus of a single filament of bacterial cellulose measured by Raman spectroscopy has been estimated in 114 GPa [23], whereas Young´s modulus of bacterial cellulose pellicles has been estimated in 15-40 GPa [24-26]. Applications of *bacterial cellulose* include i.e. reinforcement of polymer matrices [27], preparation of optically transparent films, and biomedical applications [28].

A number of reviews on academic articles dealing with nanocellulose have been published in the last years [1-2, 4, 6]. However, reviews on nanocellulose patents are less common [29]. In the article of Durán *et al.* (2012), authors illustrated the actual impact of nanocellulose-based materials in different areas based on recent patent databases [29]. In the current review, published patents on cellulose nanocrystals, microfibrillated cellulose and bacterial cellulose are revised and analyzed by use of specific software which allows access to more than 40 databases from different countries. Parameters analyzed include not only chronological patent publishing trends, but also most cited patents, top patent owners (assignees), most prolific inventors, mos cited documents, and the classification of patents among technology areas according to the International Patent Classification (IPC). Moreover, nanocellulose applications that have been patented throughout the years are screened. The analysis by subgroups according to the method of production of nanocellulose, is expected to help in illustrating the differences and similarities in the trends observed for each of them.

2. METHODOLOGY

The search of patents was performed by use of the Thomson Innovation Database, which is a web-based IP intelligence and collaboration platform for searching and analyzing global patents, scientific literature and business information integrated with analytics and workflow tools. For each particular group of nanocellulosic particles, specific keywords (descriptors) were selected for performing the search. Descriptors were chosen based on the synergy of two approaches: the search of specific keywords and concepts used in academic publications, and the selection of additional descriptors from specific patent vocabulary. The presence of the chosen descriptors was checked in the title, abstract and claims of existing patents, considering documents published between years 1920 and 2011. More than forty technology patent and patent application databases were used for patents search, including the Spanish OEPM, the American USPTO, the worldwide WIPO, the European EPO, the patent offices of France, Germany, Great Britain and the Oriental patent offices of Japan, China and South Korea.

Analysis of the recovered documents included the annual number of published patents, the most prolific inventors in the area, the top assignees, the identification of the documents that have received more citations, and the classification of patents according to international patent classification by use of the International Patent Classification (IPC). The IPC provides for a hierarchical system of language independent symbols for the classification of patents into sections, classes, subclasses and groups, according to the different areas of technology to which they pertain. The classification system has more than 70000 entries.

It is important to note that a definite patent can be published in different countries under different national numbers. This is called the *family* of the patent. In the search performed in the current contribution care was taken in order to include just *one* patent per family. Otherwise, certain variables such as for example top assignees might get distorted by owners which can undergo the cost of publishing the same document in different countries. In the case of patents with a family, the selection of the document to be considered in patent trends was the one that was published first. To do so the parameter considered was their "early priority date". In the case of tables with information on patents that have received more citations throughout the years, all family patents have been considered since it may occur that the earliest document is not necessarily the most cited one.

3. NOMENCLATURE

Nomenclature of nanocellulosic particles has not yet been standardized and because of that different terminologies have been and are still used to describe a given set of nanocellulose particles. Actually, TAPPI has recently established a Nanotechnology Division devoted to the standardization of cellulose nanomaterial definitions (TAPPI WI 3021: Standard Terms and their Definition for Cellulose Nanomaterials), whose results have not been published yet. As pointed out in recent nanocellulosics reviews [1, 6, 30] the diversity of terminology used to describe cellulose nanoparticles leads to misunderstanding and ambiguities. The previous is particularly noticeable for the case of cellulose whiskers which have also been called cellulose monocrystals, cellulose microcrystals, cellulose crystallites, cellulose microcrystallites, microcrystalline cellulose, and more recently cellulose nanowhiskers, cellulose nanocrystals, nanocrystalline cellulose, nanorods, rod-like cellulose microcrystals, rod-like cellulose crystals, and nanowires (for original cites please refer to reviews described in references [1, 2, 4, 6, 30-34]).

In reference to microfibrillated cellulose (MFC), the variety of terminology used is somewhat less widespread, probably because since it was first produced authors gave the product the current name of microfibrillated cellulose [14, 15]. However, revision of literature shows that microfibrillar cellulose, microfibrilized cellulose, nanofibrillated cellulose, nanofibrillar cellulose, nanoscale fibrillated cellulose, and cellulosic fibrillar fines, have also been used to describe the web-like structure formed by cellulose microfibrils of high aspect ratio extracted from cell wall [1, 4, 6, 30-34]. It must be pointed out that although microfibrillated and nanofibrillated cellulose (NFC) are sometimes used as synonyms they differ from the fibrillation process, which in the case of NFC produces finer particle diameters [1]. More general terms have also been used by some authors to refer to MFC, including microfibril, microfibril aggregates, nanofiber, nanofibril, and fibril aggregates (see references included in [6] for details).

When referring to bacterial cellulose (BC) revision of literature and patents show that not only bacterial cellulose but also bacteria cellulose, bacterial nanocellulose, bacterium cellulose, bacterial nanocellulose, bacteria-produced cellulose and microbial cellulose have all been used as descriptors of BC [1, 4, 6, 22, 31, 33, 35].

In reference to general terms that have been applied to refer to nano-scaled cellulose elements; cellulose nanoparticles, cellulose nanofibers, cellulose nanofibrils, cellulose microfibrils, cellulose fibrils, nanocellulose, nanoscale cellulose, nanocellulosics and nanosized cellulose fibrils, are just some of the terms that have been frequently used [6, 30-31, 33]. In the case of the word “fibril” it is important to note that the word is somehow ambiguous for nanocellulosic search since the word is also used by papermakers to denote thin cellulosic strands that remain attached on the outer of cellulose fibers, especially in the case of refined pulps [36]. Thus the word nanofiber has come into increasing use to partly avoid ambiguity [4].

4. NANOCELLULOSE PATENTS

As it was previously discussed, diverse methods of extraction/production of nanocellulosics lead to different structures and ensuing nomenclature. In the following sections patent analysis will be sequentially revised covering nanofibers extracted by acid hydrolysis (nanocrystals), mechanical treatment (microfibrillated cellulose), and microbially produced nanofibrils (bacterial cellulose). Patents belonging to other less widespread nanocellulose production methods such as electrospinning or steam explosion, will not be specifically covered by this review.

4.1. Cellulose Nanocrystals

As described in the Introduction section, cellulose microfibrils contain crystalline cellulosic domains as well as less ordered amorphous domains located at the surface and along their main axis. Upon contact with strong acid solutions (i.e. H_2SO_4 [37, 38], HCl [17, 39], HBr [40]) amorphous domains are preferentially cleaved whereas crystalline regions that have a higher resistance to acid attack (cellulose nanocrystals) remain essentially intact. De Souza Lima and Borsali (2004) explained that hydronium ions can penetrate the cellulosic material in the amorphous domains promoting the hydrolytic cleavage of the glycosidic bonds releasing individual crystallites [41].

As previously introduced in the Nomenclature section, cellulose whiskers have received a wide variety of names throughout the years, including monocrystals, microcrystals, crystallites, microcrystallites, nanowhiskers, nanocrystals, nanocrystalline cellulose, nanorods, rod-like cellulose microcrystals, rod-like cellulose crystals, and nanowires (for original cites please refer to reviews referenced in [1, 2, 4, 6, 30-33]). Fig. (**1**) illustrates the evolution of the number of annual patents on cellulose whiskers considering all mentioned descriptors. The total number of patents found by the search performed was 187.

Fig. (**1**) shows the presence of two maxima: the first one in the mid- sixties, and the second one in recent years. The previous result implies either that interest in cellulose nanocrystals received attention in two different moments, or otherwise that two different technological profiles are being considered. Revision of cellulose hydrolysis history will help in finding the answer.

The pioneers in the cellulose hydrolysis process were Ranby and Ribi who in the very early fifties produced stable suspensions of colloidal-sized cellulose crystals by sulfuric acid hydrolysis of wood and cotton cellulose [42-44]. After treating wood pulp with boiling 2.5 N sulfuric acid for 12 hours, authors obtained colloidal suspensions of rod-like particles with lengths between 50 and 60 nm and widths between 5 and 10 nm [45]. Soon after the report of Ranby and Ribi, Mukherjee *et al.* (1951) examined the effect on cotton and ramie of more concentrated acid at lower temperatures, and also obtained colloidal suspensions of rod-like particles [46]. Authors found that by increasing the severity of the acidic treatment the ultimate product of the dissolution consisted of particles between 50 and 250 nm in length with a roughly constant cross-section of 5nm and 15-20nm wide; whereas in the earlier stages of disintegration larger flat aggregates were obtained [46]. The following works of Mukherjee and co-workers demonstrated by transmission electron microscopy that dried suspensions of cellulose fibers boiled in acidic solutions led to needle-shaped particle aggregates, and by X-ray that they had the same crystalline structure as the original fibers [47, 48].

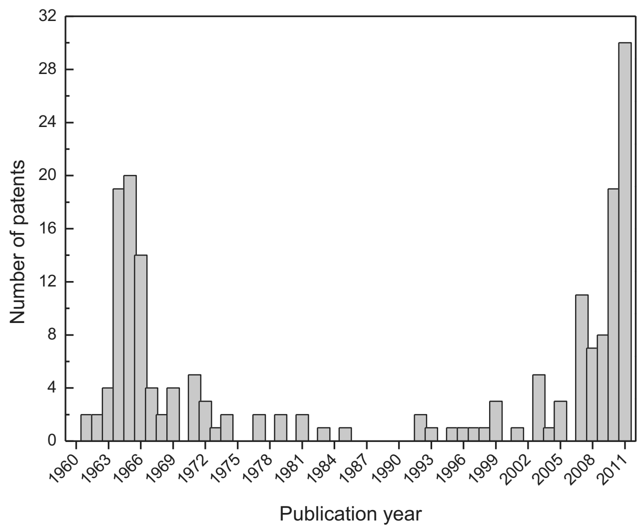

Fig. (1). Evolution of the annual number of patents on cellulose whiskers considering all the descriptors found in academic literature. Descriptors: cellulose whisker/s, cellulose monocrystal/s, cellulose microcrystal/s, cellulose crystallite/s, cellulose microcrystallite/s, cellulose nanowhisker/s, cellulose nanocrystals, nanocrystalline cellulose, cellulose nanorod/s, rod-like cellulose microcrystal/s, rod-like cellulose crystal/s, and cellulose nanowire/s.

In the meantime, Battista and co-workers were also working on the acidic hydrolysis of cellulosic substrates. By HCl hydrolysis of cellulose fibers derived from high-quality wood pulps followed by sonication, in the early fifties Battista *et al.* obtained what they called *cellulose crystallite aggregates* [49, 50]. The discovery of Battista led to an outstanding number of patents which were published in the following years dealing with micrometric cellulose crystallite aggregates obtained by acid hydrolysis. Fig. (**2**) illustrates the annual number of patents dealing with cellulose crystallite aggregates that were published in the sixties which had Battista, FMC Corporation or American Viscose Corporation (companies which owned Battista inventions), in the role of patents inventors or assignees. Descriptors used for the search are included below the figure.

Patents published by Battista and FMC Corporations/American Viscose Corporation covered the use of cellulose crystallite aggregates and their derivatives in a wide range of applications, namely separation, purification and recovery processes; coating of polymer surfaces; adsorbents in separation processes; pharmaceutical compositions; molding composition; haemostatic wound covering; chromatographical adsorption; foamable products; molding resin compositions; cosmetic preparations; pharmaceutical preparations; food compositions; beverages; coating of sheets or filaments; production of viscose; radiopaque media; coloring foods; protection of unstable organic substances; catalyst support; cigarette filter; ceramic glaze; and salad dressing among others. Oxidized, acetylated, etherified, esterified and partially methylenated derivatives were also proposed. Considering the IPC classification, patents published by Battista and FMC/American Viscose Corporation dealt mainly with codes belonging to fractionation of cellulose, e.g. separation of cellulose crystallites (C08B15/08), compositions based on cellulose and modified cellulose (C08L1/02), and the use of cellulose and their derivatives in preparations for medical, dental, or toilet purposes such as bringing pharmaceutical products into particular physical or administering forms, materials for deodorization of air, disinfection or sterilization, bandages, dressings, absorbent pads, surgical articles and soap compositions (A61K47/38).

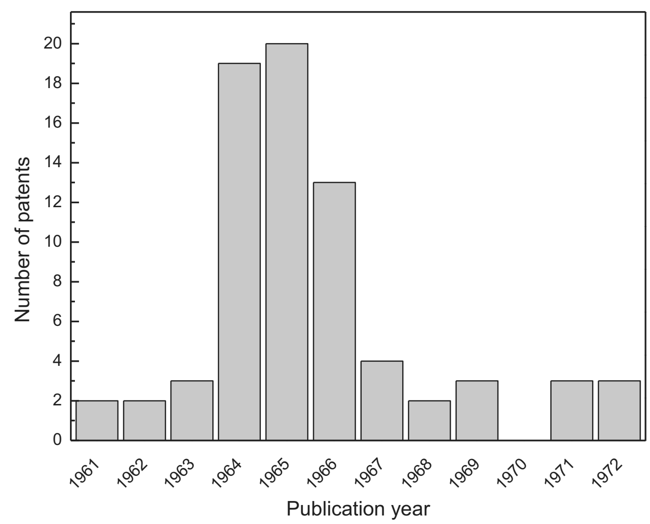

Fig. (2). Evolution of the annual number of patents on cellulose crystallite aggregates produced by Battista and FMC Corporation/American Viscose Corporation during the sixties. Descriptors: (cellulose crystallite aggregate/s or cellulose crystallite/s) and (Battista or FMC Corp or FMC Corporation or American Viscose Corporation or American Viscose Corp).

Comparison of Figs. (**1** and **2**) evidences that published patents found in the first wave of Fig. (**1**) in which *all whiskers descriptors* recalled by academic reviews were used-, are mainly those published by Battista and FMC/American Viscose Corporation on cellulose crystallite aggregates during 1960-1970. However, and as implied by the word aggregate, though the component fibrils may be in the 1-100nm rage of widths the fibrils present in the cellulose crystallite aggregates have not been completely separated from each other, leading to particles in the micrometric range. It is worth noting that individual inspection of patents containing the variety of terms assigned to rod-like cellulose particles, showed that in the first decades after Ranby and Riby discovery, the descriptors “cellulose microcrystallite”, “cellulose crystallite” and “cellulose microcrystal” all lead to patents in which cellulose particles were *explicitly* reported to have sizes in the micrometer range.

Patents related to mechanical disintegration published in the early 60s by Battista and FMC, also refer to cellulose crystallites with sizes close to a micron. In this context, two of the most cited patents published by Battista and co-workers and/or FMC Corporation are "Level-off d.p. cellulose products" (US2978446A, assignee/applicant: American Viscose Corporation, inventors: Battista and Smith, earliest priority year: 1957, publication year: 1961 [51]), and "Crystallite aggregates disintegrated in acid medium" (US3141875A, assignee/applicant: FMC Corporation, inventors: Battista and Smith, earliest priority year: 1961, publication year: 1964 [52]). In the first patent cellulose material is hydrolyzed to remove amorphous cellulosic material and the cellulosic structure remaining is termed level-off DP, in reference to a substantially constant molecular weight which is progressively reached with time during acid hydrolysis. The recovered cellulose consists essentially of large aggregates or bundles of so-called crystalline cellulose [51]. It is later stated that by vigorous mechanical agitation of level-off DP cellulose, aggregates or bundles of crystals are broken to form much smaller particles, some of which are one micron or less in size. Vigorous agitation leads to the formation of what appears to be a colloidal dispersion, and depending upon the concentration of the cellulose crystallites with less than 5 microns, a thixotropic gel when the concentration of level-off cellulose is as low as about 3% by weight might be obtained. For example, a 5% dispersion of one sample which exhibited thixotropic properties was found to contain about 1% of the total cellulose particles whose dimensions were less than one micron. As stated in the patent, dilution of the dispersion to about 1% followed by standing, leads to the separation of two layers, with the upper one containing the smaller particles of one micron or less. Stable dispersions of small disintegrated aggregates obtained by adjusting the pH of the medium between substantially neutral and 11, are claimed to form very adherent films when dispersed and dried on glass. On the other hand, the American patent "Crystallite aggregates disintegrated in acid medium" (US3141875A), is in fact continuation in part of "Level-off d.p. cellulose products" patent just described. In this patent a method for forming small disintegrated aggregates of level-off DP cellulose crystallites which comprises subjecting the aggregates to mechanical disintegration in an aqueous acidic medium is described. Small disintegrated aggregates of cellulose crystallites are reported to be such that at least about 1% of the disintegrated aggregates have a particle size not exceeding one micron [52]. Application of level-off DP cellulose material in storage and shipping purposes readily convertible into stable suspensions of any desired concentration is proposed.

The research of Battista soon led to the now well-known commercial product microcrystalline cellulose (MCC). In 1962, O. A. Battista and P. A. Smith reported the preparation by the American Viscose Company of microcrystalline cellulose from cellulose, under the name "Avicel® PH" (the "PH" designation indicates that the product is suitable for pharmaceutical use) [53]. Avicel® was introduced by FMC in 1964 in selected particle sizes and moisture contents as an ingredient for direct compression tableting [53]. Because of its desirable properties such as stability, physiological inertness, excellent moisture absorption and attractive binding conditions; MCC has found plenty of applications in the pharmaceutical industry as tablet binder, as texturizing agent, rheology agent and fat replacer in food applications, additive in paper and composites applications, etc. Although derived from mineral acid treatment of bleached kraft wood fibers – and as such sometimes used as synonym of cellulose nanocrystals-, the spray-drying process used for obtaining MCC results in re-agglomeration of smaller nano-sized crystalline domains, which become strongly attached together through hydrogen bonding. The resulting product has micrometric dimensions [6, 53, 54], and thus -as in the case of cellulose crystallite aggregates and other disintegrated smaller particles with diameters in the micron range-, will not be specifically covered by the present review. Fig. (**3**) shows the evolution of published patents dealing with MCC. More than ten thousand patents have been published since 1965.

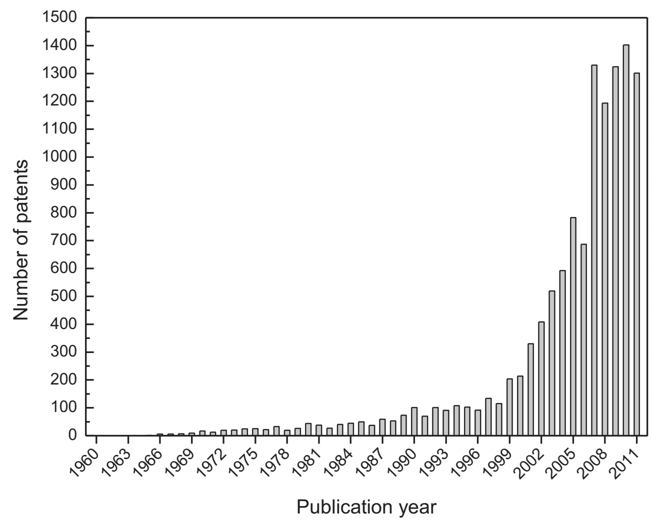

Fig. (3). Evolution of the annual number of patents on microcrystalline cellulose. Descriptors: microcrystalline cellulose.

As it is shown in Fig. (**3**), MCC technology has experienced a continuous rise since FMC Corporation introduced Avicel® in the middle sixties. At that time, the introduction of Avicel PH was a catalyst for the pharmaceutical industry's conversion to direct compression tablet technology. MCC technology is still growing these days. Since 2006, more than thousand patents on MCC are published every year, which all together account for 50% of the total patents published since its invention.

Although discovered in the very early fifties by Ranby and Ribi [42-44], *nanometric* cellulose nanocrystals did not receive much attention until 1992, when their colloidal suspensions unexpectedly showed liquid crystalline properties. Between 1949 and 1992, revision of nanocrystals history shows the importance of the work of Mukherjee and Woods who soon afterwards discovered that more drastic hydrolysis conditions than those applied by Ranby and Ribi yielded more satisfactory disintegration of the rod-like particles [46-48]; as well as the contribution of Marchessault *et al.* who in 1959 were the first to report the birefringence of colloidal dispersions of cellulose crystallites [55]. In 1992 the ability of cellulose nanocrystal suspensions to form stable chiral nematic liquid-crystalline phases with unusual optical properties brought a renaissance of interest to the nanosized rod-like cellulose particles [56]. Following the mentioned discovery, the optical and liquid-crystalline properties of cellulose suspensions were the focus of several studies and reviews [33]. Interest in cellulose nanocrystals is not only evident in scientific literature but also in patent statistics. Some of the authors of the referenced article from 1992 on stable chiral nematic liquid-crystalline phases formed by cellulose whiskers, published in 1995 a patent on liquid crystals of cellulose [57]. The patent dealt with solid films with novel optical properties produced from colloidal suspensions of cellulose crystallites prepared by acid hydrolysis of crystalline cellulose under carefully controlled conditions. The films reflected left circular polarized light over a spectrum from UV to near-IR, and they were claimed to be useful for optical authenticating devices such as paper of value, identity cards or credit cards, since the articles could not be printed or photocopied [57].

In the meantime, Favier and co-workers demonstrated for the first time the reinforcing properties of cellulose nanocrystals [58, 59]. Following this advance, the incorporation of cellulose nanocrystals from different sources into composite materials for mechanical properties enhancement was largely investigated and reviewed [2, 32, 33]. The discovery of Revol and coworkers on liquid crystal behavior, together with the improvements in the mechanical properties of nanocomposites containing cellulose nanocrystals demonstrated by Favier *et al.* defined in the middle nineties the beginning of the second technology breakthrough shown in Fig. (**1**). Whereas the first wave shown in Fig. (**1**) can be mainly attributed to the *micrometric* cellulose crystallite aggregates developed by Battista and FMC Corporation, the developments of Revol *et al.* and Favier *et al.* in the middle nineties motorized a renewed interest in truly *nanometric* cellulose crystallites. Fig. (**4**) illustrates the evolution of annual patent publishing trends on *nanosized* cellulose nanocrystals since 1995. Descriptors used for the search are the same as those used in Fig. (**1**), but manual inspection of retrieved documents was performed to guarantee that they actually referred to nano-sized cellulose whiskers (this was necessary mainly in the nineties were proper "nano" nomenclature had not still been not developed). The total number of patents found by the search performed was 70.

Fig. (**4**) illustrates the increasing interest for cellulose nanowhiskers technology exhibited during the last decade. As it is shown, in the last five years the volume of patents per year exhibits an increasing profile. The increase in nanocrystals patents after 2009 is especially high with a 100% increase in the annual patents in 2010, and almost a 70% rise in 2011. The profile observed suggests that nanocrystals technology will continue increasing at a high rate in the next years.

Before going on with the analysis of patents on nanometric cellulose whiskers published in the last two decades, it is worth analyzing the evolution of ensuing nomenclature. Individual analysis of patents showed that even if the patent published in 1995 by Revol and coworkers referred to nanowhiskers by the descriptor "cellulose crystallites", later on the terminology used was substantially concentrated on *cellulose nanocrystals*, *cellulose whiskers*, *cellulose nanowhiskers* and *nanocrystalline cellulose*. In fact, point by point inspection of patents on nanometric whiskers included in Fig. (**4**) evidenced that the contribution of other terms (i.e. *cellulose crystallites*, *cellulose crystals* and *cellulose microcrystals*) was lower than 10%. Other terms used in scientific articles such as cellulose monocrystals, cellulose nanorods, rod-like cellulose microcrystals, rod-like cellulose crystals, and cellulose nanowires; are not usually found in patent vocabulary.

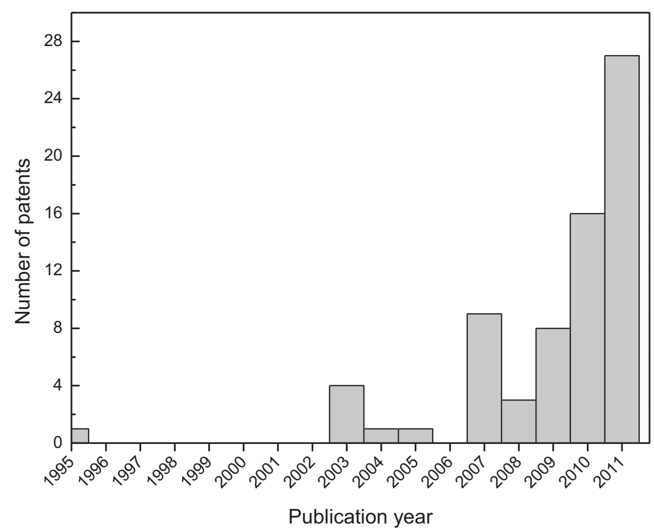

Fig. (4). Evolution of the annual number of patents on cellulose whiskers since 1995 considering all the descriptors found in academic literature, followed by manual inspection to confirm nanometric dimensions of cellulose particles described in early documents. Descriptors: cellulose whisker/s, cellulose monocrystal/s, cellulose microcrystal/s, cellulose crystallite/s, cellulose microcrystallite/s, cellulose nanowhisker/s, cellulose nanocrystals, nanocrystalline cellulose, cellulose nanorod/s, rod-like cellulose microcrystal/s, rod-like cellulose crystal/s, cellulose nanowire/s.

Fig. (**5**) illustrates the evolution of the relative use of cellulose whiskers descriptors throughout the years, including "cellulose nanocrystals", "cellulose whiskers", "cellulose nanowhiskers" and "nanocrystalline cellulose". It is illustrated that in the first years of this century the word of choice to refer to rod-like nanosized cellulose particles produced by acid hydrolysis was "cellulose whiskers". Although "cellulose whiskers" is still used in patent vocabulary, in the last five years the preferred terms in patents have been "cellulose nanocrystals" and "nanocrystalline cellulose", which have both experienced a noticeable rise mainly in the years 2010 and 2011. The boom of nanotechnology and the interest in nanoparticles properties experienced in the last years, has surely played a key role in the definition and further use of more precise nomenclature, by which specifically refers to the *nanometric* dimensions of cellulose particles.

Patents published on nanocrystals cover different applications which will be herein briefly described. One of the main applications of nanocrystals is composite materials. As previously stated, the first report of the use of cellulose nanowhiskers in composite materials was by Favier *et al.* in 1995 [58, 59]. They investigated the percolation of nanowhiskers extracted from sea animals called tunicates. Since then much scientific research has been devoted to the

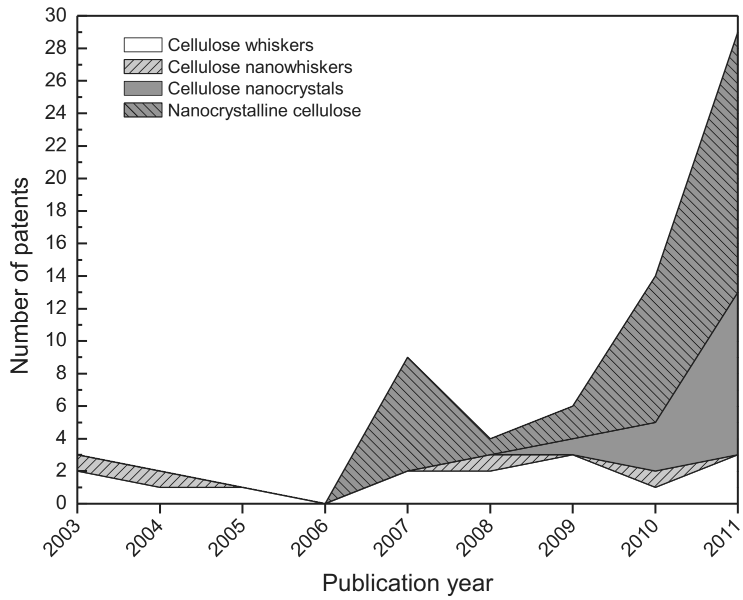

Fig. (5). Evolution of cellulose nanocrystals nomenclature used in patent literature.

preparation of composites involving cellulose nanocrystals. The interest in composite materials which include cellulose nanocrystals is also evidenced in patents. Patents on composite materials which contain cellulose whiskers include for example the manufacture of silk fibroin cellulose fine crystal composite material with high strength [60]; ionic conductor materials useful in lithium batteries or fuel cells made of a polymer matrix, ionic species and cellulose whiskers as reinforcement [61]; nanocomposites based on cellulose whiskers and cellulose plastics useful in packaging film, food packaging, electronics, and biomedical applications [62]; composite building materials comprising cementitious matrix, cellulose fibers and nanocrystalline cellulose in which cellulose nanocrystals promote a 10% increase in the modulus of elasticity [63]; cellulose acylate films with enhanced mechanical properties and optical durability by addition of cellulose nanocrystals [64]; production of nanocrystalline cellulose and polylactic acid nanocomposites useful in packaging [65]; synthesis of hydrophobic nanocomposites of nanocrystalline cellulose and hydrophobic polymerized vinyl monomer for medical use [66]; and optically transmissive and electrically conductive nanocomposite films useful in electrostatic discharge coating and liquid crystal device which comprise cellulose nanoparticles coated with a conductive polymer [67]. Other patented applications which involve cellulose nanocrystals include for instance microscale fluid purification devices useful for hemodialysis, hemofiltration and hemoreaction [68]; preparation of tablets used for treating headache [69] and reducing blood pressure [70]; magnetic nanometer particles-patterned macromolecular membranes used in information field [71]; aircraft anti-icing composition useful for cleaning airplane wings and other aerodynamically sensitive areas in which nanocrystalline cellulose is used as thickener [72]; treatment of neoplasia by administration of nanoparticles that come in close proximity to neoplastic cells [73]; synthesis of iridescent solid nanocrystalline cellulose films containing patterns generated by differential heating of aqueous suspensions of cellulose nanorods useful for optical authenticating devices [74]; cellulose aerogels comprising a plurality of cellulose nanoparticles (at least 50% or 80% by weight are cellulose nanocrystals) useful as a thermal, sound or electrical insulator, catalyst support, electronics component, and particle filter and storage media for substances [75]; preparation of compositions useful for coating wooden elements and improving the surface property of coatings which comprises wood coating element and nanocrystalline cellulose or nanocrystalline cellulose modified with organofunctional silane [76]; synthesis of mesoporous siliceous materials with chiral nematic order obtained by reaction of siliceous precursor in an aqueous suspension of nanocrystalline cellulose [77]; and a method of bonding compressing of two surfaces in which nanocrystalline cellulose suspensions obtained by sulfuric acid hydrolysis are used as adhesive [78]. Methods for the preparation of nanocrystalline cellulose by dissociating zinc chloride solution [79], and by hydrolysis of cellulose in presence of acid in gas phase [80]; for the preparation of dried forms of nanocrystalline cellulose with controllable redispersibility in water [81]; and for the control of the wavelength of iridescence in a solid nanocrystalline cellulose film [82]; have all been described. In terms of international patent classification, most nanocrystal patents pertain to the class of compositions based on polymerizable monomers; artificial filaments or fibers (CO8L), compositions of cellulose, modified cellulos, or cellulose derivatives (CO8L1/00), and manufacture of films or sheets (CO8J5/18).

Table **1** shows the most cited patents on cellulose nanocrystals. It is worth noting that for the preparation of tables enumerating the most cited patents of a topic, patent families have been considered. This was done aiming to consider that the patent of a family that has been published first is not always the one that has received most citations throughout the years. By including the patents families the total number of patents considered raised from 70 to 128.

Table 1. Most Cited Patents on Cellulose Nanocrystals. Descriptors Used are the same as those Used in Figure 4.

Publication Number	Reference Title	Assignee	Inventors	Publication Year	Citations	Ref.
US5629055A	Solidified liquid crystals of cellulose with optically variable properties	Pulp & Paper Res Inst Canada	Revol Jean-François, Godbout Joseph Donat Louis, Gray Derek Geoffrey	1997	148	[83]
WO1995021901A1	Solidified liquid crystals of cellulose with optically variable properties	Pulp & Paper Res Inst Canada	Revol Jean-François, Godbout Joseph Donat Louis, Gray Derek Geoffrey	1995	19	[57]
US20040177451A1	Composite fiber reforming method and uses	Cent Nat Rech Sci, Cnrs Cent Nat Rech Sci, Bernier P, Launois P, Poulin P, Vigolo B	Poulin Philippe, Vigolo Brigitte, Launois Pascale, Bernier Patrick	2004	9	[84]
FR2828500A1	Procede de reformage de fibers composites et applications	Cent Nat Rech Sci, Cnrs Cent Nat Rech Sci, Bernier P, Launois P, Poulin P, Vigolo B	Poulin Philippe, Vigolo Brigitte, Launois Pascale, Bernier Patrick	2003	9	[85]
FR2841255A1	Materiau a conduction ionique renforce, son utilization dans les electrodes et les electrolytes	Alloin F, Azizi S M A S, Cavaille J, Dufresne A, Inst Nat Polytech Grenoble, Inst Nat Polytechnique Grenoble, Paillet M, Sanchez J	Cavaille Jean Yves, Dufresne Alain, Paillet Michel, My Ahmed Said Azizi Samir, Alloin Fannie, Sanchez Jean Yves	2003	8	[61]
US20070173630A1	Macrocyclic polyester oligomers as flow modifier additives for thermoplastics	Cyclics Corp	Bahr Steven R, Doyle, Nathan, Wang Jing, Winckler Steven, Takekoshi Tohru	2007	4	[86]
JP2005526186A	n.a.	Cent Nat Rech Sci, Cnrs Cent Nat Rech Sci, Bernier P, Launois P, Poulin P, Vigolo B	Bernier Patrick, Vigolo Brigitte, Launois Pascale, Poulin Philippe	2005	4	[87]
US20070125489A1	Microfluidic welded devices or components thereof and method for their manufacture	Univ Oregon State	Paul Brian Kevin, Jovanovic Goran	2007	3	[88]
US20070216067A1	Macrocyclic polyester oligomers as carriers and/or flow modifier additives for thermoplastics	Cyclics Corp	Bahr Steven R, Doyle Nathan, Wang Jing, Winckler Steven, Takekoshi Tohru, Wang Yi Feng	2007	2	[89]
WO2007011684A2	Oligomeres de polyester macrocycliques comme supports et/ou additifs de modification de flux pour matieres thermoplastiques	Cyclics Corp	Bahr Steven, Doyle Nathan, Wang Jing, Winckler Steven, Takekoshi Tohru, Wang Yi Feng	2007	2	[90]
US7288317B2	Composite fibre reforming method and uses	Cent Nat Rech Sci, Cnrs Cent Nat Rech Sci, Bernier P, Launois P, Poulin P, Vigolo B	Poulin Philippe, Vigolo Brigitte, Launois Pascale, Bernier Patrick	2007	2	[91]

When patents are written, national patent officers require applicants to describe the state of art of their invention, and thus relevant previous patents and academic articles on the topic need to be cited. Besides, patent examiners also include additional relevant cites during the revision process. The analysis of patent citations allows the identification of patents which have been most useful for later researchers and for the development of new technologies. Even if patents that have received most citations are not always the most relevant ones, -as well as most relevant are not always the most cited ones-; a number of empirical studies demonstrate a strong correlation between those variables [92]. The analysis of citations received and made by a definite patent may illustrate the diffusion of technical knowledge and its different concrete applications throughout the years.

Table **1** evidences the importance of the works of Revol *et al.* (1995) previously described. Their American [83] and WIPO [57] patents on solidified liquid crystals of cellulose with optically variable properties are the most cited ones on the topic of cellulose whiskers with 148 and 19 citations, respectively. The following most cited patents included in Table **1** were published in the first years of this century [61, 84, 85]. Table **1** suggests that it was between the middle nineties and the first years of the following decade that the technical bases of many of the current cellulose nanocrystals technologies were settled up. Newer most cited patents [86-91] have in general not received a significant number of citations yet, which implies that their influence in later technological developments is still moderate. Finally, it is interesting to note that most cited patents are owned by public institutions and not by companies (see discussion on nanocrystal patents assignees later on).

In Fig. (**6**) the main assignees of nanocrystals patents are shown in terms of the total number of patents owned by each of them. The analysis was performed considering all patents included in Fig. (**4**) (irrespectively of their number of citations), and it is aimed at providing a general picture of the main competitors in the area throughout the years.

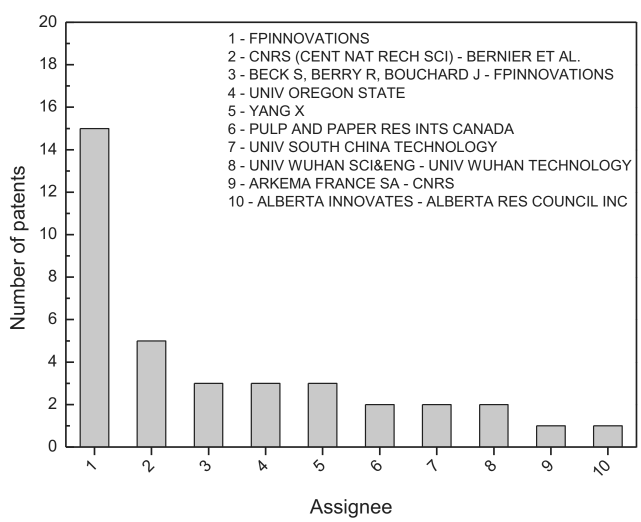

Fig. (6). Main nanocrystals patent owners/applicants. Descriptors used are the same as those used in Fig. (**4**).

Fig. (**6**) evidences the technological leadership of FPInnovations, which is a Canadian non-profit member organization that carries out scientific research and technology transfer for the forest industry. The company develops forestry and transportation processes, wood products and living-with-wood solutions, pulps and papers, nanoproducts and applications, and energy and chemical products derived from forest biomass. The second most important applicant among cellulose nanocrystals patents is the French Centre National de la Recherche Scientifique (CNRS - National Center for Scientific Research), which is a government-funded research organization. Besides, a high number of assignees which own one or two patents on cellulose nanocrystals were found (all data could not be included in Fig. (**6**)). It is worth noting the high percentage of public institutions among nanocrystals patents assignees, which account for nearly 50%. The previous implies that most of the technology has not still been transferred to the private sector.

In reference to main nanocrystals inventors, search results show that the most prolific ones have by far been Richard Berry, Jean Bouchard and Stephanie Beck, who together with FPinnovations have developed nearly 10 patents on cellulose whiskers.

4.2. Microfibrillated Cellulose

Strong mechanical treatment that imposes high shear forces to cellulose fibers, allows the extraction of microfibrils and microfibrils aggregates with high aspect ratio (lateral dimensions in the 10-100 nm range and length generally in the micrometer scale) which form highly entangled networks. Constituting elements typically have a wide size distribution down to nanoscale, and usually low degree of crystallinity since most non-crystalline domains remain essentially intact [16]. This kind of cellulosic material was first obtained in 1977, when researchers at the ITT Rayonier Eastern Research Division Lab in Whippany, USA used a high-pressure Manton Gaulin Milk Homogenizer to fibrillate a 3% slurry of chopped pulp fibers [13]. The product obtained was a translucent firm "gel" that they called "microfibrillated cellulose". The first articles on the topic were presented at the Ninth Cellulose Conference in 1981, and later published in the conference proceedings in 1983 [14, 15]. In the meantime several patents were issued by the Rayonier Division covering the preparation and a number of uses of MFC, i.e. inclusion of microfibrillated cellulose in suspension of finely comminuted materials such as foodstuffs, cosmetics, pharmaceutical products, and industrial products such as paints and boron sludge for improved homogeneity and stability; use of MFC suspensions in medicine, in drilling muds; and for the improvement of the strength of paper and nonwoven products [93-103]. Table **2** details the American patents published by the Rayonier Division. Assignees were not included since in all cases the assignee was the International Telephone and Telegraph Corporation, New York, NY, US.

Patents included in Table **2** are the American versions of Rayonier Division patents. Besides, the works of Turbak and co-workers and those of Herrick on MFC were also patented in several other countries such as Great Britain, Japan, Germany and France. This family of patents contributed to a very high exposition of their discovery. To illustrate the international exposition achieved, Table **3** summarizes the ten most cited patents considering those belonging to *all* countries. As it is shown in Table **3**, US patents played an outstanding role in the exposition of MFC technology and applications. Most cited patents include those related to the production of MFC by passing a liquid suspension of cellulose through a small diameter orifice in which the suspension is subjected to a high pressure drop and a high velocity shearing action followed by a high velocity decelerating impact [94]; manufacture of suspensions with improved homogeneity and stability in which the suspending medium contains swollen MFC, and which are useful in a variety of end use products including foods, cosmetics, pharmaceuticals, paints and drilling muds [103]; and treatment of MFC fibers to aid redispersion after drying by addition of compounds able to prevent hydrogen bond formation between fibrils [100].

Table 2. American patents of the ITT Rayonier Eastern Research Division Lab on microfrillated cellulose. Assignee: International Telephone and Telegraph Corporation, New York, NY, US.

Publication Number	Reference Title	Inventors	Publication Date	Citations	Ref.
US4341807A	Food products containing microfibrillated cellu-lose	Turbak Albin F, Snyder Fred W, Sandberg Karen R.	27/07/1982	34	[93]
US4374702A	Microfibrillated cellulose	Turbak Albin F, Snyder Fred W, Sandberg Karen R.	22/02/1983	78	[94]
US4378381A	Suspensions containing microfibrillated cellulose	Turbak Albin F, Snyder Fred W, Sandberg Karen R.	29/03/1983	30	[95]
US4452722A	Suspensions containing microfibrillated cellulose	Turbak Albin F, Snyder Fred W, Sandberg Karen R.	05/06/1984	12	[96]
US4452721A	Suspensions containing microfibrillated cellulose	Turbak Albin F, Snyder Fred W, Sandberg Karen R.	05/06/1984	8	[97]
US4464287A	Suspensions containing microfibrillated cellulose	Turbak Albin F, Snyder Fred W, Sandberg Karen R.	07/08/1984	4	[98]
US4481077A	Process for preparing microfibrillated cellulose	Herrick Franklin W.	06/11/1984	37	[99]
US4481076A	Redispersible microfibrillated cellulose	Herrick Franklin W.	06/11/1984	50	[100]
US4483743A	Microfibrillated cellulose	Turbak Albin F, Snyder Fred W, Sandberg Karen R.	20/11/1984	32	[101]
US4487634A	Suspensions containing microfibrillated cellulose	Turbak Albin F, Snyder Fred W, Sandberg Karen R.	11/12/1984	13	[102]
US4500546A	Suspensions containing microfibrillated cellulose	Turbak Albin F, Snyder Fred W, Sandberg Karen R.	19/02/1985	59	[103]

Table 3. Most Cited Patents of the ITT Rayonier Eastern Research Division Lab on Microfrillated Cellulose. Assignee: International Telephone and Telegraph Corporation

Publication Number	Reference Title	Inventors	Publication Year	Citations	Ref.
US4374702A	Microfibrillated cellulose	Turbak Albin F, Snyder Fred W, Sandberg Karen R	1983	78	[94]
US4500546A	Suspensions containing microfibrillated cellulose	Turbak Albin F, Snyder Fred W, Sandberg Karen R	1985	59	[103]
US4481076A	Redispersible microfibrillated cellulose	Herrick Franklin W	1984	50	[100]
US4481077A	Process for preparing microfibrillated cellulose	Herrick Franklin W	1984	37	[99]
JP56100801A	Microfibrous cellulose and its manufacture	Taabaku Arubin F, Sunaidaa Furetsudo U, Sandobaagu Karen R / Sandberg Karen R, Snyder Fred W, Turbak Albin F	1981	36	[104]
US4341807A	Food products containing microfibrillated cellulose	Turbak Albin F, Snyder Fred W, Sandberg Karen R	1982	34	[93]
US4483743A	Microfibrillated cellulose	Turbak Albin F, Snyder Fred W, Sandberg Karen R	1984	32	[101]
US4378381A	Suspensions containing microfibrillated cellulose	Turbak Albin F, Snyder Fred W, Sandberg Karen R	1983	30	[95]
EP120471A2	Redispersable microfibrillated cellulose	Herrick, Franklin W	1984	25	[105]
GB2066145A	Microfibrillated cellulose	Sandberg Karen R, Synder Fred W, Turbak Albin F	1981	24	[106]

The discovery of Turbak and co-workers received much attention in the following years, and both scientific articles and published patents evidenced a huge rise. MFC is now a commercial product available from various companies such as Daicel (Japan), Rettenmaier (Germany), Innventia AB (Sweden), UPM Kymmene and VTT (Finland), Borregaard (Norway) [6, 13]. Fig. (**7**) illustrates the evolution of the number of annual patents published on microfibrillated cellulose since it was first produced. The total number of patents found by the search performed was 252 (without their families). Descriptors used were chosen from specialized academic reviews and articles on the topic and by inspection of specific patent vocabulary, and are included below the figure.

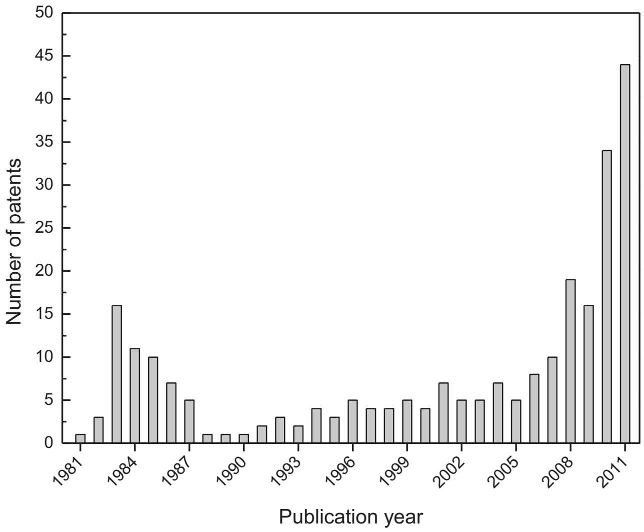

Fig. (7). Evolution of the annual number of patents on microfibrillated cellulose since 1981. Descriptors: microfibrillated cellulose, microfibrillar cellulose, microfibrilized cellulose, nanofibrillated cellulose, nanofibrillar cellulose, micro-fibrillated cellulose, micro:fibrillated cellulose.

As it happened in Fig. (**1**) (when *all* descriptors used throughout the years to refer to particles produced by acid hydrolysis of cellulose were included in the search), Fig. (**7**) also shows the presence of two maxima: one in the early eighties, and the second one in recent years. While in Fig. (**1**) the analysis carried out in the previous section demonstrated that the profile observed was the result of two different technologies dealing with acid hydrolysis of cellulose substrates; in the case of microfibrillated cellulose the profile shown in Fig. (**7**) can be attributed to two different moments of history in which MFC technology received much attention. The first one took place in the middle eighties, when Turbak and co-workers published a huge number of patents in only a few years. The Japanese company Daicel became also very active in patent publishing during the early eighties, when they patented a number MFC applications, such as water absorptive sheet usable in houses and buildings which comprises a surface layer of MFC on base sheet [107]; a fertilizer granulation in which MFC provides improved moisture absorbability, good drying and granulating operabilities [108]; a solid fuel composition with excellent ignitability and combustibility and evolving no odor during combustion (claimed) by addition an aqueous MFC suspension to a raw carbon powder [109]; composition for multilayer coating with decorative pattern purpose in which MFC addition to base coating enhances sprayability [110]; water-color paints with shortened tack-free time capable of giving a uniformly colored surface without shading by incorporation of MFC to conventional water-color paint [111]; fluid retorted food (e.g. soup) with addition of MFC to maintain stable viscosity during pasteurization [112]; seasonings comprising MFC to provide thixotropy and dispersion stability [113]; sweet bean jam comprising MFC for improved texture [114]; paper with increased strength by addition of MFC to pulp slurry [115]; a method for measuring cellulase activity easily with a high sensitivity by using MFC as substrate [116]; preparation of a highly active immobilized biocatalyst by using MFC having a large surface area as a carrier [117]; shape-retaining dentifrice including cellulose microfibrils [118], etc.

The second rise in patents publication shown in Fig. (**7**) starts in the second half of last decade, triggered by the worldwide interest in nanotechnology and also probably because protection set by most patents of the eighties had finished. In the last five years the number of patents published accumulated nearly 45% of the total number of patents published on the topic, with 2010 and 2011 being the most prolific years. The profile observed suggests that MFC technology will continue increasing in the next years.

Patents on MFC published during the last two decades include clinical examination and filter papers in which porous calcium phosphate-based material is bonded with microfibrillated cellulose [119], acoustic diaphragm comprising a web of MFC [120], burn control wrappers for smoking articles e.g. cigarettes comprising conventional paper wrappers with region(s) of MFC bonded on [121], polyester paper having excellent strength and water-resistance and free from strike-through of ink useful as integer material for houses and cars prepared from polyester fiber, polyester binder and MFC [122], separator for alkaline secondary cells that comprises polyolefin fiber unwoven cloth containing MFC which imparts improved hydrophilic properties [123], manufacture of absorbent sheet for use as nappy for adults and children [124], supplement materials for compost production containing specific amounts of MFC with controlled particle size which are claimed to provide excellent air permeability and shape retention [125], sheet-like absorber for female sanitary products comprising an absorption layer with a preset amount of fibrillated cellulose and water absorbing resin [126], pack agent for cosmetics which contains polyvinyl alcohol and MFC as essential component and is claimed to have excellent film forming-ability and appropriate rate of drying and to be easily peel-able [127], composite material for resin composition used for motor vehicle component obtained by coating polylactic acid on the surface of MFC [128], diagnostic test device for e.g. pregnancy test or for diagnosing gluose meters for diabetics, which has different zones with respective reagents which react with the sample [129], optical components such as lens and prism which have a reflective surface with metal thin film and nanocomposite obtained by impregnating synthetic resin into MFC [130], resin composite materials used for forming molded products in which surface-treated MFC is used as reinforcement base material [131], polyphenol-containing composition useful in food and beverages for suppressing hypertension prepared by contacting a polyphenol containing solution with MFC [132], layered mechano-active material for packaging applications which comprises a layer MFC and whose extension is anisotropically controllable by heat and/or moisture [133], separator for electrochemical element which is claimed to be superior in heat resistance, favorable in handling, and small in pore diameter, obtained by filling the interspaces of a fiber matrix with aluminium oxides and MFC [134], film substrate used for flexible display apparatus comprising gas barrier layer provided on film support body which contains MFC [135], reflective mirror for solar thermal power generation system which made of microfibrillated cellulose resin provided on metal film for reflecting sunlight [136], fiber cord used as reinforcing cord of pneumatic radial tire obtained by coating fiber cord with adhesive agent, latex rubber and MFC [137], barrier layer useful for packaging a container [138], carbon-fiber-reinforced composite material useful in brake material and motor vehicle which contains carbonized MFC [139], cement mixture containing MFC useful for the production of a cementitious composition such as concrete, self compacting concrete, mortar, grout or injection grout, used as construction element, rheology modifier or segregation control [140], strong nanopapers with good thermal stability, high storage modulus, high oxygen gas-barrier properties, high strength and cracking resistance (claimed) useful as e.g. filter paper which comprise MFC nanofibers, a water soluble crosslinker and layered clay [141], paper or paperboard substrate having barrier properties for producing package used as food or liquid package, which comprises a first fiber based layer, a second layer comprising MFC, and a third layer comprising a polymer [142], rheology modifying agent and sealing agent which comprises nanofibrillar cellulose useful for oilfield applications [143], wound dressing useful for wound healing at hemorrhaging wound site which comprises MFC having defined particle size with elevated free radical level [144], composition useful for providing a barrier to a permeable substrate which comprises MFC, partially hydrolyzed vinyl acetate polymer and at least one anionic polymer [145], vehicle panel useful as e.g. automotive panel and door panel which comprises a naturally-sourced composite with MFC as strengthening agent[146], etc. Diverse methods for the preparation of microfibrillated cellulose have been patented including e.g. the obtention of ultra microfibrillated cellulose for coated and dyed paper by passing pulp slurry through whetstone plate fitting apparatus and ultra-micronising using high pressure homogenizer [147], method of producing MFC which involves treating a slurry containing pulp with a disc refiner to obtain MFC having preset average fiber length [148], preparation of unbleached microfibrillar cellulose by treating polysaccharide in aqueous suspension comprising an oxidant such as hydrogen peroxide and transition metal such as iron and mechanically delaminating the polysaccharide [149], treatment of chemical pulp for manufacture of MFC for use in e.g. food or cosmetic products, involves treating refined hemicellulose containing pulp with wood degrading enzyme(s) and homogenizing [150], production of MFC by passing a suspension of cellulose and a solvent through an orifice such that the said suspension is subjected to a pressure drop which has a maximum value of 100 MPa [151], treating cellulosic fibers of kraft pulp to produce MFC by mechanically pre-treating fibers of kraft pulp by shredding or refining, and treating fibers with enzyme such as cellulose [152], and production of MFC by providing a slurry comprising fibers, adding the slurry to extruder and treating the slurry in the extruder so that the fibers are defibrillated [153]. Methods on the drying of MFC have also been patented including e.g. the partially freezing of MFC followed by drying by use of a cold moving gas stream, which is claimed to enhance product quality and capacity in a cost effective manner [154]: and the atomization of an aqueous suspension of cellulose nanofibrils which is later introduced into a drying chamber [155]. According to IPC classification the technological areas to which most MFC patents pertain are production of cellulose by removing non-cellulose substances/after-treatment of cellulose pulp, e.g. of wood pulp, or cotton linters (D21C9/00A); impregnating or coating of paper and treatment of finished paper/pulp or paper comprising cellulose or lignocellulose fibers of natural origin (D21H11/00); compositions of cellulose, modified cellulose, or cellulose derivatives (C08L1/00); and absorbent pads, e.g. sanitary towels, swabs or tampons for external or internal application to the body (A61F13/15). Table **4** summarizes the ten most cited patents found for the search performed for MFC. By including the patents families the total number of patents covered by the raised from 252 to 701 documents.

Table **4** illustrates the relatively high number of citations received by some documents, which implies that they have had a significant influence on several later developments. The importance of the documents patented during the eighties by the International Telephone and Telegraph Corporation (ITT) with Turbak, Snyder and Sandberg or Herrick, is illustrated. The mentioned Japanese company Daicel also appears with a highly referenced patent of the middle eighties. It is worth noting the relatively high number of citations of the patent from Hercules Inc published in the year 2000, considering that this document appeared nearly twenty years later than documents by Turbak *et al.*

Fig. (**8**) shows the most prolific assignees of microfibrillated cellulose patents in terms of the total number of patents they own. The analysis was performed considering all patents included in Fig. (**7**) (irrespectively of their number of citations). Fig. (**8**) illustrates the importance of the Japanese company Daicel Chemical Industries which is engaged in the manufacture of cellulose and organic synthesis products, including acetate tow for cigarette filters, carboxymethyl cellulose, cellulose acetate, hydroxyethyl cellulose and microfibrillated. The analysis of annual patent applications of Daicel evidence the permanent interest of the company on MFC since the early eighties until these days (data not shown). Other prolific assignees are Stora Enso Oyg which is an integrated paper, packaging and forest products company headquartered in Helsinki (Finland) which in the year 2011 published seven new patents; Akzo Nobel which is engaged in the production of paints, coatings, and specialty chemicals; and UPM-Kymmene Corporation which is one of the leading European manufacturers of integrated paper and forest based products, also headquartered in Helsinki.

Table 4. Most Cited Patents on MFC

Publication Number	Reference Title	Assignee	Inventors	Publication Year	Citations	Ref.
US4374702A	Microfibrillated cellulose	Int Telephone & Telegraph Corp	Turbak Albin F, Snyder Fred W, Sandberg Karen R	1983	78	[94]
US4500546A	Suspensions containing microfibrillated cellulose	Deut ITT Ind Gmbh, Itt Ind Inc	Turbak Albin F, Snyder Fred W, Sandberg Karen R	1985	59	[103]
US4481076A	Redispersible microfibrillated cellulose	Deut ITTInd Gmbh	Herrick Franklin W	1984	50	[100]
US5417228A	Smoking article wrapper for controlling burn rate and method for making same	Philip Morris Inc, Philip Morris Prod Inc	Baldwin Sheryl D, Gautam Navin, Houghton Kenneth S, Rogers Robert M, Ryder Judith L	1995	41	[156]
US5263999A	Smoking article wrapper for controlling burn rate and method for making same	Philip Morris Inc, Philip Morris Prod Inc	Baldwin Sheryl D, Gautam Navin, Houghton Kenneth S, Rogers Robert M, Ryder Judith L	1993	40	[157]
US4481077A	Process for preparing microfibrillated cellulose	Int Telephone & Telegraph Corp	Herrick Franklin W	1984	37	[99]
US5964983A	Microfibrillated cellulose and method for preparing a microfibrillated cellulose	Gen Sucriere Sa, Saint-Louis Sucre Sa	Dinand Elisabeth, Chanzy Henri, Vignon Michel R, Maureaux Alain, Vincent Isabelle	1999	37	[158]
JP56100801A	Microfibrous Cellulose and Its Manufacture	ITT Ind Inc	Taabaku Arubin F, Sunaidaa Furetsudo U, Sandobaagu Karen R / Sandberg Karen R, Snyder Fred W, Turbak Albin F	1981	36	[104]
US4659388A	Additive composition for foods or drugs	Daicel Chem Ind Ltd	Innami Satoshi, Fukui Yoshitaka	1987	36	[159]
US4341807A	Food products containing microfibrillated cellulose	Deut ITT Ind Gmbh, ITTInd Inc	Turbak Albin F, Snyder Fred W, Sandberg Karen R	1982	34	[93]
WO2000047628 A2	Derivatized Microfibrillar Polysaccharide	Hercules Inc	Cash Mary Jean, Chan Anita N, Conner Herbert Thompson, Cowan Patrick Joseph, Gelman Robert Alan, Lusvardi Kate Marritt, Thompson Samuel Anthony, Tise Frank Peine	2000	33	[160]

Contrarily to cellulose nanocrystals patents, MFC patents are mainly owned by companies and not by universities or public institutions, which correlates with the higher extent of application of the technology and the market development of MFC. The presence of individual applicants or universities in the field of MFC is scarce. It is worth noting that there are a number of other competitors with own one, two or three patents, which have not been included in Fig. (**8**). In reference to MFC patent inventors, the main contributor has been Isto Heiskanen from Stora Enso.

The manufacture of MFC is now generally performed by refining plus high pressure homogenization [6]. However, production of MFC solely by shear forces requires multiple passes through the homogenizer and thus high energy input. Moreover, the process is prohibitively unstable as the constrictions chambers of the homogenizer quickly become blocked [16]. Then, in the last years an important topic in MFC research has been the development of pretreatments capable of reducing the energy demand of the later mechanical fibrillation process. In this context, in 2006 Saito and coworkers reported a novel way of introducing charged carboxylate groups into cellulosic materials which facilitated disintegration into microfibrils with smaller widths, and by using a much lower energy input than traditional pure mechanical treatment [18]. The approach involved oxidation of never-dried native celluloses (bleached sulfite wood pulp, cotton, tunicin, and bacterial cellulose) mediated by the 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) radical, followed by a homogenizing mechanical treatment. The resulting product consisted in long individual microfibrils which yielded transparent and highly viscous suspensions [18]. Upon TEMPO oxidation the accessible primary hydroxyls on the surface of the microfibrils become modified with anionic carboxylate groups, which resulted in repulsion between nanofibers that eased fibrillation.

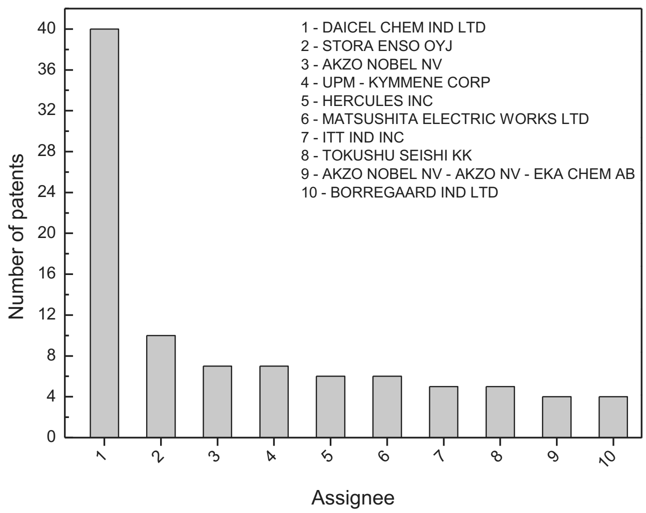

Fig. (8). Main MFC patent owners. Descriptors used are the same as those used in Figure 7.

Meanwhile, Pääkkö *et al.* (2007) and Henriksson *et al.*, (2007) proposed a novel method for the production of MFC which combines enzymatic hydrolysis and mechanical shearing [16, 17]. Authors demonstrated that a combination of high pressure shear forces and mild enzymatic hydrolysis is an efficient method to prepare MFC with well-controlled nanosized diameters. The enzymes used are monocomponent endoglucanases, which are a class of cellulases which preferentially hydrolyze unordered regions of cellulose. Enzyme-treatment was found to facilitate disintegration, and the MFC nanofibers produced also showed higher average molar mass and larger aspect ratio than nanofibers pretreated with HCl (even at what the authors called mild conditions) [17]. Furthermore, it was demonstrated that small additions of the monocomponent endoglucanase prevented the blocking of the homogenizer [16]. The process is considered environmentally friendly since no solvent or harsh chemical reactants are used, and important energy input reductions are achieved.

Figs (**9a** and **9b**) illustrate the patent publishing trends of the described oxidation and enzymatic pretreatments, respectively. The total number of patents retrieved by the search performed for oxidation was 30, whereas 17 patents dealing with cellulose-degrading enzyme pretreatment were found. Descriptors used to perform the search were chosen based on scientific articles on the topic and are included below the figure.

Fig. (**9a**) illustrates the evolution of the n-oxyl oxidation technology, which since its introduction in the year 2008 has experienced an exponential increase in new patent applications. From the profile shown in Fig. (**9a**), the oxidation technology appears as an emergent one which will continue growing in the next years.

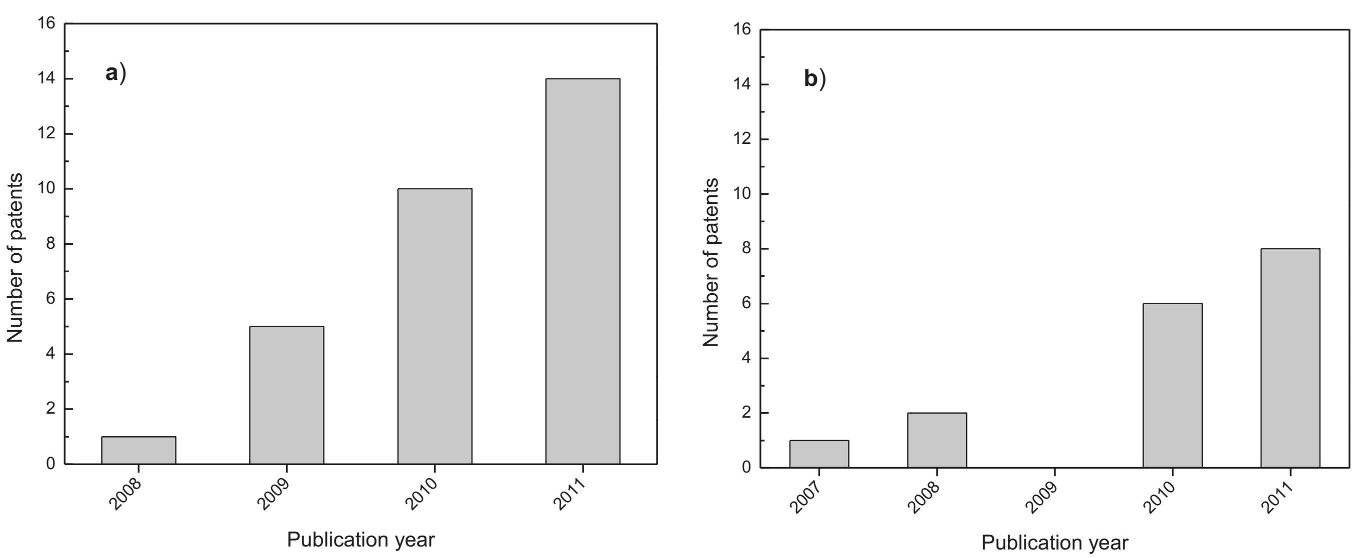

Fig. (9). Evolution of the annual number of patents on pretreatments devoted to ease fibrillation of MFC. (**a**) Oxidation technology patents; (**b**) Enzymatic pretreatment patents. Descriptors used for oxidation search: (cellulose microfibril/s, cellulose nanofiber/s, cellulose nanofibril/s, nanocellulose/s, microfibrillated cellulose, microfibrillar cellulose, nanofibrillated cellulose, nanofibrillar cellulose, microfibrilized cellulose, micro-fibrillated cellulose, micro:fibrillated cellulose) and (TEMPO, n-oxyl, 2,2,6,6-tetramethylpiperidine-1-oxyl). Descriptors used for enzymatic search: (cellulose microfibril/s, cellulose nanofiber/s, cellulose nanofibril/s, nanocellulose/s, microfibrillated cellulose, microfibrillar cellulose, nanofibrillated cellulose, nanofibrillar cellulose, microfibrilized cellulose, micro-fibrillated cellulose, micro:fibrillated cellulose) and (cellulase/s, enzyme/s, enzymatic, endoglucanase/s) followed by manual refining.

Table **5** shows the ten patents on oxidation-mediated cellulose microfibrils that have received more citations. By including the patents families the total number of patents covered by the search raised from 30 to 73. The Japanese patent JP2008001728A "Fine cellulose fiber" invented by Isogai and co-workers and owned by Asahi Kasei Corp, is by far the most cited document [161]. In the mentioned patent (whose inventors are the authors of the first article on the topic [18]), fine cellulose fibers are obtained by utilizing a surface oxidization reaction of the cellulose by an N-oxyl compound. The N-oxy compound is 2,2,6,6-tetramethyl-1-piperidine N-oxyl; and the co-oxidation agent is hypohalous acid or its salt, halous acid or its salt, perhalogen acid or its salt, hydrogen peroxide and/or per-organic acid. The fine cellulose fiber has a maximum fiber diameter of at most 1000 nm and a number-average fiber diameter of 2-150 nm, has a part of hydroxy groups of the cellulose oxidized into at least one functional group selected from the group consisting of a carboxyl group and an aldehyde group, and has a cellulose I type crystal structure. The dispersion of fine cellulose fiber is obtained by dispersion processing, homomixer processing under high speed rotation, high voltage homogenizer processing, super-high-voltage homogenizer processing, ultrasonic distributed processing, beater processing, disc type refiner processing, conical type refiner processing, double disc type refiner processing and/or grinder processing [161].

Main assignees of the oxidation technology are shown in Fig. (**10**). Only assignees with more than one patent have been included. Data shown evidences the clear leadership of the Nippon Seishi KK and Nippon Paper Industries Co. Ltd., both leaders of the Japanese pulp and paper business. Most oxidation patents are owned by companies, which correlates with the extent of technology application. In terms of patents inventors, the most prolific belong to the Nippon Paper Industries Co. Ltd., such as Shoichi Miyawaki, Shiho Katsukawa and Yuko IIjima.

In reference to the action of cellulose-degrading enzymes aimed at easing fibrillation of cellulose, Fig. (**9b**) evidences the interest that this technology has received since it was introduced in 2007. Although with a lower rate than oxidation technology, the number of patents which use cellulases to ease fibrillation evidences an important rise in the last 5 years. Most prolific years have been 2010 and 2011. As in the case of oxidation, enzymatic pretreatments appear as an emergent technology which will continue growing in the next years. Table **6** shows the most cited patents on the topic including all families.

Table **6** shows that patents on enzymatic pretreatments applied to production of MFC have still only a few citations. Most cited patents include "Method for the manufacturing of microfibrillated cellulose" by Lindström *et al.* [171], and "Method of producing and the use of microfibrillated paper" by Henriksson *et al.* [172]. The first patent provides a method for treatment of chemical pulp for the manufacturing of microfibrillated cellulose comprising a) providing a hemicellulose containing pulp, b) refining said pulp in at least one step and treating said pulp with one or more wood degrading enzymes at a relatively low enzyme dosage, and c) homogenizing said pulp thus providing MFC [171]. The document from Henriksson *et al.* deals with a method of producing a cellulose based paper that exhibits enhanced mechanical properties. The method involves providing a suspension of well dispersed modified cellulose at a low concentration. The nanofibrils have been treated with enzymes and/or by mechanical beating. The properties and the chemical structure of the paper make it suitable for *in vivo* applications such as implant material [172].

Assignees of patents on enzymatic-mediated MFC are shown in Fig. (**11**). As it is shown, the technology is still concentrated in a scarce number of competitors (only ten were found). The most prolific one is the Finnish pulp and paper manufacturer Stora Enso Oyj, one of the world's largest pulp and paper manufacturer in terms of production capacity. Another important competitor is the Swedish STFI-Packforsk which in 2009 changed its name for INNVENTIA, a customer oriented research company in pulp and papermaking which started as a collective research institute. Other main patent owners are the Japanese Nippon Paper Industries Co. Ltd.; as well as the Swedish plant and forest biotechnology company SweTree Technologies. Most patents are owned by companies, which correlates with the extent of technology application. In terms of patents inventors, the most prolific ones have been Isto Heiskanen and Kaj Backfolk from Stora Enso, and Lars Berglund (Sweden).

4.3. Bacterial Cellulose

Although cellulose source is generally associated with plant biomass, it is now well-known that cellulose is also produced by tunicates (sea squirts), some algae, amoebae, fungi and bacteria. The bacteria-derived cellulose is of particular interest due to its light weight, high mechanical properties, non-toxicity, renewability, biodegradability, and high chemical purity which avoids chemical treatments used in plant-derived celluloses for the removal of hemicellulose and lignin [178, 179]. Most important, microbial production of cellulose represents a very attractive source of cellulose nanofibers based on a variety of cheap carbon sources such as agroindustrial residues and wastewaters.

Bacterial cellulose (BC) is produced as an extracellular primary metabolite by bacteria belonging to the genera *Acetobacter*, *Agrobacterium*, *Alcaligenes*, *Pseudomonas*, *Rhizobium*, *Aerobacter*, *Achromobacter*, *Azotobacter*, *Salmonella* or *Sarcina* [180, 181]. Its most efficient producers are gram-negative acetic acid bacteria *Acetobacter xylinum* which has been reclassified and included within the novel genus *Gluconacetobcater*, as *G. xylinus* [182, 183]. Culture is normally carried out in static conditions at temperatures around 28-30°C. The system initially becomes turbid and later on a white pellicle appears on the surface of the fermentation vessel. Since bacteria used are aerobic, cellulose pellicle is formed only in the vicinity of the oxygen-rich air-liquid surface, and it adopts its shape. Several reasons for the formation of the cellulose pellicle by bacteria have been proposed, such as a mean of maintaining their position close to the surface of culture solution [184], and also as a protective coating to guard bacteria from ultraviolet radiation [185], or from enemies and heavy-metal ions whereas nutrients diffuse easily along the pellicle [22]. It is believed that cellulose molecules are synthesized in the interior of the cell and spun out to form protofibrils of ca. 2-4 nm diameter, which

Table 5. Most Cited Patents on TEMPO Oxidation of Cellulose

Publication Number	Reference Title	Assignee	Inventors	Publication Year	Citations	Ref.
JP2008001728A	Fine cellulose fiber	Asahi Kasei KK	Isogai Akira, Saito Tsuguyuki, Nishiyama Yoshiharu, Pataux Jean-Luc, Vignon Michel.	2008	24	[161]
WO2009069641A1	Cellulose nanofiber and process for production thereof, and cellulose nanofiber dispersion	Sharp KK, Univ Tokyo, Isogai A, Saito T	Isogai Akira, Saito Tsuguyuki	2009	5	[162]
JP2009263850A	Printing paper - Print sheet	Jujo Paper Co Ltd, Nippon Paper Ind Co Ltd, Nippon Seishi Kk , Abe H, Iijima Y, Isogai A, Katsukawa S, Miyawaki S	Kawasaki Kentaro, Higata Tomohiro, Miyawaki Shoichi, Katsukawa Shiho, Abe Yutaka, Iijima Yuko, Isogai Akira	2009	3	[163]
WO2009084566A1	Process for production of cellulose nanofiber, catalyst for oxidation of cellulose, and method for oxidation of cellulose	Jujo Paper Co Ltd, Nippon Paper Ind Co Ltd, Nippon Seishi Kk, Abe H, Iijima Y, Isogai A, Katsukawa S, Miyawaki S	Miyawaki Shoichi, Katsukawa Shiho, Abe Hiroshi, Iijima Yuko, Isogai Akira	2009	2	[164]
WO2009122982A1	Additive for papermaking and paper containing the same	Jujo Paper Co Ltd, Nippon Paper Ind Co Ltd, Nippon Seishi KK, Abe H, Iijima Y, Isogai A, Katsukawa S, Miyawaki S	Miyawaki Shoichi, Katsukawa Shiho, Abe Hiroshi, Iijima Yuko, Isogai Akira	2009	2	[165]
JP2009161613A	Method for oxidizing cellulose, oxidation catalyst for cellulose, and method for producing cellulose nanofiber	Jujo Paper Co Ltd, Nippon Paper Ind Co Ltd, Nippon Seishi KK, Abe H, Iijima Y, Isogai A, Katsukawa S, Miyawaki S	Miyawaki Shoichi, Katsukawa Shiho, Abe Yutaka, Iijima Yuko, Isogai Akira	2009	1	[166]
JP2009263848A	Additive for papermaking and paper containing the same	Jujo Paper Co Ltd, Nippon Paper Ind Co Ltd, Nippon Seishi KK, Abe H, Iijima Y, Isogai A, Katsukawa S, Miyawaki S	Miyawaki Shoichi, Katsukawa Shiho, Abe Yutaka, Iijima Yuko, Isogai Akira	2009	1	[167]
JP2009263854A	Coated paper for gravure printing	Jujo Paper Co Ltd, Nippon Paper Ind Co Ltd, Nippon Seishi KK, Abe H, Iijima Y, Isogai A, Katsukawa S, Miyawaki S	Yamada Yoshitake, Okamoto Tadashi, Miyawaki Shoichi, Katsukawa Shiho, Abe Yutaka, Iijima Yuko, Isogai Akira	2009	1	[168]
JP2010235679A	Method for manufacturing cellulose nano-fiber	Nippon Paper Ind Co Ltd, Nippon Seishi KK	Miyawaki Shoichi, Katsukawa Shiho, Abe Yutaka, Iijima Yuko, Isogai Akira	2010	1	[169]
JP2010242063A	Cellulose nanofiber compound polyvinyl alcohol-based polymer composition	Kuraray Co Ltd	Endo Ryokei, Oishi Kimiko, Yasushiro Hideki	2010	1	[170]

Table 6. Most Cited Patents on Enzymatic Pretreatments of MFC

Publication Number	Reference Title	Assignee	Inventors	Publication Year	Citations	Ref.
WO2007091942A1	Method for the manufacturing of microfibrillated cellulose	Stfi-Packforsk Ab, Lindström Tom, Ankerfors Mikael, Henriksson Gunnar	Lindström Tom, Ankerfors Mikael, Henriksson Gunnar	2007	3	[171]
US20100065236A1	Method of producing and the use of microfibrillated paper	n.a.	Henriksson Marielle, Berglund Lars, Zhou Qi, Bulone Vincent	2010	3	[172]
JP2008150719A	Cellulose nano-fiber and method for producing the same	Forestry & Forest Products Research Institute	Shibuya Hajime, Hayashi Noriko	2008	1	[173]
EP2196579A1	Method for producing microfibrillated cellulose	Borregaard Industries Limited Norge	Wichmann Jens-Uwe, Haugen Øivind	2010	1	[174]
WO2010116826A1	Process for producing cellulose nanofibers	Nippon Paper Industries Co. Ltd., Miyawaki Shoichi, Katsukawa Shiho, Abe Hiroshi, Iijima Yuko, Isogai Akira	Miyawaki Shoichi, Katsukawa Shiho, Abe Hiroshi, Iijima Yuko, Isogai Akira	2010	1	[175]
JP2010235679A	Method for manufacturing cellulose nano-fiber	Nippon Paper Industries Co Ltd	Miyawaki Shoichi, Katsukawa Shiho, Abe Hiroshi, Iijima Yuko, Isogai Akira	2010	1	[176]
WO2011001036A1	Liquid-repellent material	Aalto-Korkeakoulusäätiö Fi, Jin Hua, Pääkkö Marjo, Ikkala Olli, Ras Robin H. A.	Jin Hua, Pääkkö Marjo, Ikkala Olli, Ras Robin H	2011	1	[177]

are crystallized into microfibrils, these into bundles and the latter into ribbons [22, 35]. BC ribbons have been reported to have a thickness of approximately 3-4nm, 70-100nm in width, and 1-9μm in length [22, 35]. Produced BC ribbons form a dense reticulated structure stabilized by extensive hydrogen bonding whose solid portion is less than 1%, and the rest is water.

Besides the current interest in bacterial cellulose as biomaterial, BC obtained from coconut water has long been known as the raw material of an indigenous dessert food of South-East Asia called *nata-de-coco*. In 1886, A.J. Brown reported for the first time the synthesis of an extracellular gelatinous mat whose chemical composition and reactivity was the same as cell-wall cellulose [186, 187]. In the second half of the following century, Hestrin *et al.* and Colvin (1957) made important advances in terms of cellulose production by lyophilized cells and cell-free extracts of *A. xylinum* using glucose as carbon source [188-190]. In the mid- 1980s the remarkable mechanical properties of BC pellicles were reported by Iguchi and co-workers [24, 25], and interest in microbial cellulose grew rapidly thereafter. In the mid-1990s the use of BC for composite materials was reported by several authors [26, 191]. In the following decade the possibility of obtaining cellulose nanofibrils of high purity without high energy input as required for traditional MFC preparation, brought a resurgence in this research area.

Fig. (**12**) illustrates the evolution of the number of annual patents published on the field of bacterial cellulose during the last thirty years. The total number of patents found by the search performed was 815. Descriptors used were chosen from specialized academic reviews and articles on the topic and by inspection of specific patent vocabulary, and are included below the figure.

The search performed showed that a patent on bacterial cellulose was published as early as in the early fifties, when bacterial cellulose was one of the substrates assayed in the esterification of hydroxy-compounds by reacting with a carboxylic acid in the presence of trifluoracetic anhydride [192]. During the seventies, applications on membranes for filtration and other separation processes such as dialysis and ion exchange based on bacterially grown cellulose skins were made; and pulp-based electrical insulation containing bacterial cellulose for higher breakdown strength and lower loss factor was patented [193]. Evolution of bacterial cellulose technology since 1980 is shown in Fig. (**12**), in which two maxima were found. The first one took place in the years 1997-1998 and the second one in recent years. The first noticeable rise in annual patents was surely triggered by the discovery of the high mechanical properties of BC pellicles [24, 25], and their subsequent use as reinforcement of composite materials. Most patents of those years include BC applications in paper reinforcement and acoustic membranes; as well as optimization of cellulose cultivating conditions (see next paragraph). The annual patents on bacterial cellulose experienced an abrupt decrease in the following years; a tendency that was reverted by the year 2002 when interest in BC technology experienced the beginning of a second rise, which by the end of the decade accumulated nearly 50 % of the total number of documents on microbial cellulose technology in only 5 years. Similarly to cellulose nanocrystals and microfibrillated cellulose, the years 2010 and 2011 have been the most prolifics in terms of patent applications, a phenomenon which finds correlation with the increasing worldwide interest on new outstanding properties shown by nanoparticles. From the profile found, it can be inferred that in next years the field will go on rising at a high rate.

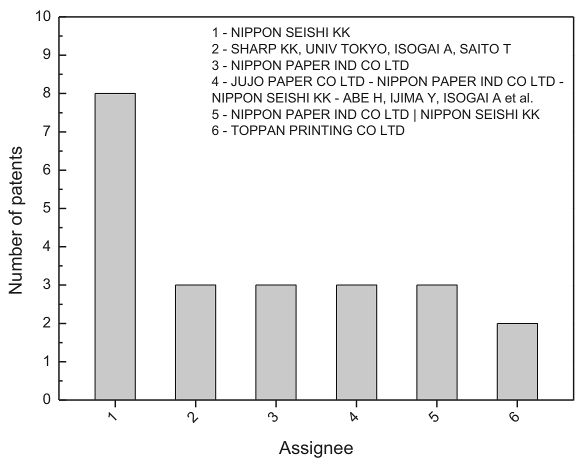

Fig. (10). Main n-oxyl oxidation patent owners. Descriptors used are the same as those used in Fig. (**9a**).

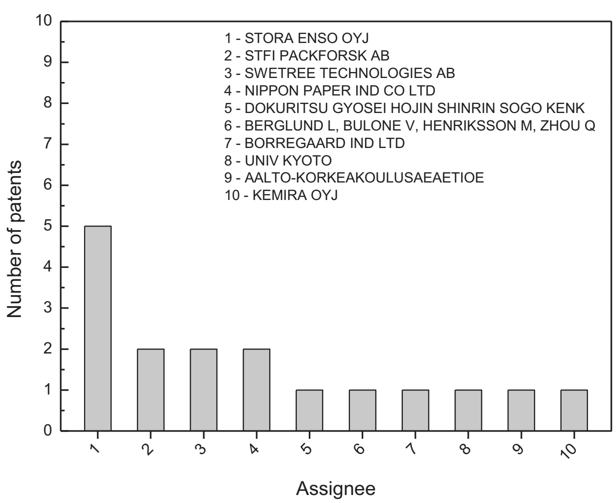

Fig. (11). Main enzymatic-mediated MFC patent owners. Descriptors used are the same as those used in Fig. (**9b**).

Published patents on microbial cellulose applications include e.g. medicinal pads for topical application made of a pellicle of microbially produced cellulose impregnated with a physiologically acceptable liquid [194]; molded materials of high dynamic strength formed from bacteria-produced cellulose comprising ribbon-like microfibrils [195]; use of bacterial cellulose as carrier for immobilizing biological material such as cells, enzymes or biological active molecules [196]; microbially produced reticulated cellulose useful for production of novel sheet materials [197]; glass fiber sheets of high strength manufactured by forming an aqueous slurry of glass fiber and BC [198]; oral plasters for treatment stomatitis or gingivitis comprising a supporting base made of bacterial cellulose on which dermal absorption medicine are set [199]; membrane filter for reverse osmosis comprising bacterial cellulose which imparts high dynamic strength [200]; speaker diaphragm having waterproof ability mainly composed of esterified bacterial cellulose fiber [201]; use of bacterial cellulose for binding cholesterol, e.g. in the digestive tract and for providing a source of dietary fiber [202]; microcapsules with stable water retaining function for photosensitive material containing in their core BC as water holding agent [203]; hydraulic fracturing fluids for recovery of hydrocarbons containing proppant, gelling agent and bacterial cellulose, in which the addition of relatively small quantities of BC improve fracturing fluids rheological properties and thus reduce pumping energy requirements [204]; hollow microbial cellulose useful in novel artificial blood vessels and in other medical material [205]; rubber compounded composition with light weight and good strength by addition of BC [206]; artificial soil composition that retains seeds and holds water comprising bacterial cellulose and fertilizers [207]; paper for wrapping prepared from pulp containing bacterial cellulose which imparts high sheet denseness, transparency, strength and barrier property [208]; edible material comprising bacterial cellulose which improves viscosity, fluidity and water-retentivity and texture of products [209]; photocatalyst sheets used as filter member of air-cleaner consisting of photocatalyst, absorbent, BC and coagulating agent [210]; high absorption composites such as nappies and sanitary products for children and women [211]; preparation of shaped articles of microbial cellulose useful in microsurgery by culturing microorganism between shape-defining walls [212]; coagulant for water treatment such as city water, sewage water and industrial waste liquid, based

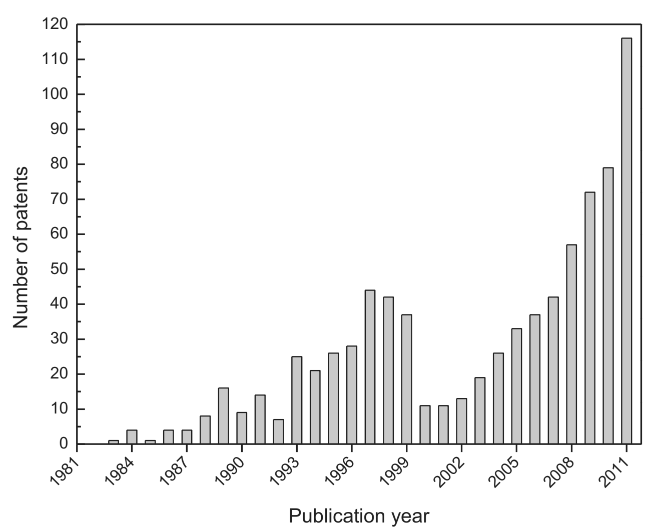

Fig. (12). Evolution of the annual number of patents on bacterial cellulose. Descriptors: bacterial cellulose, bacteria cellulose, bacterium cellulose, microbial cellulose, bacteria-produced cellulose, bacterial nanocellulose.

Table 7. Most Cited Patents on Bacterial Cellulose

Publication Number	Reference Title	Assignee	Inventors	Publication Year	Citations	Ref.
US4588400A	Liquid loaded pad for medical applications	Johnson & Johnson Products Inc., New Brunswick, NJ, US	Ring David F, Nashed, Wilson, Dow Thurman	1986	123	[223]
US5417228A	Smoking article wrapper for controlling burn rate and method for making same	Philip Morris Incorporated, New York, NY, US	Baldwin Sheryl D, Gautam Navin, Houghton Kenneth S, Rogers Robert M, Ryder Judith L.	1995	41	[224]
JP62036467A	Bacterial cellulose-containing molding material having high mechanical strength	Agency of Ind Science & Technol - Ajinomoto Co Inc - Sony Corp	Iguchi Masatoshi, Mihashi Shigenobu, Ichimura Kunihiro, Yamanaka Shigeru , Watabe Otohiko, Nishi Mio, Uryu Masaru	1987	40	[224]
US5263999A	Smoking article wrapper for controlling burn rate and method for making same	Philip Morris Incorporated, New York, NY, US	Baldwin Sheryl D, Gautam Navin, Houghton Kenneth S, Rogers Robert M, Ryder Judith L.	1993	40	[225]
US4863565A	Sheeted products formed from reticulated microbial cellulose	Weyerhaeuser Company	Johnson Donald C, Neogi Amar N.	1989	38	[226]
US5198399A	Polymerization catalyst and method	Quantum Chemical Corporation	Hoff Raymond E, Cribbs Leonard V.	1993	38	[227]
US4742164A	Bacterial cellulose-containing molding material having high dynamic strength	Ajinomoto Co. Inc., Tokyo,JP - Sony Corporation, Tokyo, JP - Agency of Industrial Science and Technology, Tokyo, JP	Iguchi Masatoshi, Mitsuhashi Shigenobu, Ichimura Kunihiro, Nishi Yoshio, Uryu Masaru, Yamanaka Shigeru , Watanabe Kunihiko	1988	31	[228]
US5207826A	Bacterial cellulose binding agent	Weyerhaeuser Company, Tacoma, WA, US	Westland John A, Stephens R Scott, Johnston Jr. William C, Rosenkrans Harold J.	1993	29	[229]
GB2131701A	Liquid loaded pad for medical applications	Johnson & Johnson Products Inc(US-NEW),US	Ring David Francis, Nashed Wilson, Dow Thurman	1984	28	[230]
US4655758A	Microbial polysaccharide articles and methods of production	Johnson & Johnson Products Inc., New Brunswick, NJ, US	Ring David Francis, Nashed Wilson, Dow Thurman	1987	28	[231]
US4942128A	Microbial cellulose modified during synthesis	Board of Regents the University of Texas System, Austin, TX, US	Brown Jr. R. Malcolm	1990	28	[232]

on BC fiber and aluminum/iron hydroxide [213]; fuel cell electrode comprising BC as support structure on which transition metal catalyst is disposed on [214]; scaffold useful for inducing *in vivo* or *ex vivo* tissue formation [215]; thermally low expandable optical-waveguide film for compact disks [216]; honeycomb porous component used as support of cell cultivation substrate comprising BC [217]; edible food packaging films made of BC for e.g. processing, refreshing and facilitating fruits and vegetables, meats and aquatic products [218]; etc. Biomedical uses of BC have contributed at a high extent to patents on BC, including e.g. transparent polymeric composite material for use in osseous tissue support material, blood vessel prosthesis, and artificial skin biomedical material, made of BC membrane and poly(beta-hydroxyethyl methacrylic acid) [219]; cartilage-like biomaterial designed for reconstructive surgery comprising purified and modeled BC [220]; implantable support material used for culturing cells, maintaining and transporting viable cell sheets, in implants for e.g. cornea repair, cartilage repair, connective tissue repair and ligament repair [221]; bone cement useful in tool for fixing bone for preventing infectious diseases and infected fractures obtained by mixing bacterial cellulose powder carrying a medicinal agent [222]; etc. According to the IPC classification most BC patents correspond to fermentation or enzyme-using processes to synthesize a desired chemical compound or composition: polysaccharides (C12P19/04); as well as to indexing scheme relating to microorganisms/*Acetobacter* (C12R1/02). Table **7** summarizes the ten most cited patents on BC. By including the patents families the total number of patents covered by the search achieved 1762 documents.

Table 7 evidences the relevance of the American patent US4588400A on ¨Liquid loaded pad for medical applications¨ invented by Ring and coworkers in the mid- eighties. In the mentioned patent a medicinal pad for topical applica-

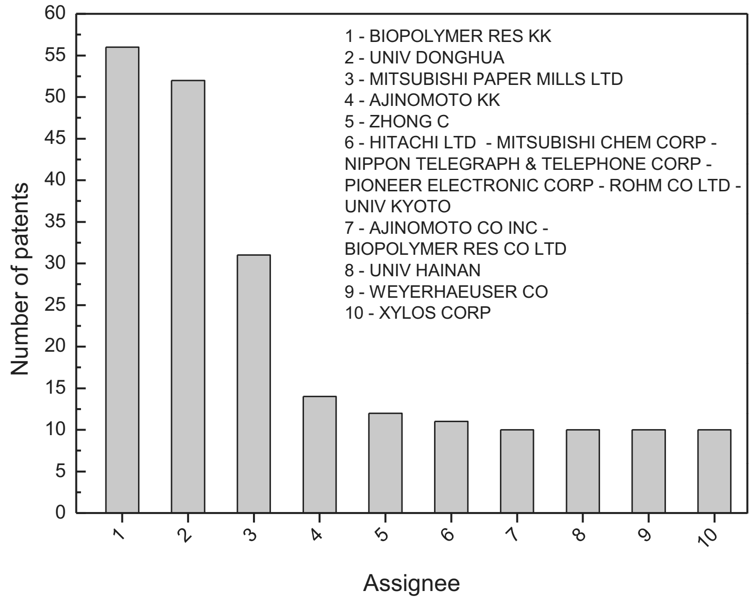

Fig. (13). Main bacterial cellulose patent owners. Descriptors used are the same as those used in Fig. (**12**).

tion consisting of a pellicle of microbially produced cellulose impregnated with a physiologically acceptable liquid is claimed [223]. Other documents included in Table 7 also have had a high number of citations, which implies that they had a significant influence on several later developments. Most of those technologies originated in the second half of the nineties, when composite materials had their break-through, and also when bacterial cellulose cultivation processes under different conditions and by use of a number of different strains were developed.

Fig. (**13**) summarizes the most prolific owners in the field of bacterial cellulose in terms of the total number of patents they own. The analysis was performed considering all patents included in Fig. (**12**). It is illustrated that a great part of bacterial cellulose technology is concentrated in three main competitors, namely the Japanese Biopolymer Res: KK -whose participation in the field of BC patents finished in 1999 (data not shown)-, the Chinese public University of Donghua which was originally a single-discipline textile institute; and Mitsubishi Paper Mills Ltd., a Japanese company involved in the production, processing, and sale of pulp, paper, and photosensitive materials. Many prolific competitors in the field are companies, which implies a high extent of technology application. Public institutions are also present in microbial cellulose field as it is the case of Donghua University, followed by the University of Kyoto (Japan), and the University of Hainan (China).

The analysis of the annual patents published by top assignees (data not shown) yields a profile with two maxima that resembles the one shown in Fig. (**12**) for total annual patents published on BC. Since the late eighties and till the last years of last century, the technology developed by Ajinomoto KK, Mitsubishi Paper Mills Ltd Mitsubishi, and Biopolymer Res: KK led to a high and continuously increasing number of patents, which had its maximum (close to 20 patents per year) in the years 1997-1998. The annual patents published by those companies experienced an abrupt decrease in the year 1999; and in the following years their participation on BC technology development was only marginal. By 2006 no patents by those once huge competitors were published, and the University of Donghua appeared as the main competitor in the field with more than fifty patents published in the last 6 years.

In terms of inventors, the most prolific one has been Kunihiko Watanabe (China), most of whose patents are owned by Bio Polymers: KK or Ajinomoto Co. Inc. Ajinomoto Co. Inc. is a Japanese company which makes foodstuffs, beverages, aspartame, amino and nucleic acids used in sweeteners, and cosmetics.

CURRENT & FUTURE DEVELOPMENTS

Although discovered several decades ago, interest in nanocellulose particles has experienced an outstanding rise during the last decade [29, 33]. The previous is based in the very attractive properties of nanocellulosics such as i.e. renewability, biodegradability, low density, high strength and stiffness, low thermal expansion, and high aspect ratio. Moreover, worldwide interest in nanotechnology and in the new properties that nanomaterials may have, has also played a role in the revived interest on nanocellulosic particles [233]. In the current review cellulose nanocrystals, microfibrillated cellulose, and bacterial cellulose have all shown to be technologies in which public institutions and companies are focused on. Patent trends analyzed in terms of the number of documents published every year, demonstrate that the years 2010 and 2011 have been the most prolific, and that figures are expected to go on rising in the next years.

In terms of patents transfer, cellulose nanocrystals show the lowest number of patents and their owners are mainly universities and public institutions. The previous suggests that nanowhiskers technology has not still been transferred to the private sector. Contrarily, a number of well-known huge companies are found among the assignees of microfibrillated cellulose and bacterial cellulose patents. Companies involved in nanocellulose field come mainly from the pulp and paper industry; and Japan, China, Canada, Finland, and Sweden appear as the countries which are pushing the advance of nanocellulose technology.

There are still a number of challenges to be addressed in nanocellulose technology which include e.g. reducing the amount of harsh acids used in nanocrystals preparation and finding easier recovery methods; and reducing the energy input and clogging problems in MFC production [6, 236]. In the case of MFC, oxidation and enzymatic pretreatments appear as emerging technologies which will make mechanical fibrillation a less demanding process. Microbially-produced cellulose is shown as a very promising route for the production nanocellulose, since fibers with nanosized diameters and with no need of hemicellulose/lignin removal, are relatively easily obtained. A challenge to address in bacterial cellulose technology is to find suitable carbon sources that are cheap and that do not compete with food production. In this context, agricultural residues may provide an interesting opportunity for introducing high-added-value nanocellulose technology in developing countries [178, 234, 235].

CONFLICT OF INTEREST

The authors have no conflicts of interest that are directly relevant to the content of this review.

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PATIENT CONSENT

Declared none.

REFERENCES

[1] Moon RJ, Martini A, Nairn J, Simonsen J, Youngblood J. Cellulose nanomaterials review: structure, properties and nanocomposites. Chem Soc Rev 2011; 40: 3941-94

[2] Azizi Samir MAS, Alloin F, Dufresne A. Review of recent research into cellulose whiskers: their properties and their application in nanocomposite field. Biomacromolecules 2005; 6: 612-26.

[3] Montanari S, Roumani M, Heux L, Vignon MR. Topochemistry of carboxylated cellulose nanocrystals resulting from TEMPO-mediated oxidation. Macromolecules 2005; 38: 1665-71.

[4] Hubbe MA, Rojas OJ, Lucia LA, Sain M. Cellulosic nanocomposites: a review. BioResources 2008; 3: 929-80.

[5] Sakurada I, Nukushina Y. Experimental determination of the elastic modulus of crystalline regions in oriented polymers. J Polym Sci 1962; 57: 651-60.

[6] Siro I, Plackett D. Microfibrillated cellulose and new composite materials: a review. Cellulose 2010; 17: 459-94.

[7] Ljungberg N, Bonini C, Bortolussi F, Boisson C, Heux L, Cavaillé JY. New nanocomposite materials reinforced with cellulose whiskers in atactic polypropylene: effect of surface and dispersion characteristics. Biomacromolecules 2005; 6: 2732-9.

[8] Uddin AJ, Araki J, Gotoh Y. Toward "strong" green nanocomposites: polyvinyl alcohol reinforced with extremely oriented cellulose whiskers. Biomacromolecules 2011; 12: 617-24.

[9] Xu Q, Yi J, Zhang X, Zhnag H. A novel amphotropic polymer based on cellulose nanocrystals grafted with azo polymers. Eur Polym J 2008; 44: 2830-7.

[10] Mahmoud KA, Male KB, Hrapovic S, Luong JH. Cellulose nanocrystal/gold nanoparticle composite as a matrix for enzyme immobilization. Appl Mater Interfaces 2009; 7: 1383-6.

[11] Dong S, Roman M. Fluorescently labeled cellulose nanocrystals for bioimaging applications. J Am Chem Soc 2007; 129: 13810-1.

[12] Noorani S, Simonsen J, Atre S. Nano-enabled microtechnology: polysulfone nanocomposites incorporating cellulose nanocrystals. Cellulose 2009; 14: 577-84.

[13] Birth of nanocellulose. Available at: http:// http://www.naylornetwork.com/PPI-OTW/articles/?aid=150993&issueID=22333 (Accessed on: Feb 23, 2012).

[14] Turbak AF, Snyder FW, Sandberg KR. Microfibrillated Cellulose, a new cellulose product: properties, uses, and commercial potential. *Proceedings of the Ninth Cellulose Conference* (Applied Polymer Symposia, 37: 815-27) New York, USA, 1983.

[15] Herrick FW, Casebier RL, Hamilton JK, Sandberg KR. Microfibrillated cellulose: morphology, and accessibility. *Proceedings of the Ninth Cellulose Conference* (Applied Polymer Symposia, 37: 797-813) New York, USA, 1983.

[16] Pääkkö M, Ankerfors M, Kosonen A, *et al*. Enzymatic hydrolysis combined with mechanical shearing and high-pressure homogenization for nanoscale cellulose fibrils and strong gels. Biomacromolecules 2007; 8: 1934-41.

[17] Henriksson M, Henriksson G, Berglund LA, Lindström T. An environmentally friendly method for enzyme-assisted preparation of microfibrillated cellulose (MFC) nanofibers. Eur Polym J 2007; 43: 3434–41.

[18] Saito T, Nishiyama Y, Putaux JL, Vignon M, Isogai A. Homogeneous suspensions of individualized microfibrils from tempo-catalyzed oxidation of native cellulose. Biomacromolecules 2006; 7: 1687-91.

[19] Suryanegara L, Nakagaito A, Yano H. Thermo-mechanical properties of microfibrillated cellulose-reinforced partially crystallized PLA composites. Cellulose 2010; 17: 771-8.

[20] Lu J, Wang T, Drzal LT. Preparation and properties of microfibrillated cellulose polyvinyl alcohol composite materials. Composites Part A 2008; 39: 738-46.

[21] Henriksson M, Berglund LA, Isaksson P, Lindstro□m T, Nishino T. Cellulose nanopaper structures of high toughness. Biomacromolecules 2008; 9: 1579-85.

[22] Iguchi M, Yamanaka S, Budhiono A. Review bacterial cellulose- a masterpiece of nature´s arts. J Mater Sci 2000; 35: 261-70.

[23] Hsieh Y-C, Yano H, Nogi M, Eichhorn SJ. An estimation of the Young's modulus of bacterial cellulose filaments. Cellulose 2008; 15: 507–13.

[24] Yamanaka S, Watanabe K, Kitamura N, *et al*. The structure and mechanical properties of sheets prepared from bacterial cellulose. J Mater Sci 1989; 24: 3141–5

[25] Nishi Y, Uryu M, Yamanaka S, *et al*. The structure and mechanical-properties of sheets prepared from bacterial cellulose. 2. Improvement of the mechanical-properties of sheets and their applicability to diaphragms of electroacoustic transducers. J Mater Sci 1990; 25: 2997–3001.

[26] Tajima K, Fujiwara M, Takai M, Hayashi J. Synthesis of bacterial cellulose composite by *Acetobacter xylinum*. I. Its mechanical strength and biodegradability. Mokuzai Gakkaishi 1995; 41: 749–57.

[27] Gindl W, Keckes J. Tensile properties of cellulose acetate butyrate composites reinforced with bacterial cellulose. Compos Sci Technol 2004; 64: 2407–13.

[28] Svensson A, Nicklasson E, Harrah T, *et al*. Bacterial cellulose as a potential scaffold for tissue engineering of cartilage. Biomaterials 2005; 26: 419-31.

[29] Durán N, Lemes AP, Seabra AB. Review of cellulose nanocrystals patents: preparation, composites and general applications. Recent Pat Nanotechnol 2012; 6: 16-28.

[30] Siqueira G, Bras J, Dufresne A. Cellulosic bionanocomposites: a review of preparation, properties and applications. Polymers 2010; 2: 728-65.

[31] Eichhorn SJ, Dufresne A, Aranguren M, *et al*. Review: current international research into cellulose nanofibres and nanocomposites. J Mater Sci 2010; 45: 1-33.

[32] Habibi Y, Lucia L, Rojas OJ. Cellulose nanocrystals: chemistry, self-assembly, and applications. Chem Rev 2010; 110: 3479–500.

[33] Klemm D, Kramer F, Moritz S, *et al*. Nanocelluloses: a new family of nature-based materials. Angew Chem Int Ed 2011; 50: 5438 – 66.

[34] Ioelovich M. Cellulose as a nanostructured polymer: a short review. BioResources 2008; 3: 1403-18.

[35] Bielecki S, Krystynowicz A, Turkiewicz M, Kalinowska H. In: Vandamme EJ, De Baets S, Steinbüchel A, Eds. Biopolymers, Vol 5. Germany: Wiley-VCH 2002: pp. 37-90.

[36] Clark J d'A. Pulp Technology and Treatment for Paper, 2nd ed. San Francisco: M. Freeman Publications 1985.

[37] Moran JI, Alvarez VA, Cyras VP, Vázquez A. Extraction of cellulose and preparation of nanocellulose from sisal fibers. Cellulose 2008; 15: 149-59.

[38] Beck-Candanedo S, Roman M, Gray DG. Effect of reaction conditions on the properties and behavior of wood cellulose nanocrystal suspensions. Biomacromolecules 2005; 6: 1048–54.

[39] Henriksson M, Berglund LA. Structure and properties of cellulose nanocomposite films containing melamine formaldehyde. J Appl Polym Sci 2007; 106: 2817-24.

[40] Lee SY, Mohan DJ, Kang IA, Doh G-H, Lee S, Han SO. Nanocellulose reinforced PVA composite films: effects of acid treatment and filler loading. Fibers Polym 2009; 10: 77-82.

[41] De Souza Lima MM, Borsali R. Rodlike cellulose microcrystals: structure, properties and applications. Macromol Rapid Commun 2004; 25: 771-87.

[42] Ranby BG. Aqueous colloidal solutions of cellulose micelles. Acta Chem Scand 1949; 3: 649-50.

[43] Ranby BG. Fibrous macromolecular systems. Cellulose and muscle. The colloidal properties of cellulose micelles. Discuss Faraday Soc 1951; 11: 158-64.

[44] Ranby BG, Ribi E. Uber den feinbau der zellulose. Experimentia 1950; 6: 12-4.

[45] Cellulose nanocrystals: From discovery to application (by Roman M and Winter WT). Available at: http://www.tappi.org/Downloads/unsorted/UNTITLED---06NANO09pdf.aspx (Accessed on: February 2, 2012).

[46] Mukherjee SM, Sikorski J, Woods HJ. Micellar structure of native cellulose. Nature 1951; 167: 821-2.

[47] Mukherjee SM, Sikorski J, Woods HJ. Electron-microscopy of degraded cellulose fibres. J Text Inst Trans 1952; 43: T196-T201.

[48] Mukherjee SM, Woods HJ. X-ray and electron microscope studies of the degradation of cellulose by sulphuric acid. Biochim Biophys Acta 1953**;** 10: 499–511.

[49] Battista OA. Hydrolysis and crystallization of cellulose. Ind Eng Chem 1950; 42: 502-7.

[50] Battista OA, Coppick S, Howsmon JA, Morehead FF, Sisson WA. Level-off degree of polymerization. Relation to polyphase structure of cellulose fibers. Ind Eng Chem 1956; 48: 333-5.

[51] Battista OA, Smith PA. Level-off d.p. cellulose products. US2978446A, 1961.

[52] Battista OA, Smith PA. Crystallite aggregates disintegrated in acid medium. US3141875A, 1964.

[53] Avicel PH Microcrystalline Cellulose, NF, Ph Eur., JP, BP. FMC Corp. Available at: http://www.fmcbiopolymer.com/Portals/bio/content/Docs/PS-Section%2011.pdf (Accessed on: Feb 3, 2012).

[54] FMC BioPolymer. Avicel for solid dose forms. Product Selection Table. Available at: http://www.fmcbiopolymer.com/Pharmaceutical/Products/Avicelforsoliddoseforms.aspx (Accessed on: Feb 3, 2012).

[55] Marchessault RH, Morehead FF, Walter NM. Liquid crystal systems from fibrillar polysaccharides. Nature 1959; 184: 632–3.

[56] Revol J-F, Bradford H, Giasson J, Marchessault RH, Gray DG. Helicoidal self-ordering of cellulose microfibrils in aqueous suspension. Int J Biol Macromol 1992; 14: 170-2.

[57] Revol JF, Godbout JDL, Gray DG. Solidified liquid crystals of cellulose with optically variable properties. WO1995021901A1, 1995.

[58] Favier V, Canova GR, Cavaillé JY, Chanzy H, Dufresne A, Gauthier C. Nanocomposite materials from latex and cellulose whiskers. Polym Adv Technol 1995; 6: 351-5.

[59] Favier V, Chanzy H, Cavaillé JY. Polymer nanocomposites reinforced by cellulose whiskers. Macromolecules 1995; 28: 6365-7.

[60] Kuga S, Umagoe A, Wada M, Nishiyama Y, Noisshiki Y. Silk fibroin/cellulose crystallite composite material and method for producing the same - A silk fibroin / cellulose fine-crystal composite material, and its manufacturing method. JP2003113312A, 2003.

[61] Cavaille JY, Dufresne Alain, Paillet M, Azizi Samir MAS, Alloin F, Sanchez JY. Materiau a conduction ionique renforce, son utilisation dans les electrodes et les electrolytes. FR2841255A1, 2003.

[62] Oksman K, Bondeson D, Syre P. Nanocomposites based on cellulose whiskers and cellulose plastics. US20080108772A1, 2008.

[63] Thomson SL, O'Callaghan DJ, Westland JA, Su B. Method of making a fiber cement board with improved properties and the product. US20100162926A1, 2010.

[64] Cho YG, Kim KY, Son SH, *et al*. Cellulose acylate films including cellulose nanocrystals with excellent mechanical properties and a method for manufacturing the same - The cellulose acylate film including the cellulose nano crystal and manufacturing method thereof. KR2011075991A, 2011.

[65] Hamad WY, Miao C. Nanocomposite biomaterials of nanocrystalline cellulose (NCC) and polylactic acid (PLA). US20110196094A1, 2011.

[66] Hamad WY, Su S. Thermoplastic nanocomposite material based on nanocrystalline cellulose (NCC). US20110201755A1, 2011.

[67] Pitchai-Mydeen SA, Yan N. Method of producing electrically conductive polymer and cellulose nanocomposites - Procédé de production de nanocomposites de polymère électriquement conducteur et de cellulose. WO2011140658A1, 2011.

[68] Jovanovic G, Atre SV, Paul BK, *et al.* Microfluidic devices, particularly filtration devices comprising polymeric membranes, and method for their manufacture and use. US7955504B1, 2011.

[69] Li Y-Q, Zheng Y-F. A chewable tablet for treating headache and its preparation method. CN101194965A, 2008.

[70] Wang, A-M, Li W. Bezoar pressure-reducing orally disintegratable tablet and preparation method thereof. CN101480482A, 2009.

[71] Piao GZ, Zhou K, Han Z, *et al.* Weak magnetic nanometer particle patterned macromolecule membrane, processing method and processing device. CN101428491A, 2009.

[72] Boluk Y, Zhao L. Aircraft anti-icing fluids formulated with nanocrystalline cellulose. US20100327215A1, 2010.

[73] Davalos RV, Rylander MN, Arena CB. Irreversible electroporation using nanoparticles, electroporation irréversible à l'aide de nanoparticules. WO2010151277A1, 2010.

[74] Beck S, Bouchard J, Berry R. Iridescent solid nanocrystalline cellulose films incorporating patterns and method for their production. US20100151159A1, 2010.

[75] Thielemans WAWI, Davies R. Cellulose nanoparticle aerogels, hydrogels and organogels - Aérogels, hydrogels et organogels à base de nanoparticules cellulosiques. WO2011030170A1, 2011.

[76] Landry V, Blanchet P. Coatings containing nanocrystalline cellulose, processes for preparation and use thereof - Revêtements contenant de la cellulose nanocristalline, procédés de préparation associés et utilisation associée. WO2011075837A1, 2011.

[77] Maclachlan MJ, Shopsowitz KE, Hamad WY, Qi H. Inorganic mesoporous materials with chiral nematic structures and preparation method thereof - Matériaux mésoporeux inorganiques ayant des structures nématiques chirales et procédé de préparation associé. WO2011123929A1, 2011.

[78] Jiang Z-H, Berry R, Bouchard J, Audet A. Adhesion with nanocrystalline cellulose - Adhésion à l'aide d'une cellulose nanocristalline. WO2011147029A1, 2011.

[79] Huang B, Chen X-R, Dai D-S, *et al.*Method for preparing nanocrystal cellulose by dissociating $ZnCl_2$. CN102093484A, 2011.

[80] Gardner DJ, Han Y, Peng Y. Method for drying cellulose nanofibrils. US20110260348A1, 2011.

[81] Beck S, Bouchard J, Berry R. Redispersible dried nanocrystalline cellulose - Cellulose nanocristalline séchée redispersible. WO2010066036A1, 2010.

[82] Beck S, Bouchard J, Berry R. Control of nanocrystalline cellulose film iridescence wavelength - Régulation de la longueur d'onde de l'iridescence de films de cellulose nanocristalline. WO2010124396A1, 2010.

[83] Revol JF, Godbout JDL, Gray DG. Solidified liquid crystals of cellulose with optically variable properties. US5629055A, 1997.

[84] Poulin P, Vigolo B, Launois P, Bernier P. Composite fibre reforming method and uses. US20040177451A1, 2004.

[85] Poulin P, Vigolo B, Launois P, Bernier P. Procede de reformage de fibres composites et applications. FR2828500A1, 2003.
[86] Bahr SR, Doyle N, Wang J, Winckler S, Takekoshi T. Macrocyclic polyester oligomers as flow modifier additives for thermoplastics. US20070173630A1, 2007.
[87] Bernier P, Vigolo B, Launois P, Poulin P. JP2005526186A, 2005.
[88] Paul BK, Jovanovic G. Microfluidic welded devices or components thereof and method for their manufacture. US20070125489A1, 2007.
[89] Bahr SR, Doyle N, Wang J, Winckler S, Takekoshi T, Wang YF. Macrocyclic polyester oligomers as carriers and/or flow modifier additives for thermoplastics. US20070216067A1, 2007.
[90] Bahr SR, Doyle N, Wang J, Winckler S, Takekoshi T, Wang YF. Oligomeres de polyester macrocycliques comme supports et/ou additifs de modification de flux pour matieres thermoplastiques. WO2007011684A2, 2007.
[91] Poulin P, Vigolo B, Launois P, Bernier P. Composite fibre reforming method and uses. US7288317B2, 2007.
[92] Hu AGZ, Jaffe AB. Patent citations and international knowledge flow: the cases of Korea and Taiwan. Int J Ind Organiz 2003; 21: 849-80.
[93] Turbak AF, Snyder FW, Sandberg KR. Food products containing microfibrillated cellulose. US4341807A, 1982.
[94] Turbak AF, Snyder FW, Sandberg KR. Microfibrillated cellulose. US4374702A, 1983.
[95] Turbak AF, Snyder FW, Sandberg KR. Suspensions containing microfibrillated cellulose. US4378381A, 1983.
[96] Turbak AF, Snyder FW, Sandberg KR. Suspensions containing microfibrillated cellulose. US4452722A, 1984.
[97] Turbak AF, Snyder FW, Sandberg KR. Suspensions containing microfibrillated cellulose. US4452721A, 1984.
[98] Turbak AF, Snyder FW, Sandberg KR. Suspensions containing microfibrillated cellulose. US4464287A, 1984.
[99] Herrick FW. Process for preparing microfibrillated cellulose. US4481077A, 1984.
[100] Herrick FW. Redispersible microfibrillated cellulose. US4481076A, 1984.
[101] Turbak AF, Snyder FW, Sandberg KR. Microfibrillated cellulose. US4483743A, 1984.
[102] Turbak AF, Snyder FW, Sandberg KR. Suspensions containing microfibrillated cellulose. US4487634A, 1984.
[103] Turbak AF, Snyder FW, Sandberg KR. Suspensions containing microfibrillated cellulose. US4500546A, 1985.
[104] Taabaku AF, Sunaidaa FU, Sandobaagu KR (original inventor) - Sandberg KR, Synder FW, Turbak AF (inventor DWPI). Microfibrous cellulose and its manufacture. JP56100801A, 1981.
[105] Herrick FW. Redispersable microfibrillated cellulose - Cellulose microfibrillée redispersable, Redispergierbare mikrofibrillierte cellulose. EP120471A2, 1984.
[106] Sandberg KR, Synder FW, Turbak AF. Microfibrillated cellulose. GB2066145A, 1981.
[107] Kotani M, Ueda S. Dew condensation water absorbing sheet. JP58201640A, 1983.
[108] Mori K. Fertilizer granulation. JP59039789A, 1984.
[109] Mori K. Preparation of solid fuel composition. JP59038290A, 1984.
[110] Komata M. Composition for multi-layer coating with decorative pattern. JP58198574A, 1983.
[111] Ikeda K. Water-color paint. JP58189268A, 1983.
[112] Mizuguchi K, Fujioka I, Kobayashi H. Preparation of retort food . JP58190382A, 1983.
[113] Mizuguchi K, Fujioka I, Kobayashi H. Liquid or pasty seasoning composition. JP58190369A, 1983.
[114] Mizuguchi K, Fujioka I, Kobayashi H. Bean jam or food composition prepared by using the same. JP58190352A, 1983.
[115] Takahashi O, Shiono H. Increasing of paper strength. JP58197400A, 1983.
[116] Kawai K, Kageyama S, Sugawara K. Method for determining cellulase activity. JP58202000A, 1983.
[117] Sugawara K, Kawai K, Kageyama S. Preparation of highly active immobilized biocatalyst. JP58212786A, 1983.
[118] Koyama T. Dentrifice composition. JP59033210A, 1984.
[119] Tsukamoto Y, Katsuyama A, Kurata T, *et al.* Inorganic material-containing paper. JP3113093A, 1991.
[120] Urdu M, Kurihara N. Method of producing an acoustic diaphragm - Procédé de fabrication d'une membane acoustique - Verfahren zur Herstellung einer akustichen Membran. EP457474A2, 1991.
[121] Baldwin SD, Gautam N, Houghton KS, Rogers RS, Ryder JL. Omslag foer roekningsprodukt foer reglering av foerbraenningshastigheten samt foerfarande foer framstaellning av detsamma. FI199204033A, 1993.
[122] Kawamura S, Iketani M, Tsutsui H. Polyester paper. JP6322695A, 1994.
[123] Aizawa W, Hyodo K, Ida T, Shigematsu T. Separator for alkaline secondary battery. JP10144282A, 1998.
[124] Takami K, Shibatani M. Production of absorbing sheet. JP11172558A, 1999.
[125] Shimoide A, Uemura K, Mukai K. Subsidiary material for compost preparation and preparation of compost . JP2000302801A, 2000.
[126] Okamoto F, Matsuda Y; Hata K. Sheet-like high absorbent and manufacturing method therefore. JP2002263136A, 2002.
[127] Harano Y, Nakamae T, Fuji T. Cosmetic pack agent - The pack agent for makeup, decoration. JP2006240994A, 2006.
[128] Sakuta N, Ohashi T. Polylactic acid-microfibrillated cellulose composite material and method for producing the same - A polylactic-acid-microfibril-forming cellulose composite material and its manufacturing method. JP2007238812A, 2007.
[129] Duesbury P, Davis M, Burnapp M. Diagnostic test device. GB2445160A, 2008.
[130] Takeda K. Optical component having reflecting surface - The optical component which has a reflective surface. JP2008165094A, 2008.
[131] Nakahara S. Resin composite material, its manufacturing method, and resin composite material molded article - A resin composite material, its manufacturing method, and a resin composite material molded,shaped object. JP2008184492A, 2008.
[132] Kurokawa M, Uchida N, Imazumi S, Eguchi F. Method for producing polyphenol-rich composition. US20090197942A1, 2009.
[133] Granberg H, Lindström M, Forsberg S, *et al.* Motion-controlled mechano-active materials - Matériaux mécano-actifs à mouvement contrôlé. WO2010005377A1, 2010.
[134] Takaoka K, Kato K. Separator for electrochemical element - The separator for electrochemical elements. JP2010067653A, 2010.
[135] Morii S, Betsumiya H. Film substrate - Film board, substrate. JP2010194790A, 2010.
[136] Bekku H. Reflector for solar thermal power generator - Réflecteur pour générateur d'énergie héliothermique. WO2010106844A1, 2010.
[137] Takahashi S. Fiber cord for reinforcing rubber and pneumatic radial tire using the same - The fiber cord for rubber reinforcement, and a pneumatic radial tire using the same. JP2010275642A, 2010.
[138] Albertsson AC, Edlund U. Barrier layer for a packaging laminate and packaging laminate comprising such barrier layer - Couche barrière pour un stratifié d'emballage et stratifié d'emballage comprenant une telle couche barrière. WO2011005181A1, 2011.
[139] Nakatsuji T, Fujii T, Okubo K, Kotakeuchi K, Takeuchi Y. Carbon fiber-reinforced carbon composite material and method for manufacturing the same - A carbon-fiber-reinforced carbon composite material and its manufacturing method. JP2011046543A, 2011.
[140] Laukkanen A, Teirfolk JE, Leivo M, Kuosa H, Kataja K, Nurmi A. Materiaali käytettäväksi betonin lisäaineena - Ett material för användning som betongtillsatsämne. FI200906009A, 2011.
[141] Berglund L, Liu A. Strong nanopaper - Nanopapier resistant. WO2011059398A1, 2011.
[142] Axrup L, Heiskanen I, Backfolk K. Ett pappers eller kartongsubstrat, en process för tillverkning av substratet och en förpackning bildad av substratet. SE 200950995A1, 2011.
[143] Laukkanen A, Teirfolk JE, Salmela J, Lille M. Aine ja koostumus öljykenttäsovelluksiin - Ämne och sammansättning för oljefältstillämpningar. FI201000022A, 2011.
[144] Flynn N, Kelly HT, Walter JS. Wound dressing - Pansement pour plaie. WO2011116069A1, 2011.
[145] Malmborg K, Heijnesson-Hultén AM, Sandström J. Cellulosic barrier composition comprising anionic polymer - Composition barrière cellulosique comprenant un polymère anionique. WO2011147823A1, 2011.
[146] Rasmussen RR, Govang PJ, Poppe CD, Schryver TPG, Marshall K, Vera A. Biodegradable vehicle panels - Panneaux de véhicule biodégradables. WO2011150207A1, 2011.

[147] Matsuda Y, Hirose M, Ueno K. Ultrafine fibrillated cellulose and its production, production of coated paper using the ultrafine fibrillated cellulose and production of dyed paper. JP8284090A, 1996.
[148] Suzuki M, Hattori Y. Method and apparatus for producing microfibrillated cellulose - Procede et appareil de production de cellulose microfibrillee. WO2004009902A1, 2004.
[149] Heijnesson-Hulten A. Method of preparing microfibrillar polysaccharide. AU2006262963A1, 2007.
[150] Lindstrom T, Ankerfors M, Henriksson G. Method for the manufacturing of microfibrillated cellulose - Procede de fabrication de cellulose microfibrillee. CA2641607A1, 2007.
[151] Wichmann JU, Haugen Ø. Method for producing microfibrillated cellulose - Verfahren zur herstellung von mikrofibrilierter cellulose - Procédé de fabrication de cellulose microfibrillé. EP2196579A1, 2010.
[152] Vehvilaeinen M, Kamppuri T, Peltola M, Harlin A, Nousiainen P. Metod för framställning av mikrofibrillär cellulose. SE533510C2, 2010.
[153] Heiskanen I, Harlin A, Backfolk K, Laitinen R. Process for production of microfibrillated cellulose in an extruder and microfibrillated cellulose produced according to the process - Procédé de production de cellulose microfibrillée dans une extrudeuse et cellulose microfibrillée produite selon le procédé. WO2011051882A1, 2011.
[154] Øevrebøe HH, Wichmann J-U, Opstad A, Holtan S. Method for drying microfibrillated cellulose - Procede de sechage de cellulose microfibrillee. CA2754988A1, 2010.
[155] Gardner DJ, Han Y, Peng Y. Method for drying cellulose nanofibrils. US20110260348A1, 2011.
[156] Baldwin SD, Gautam N, Houghton KS, Rogers RM, Ryder JL. Smoking article wrapper for controlling burn rate and method for making same. US5417228A, 1995.
[157] Baldwin SD, Gautam N, Houghton KS, Rogers RM, Ryder JL. Smoking article wrapper for controlling burn rate and method for making same. US5263999A, 1993.
[158] Dinand E, Chanzy H, Vignon MR, Maureaux A, Vincent I. Microfibrillated cellulose and method for preparing a microfibrillated cellulose. US5964983A, 1999.
[159] Innami S, Fukui Y. Additive composition for foods or drugs. US4659388A, 1987.
[160] Cash MJ, Chan AN, Conner HT, Cowan PJ, Gelman RA, Lusvardi KM, Thompson SA, Tise FP. Derivatized microfibrillar polysaccharide. O2000047628A2, 2000.
[161] Isogai A, Saito T, Nishiyama Y, Pataux JL, Vignon M. Fine cellulose fiber. JP2008001728A, 2008.
[162] Isogai A, Saito T. Cellulose nanofiber and process for production thereof, and cellulose nanofiber dispersion. WO2009069641A1, 2009.
[163] Kawasaki K, Higata T, Miyawaki S, *et al.* Printing paper - Print sheet. JP2009263850A, 2009.
[164] Miyawaki S, Katsukawa S, Abe H, Iijima Y, Isogai A. Process for production of cellulose nanofiber, catalyst for oxidation of cellulose, and method for oxidation of cellulose. WO2009084566A1, 2009.
[165] Miyawaki S, Katsukawa S, Abe H, Iijima Y, Isogai A. Additive for papermaking and paper containing the same. WO2009122982A1, 2009.
[166] Miyawaki S, Katsukawa S, Abe H, Iijima Y, Isogai A. Method for oxidizing cellulose, oxidation catalyst for cellulose, and method for producing cellulose nano-fiber. JP2009161613A, 2009.
[167] Miyawaki S, Katsukawa S, Abe H, Iijima Y, Isogai A. Additive for papermaking and paper containing the same. JP2009263848A, 2009.
[168] Yamada Y, Okamoto T, Miyawaki S, Katsukawa S, Abe Y, Iijima Y, Isogai A. Coated paper for gravure printing. JP2009263854A, 2009.
[169] Miyawaki S, Katsukawa S, Abe H, Iijima Y, Isogai A.Method for manufacturing cellulose nano-fiber. JP2010235679A, 2010.
[170] Endo R, Oishi K, Yasushiro H. Cellulose nanofiber compound polyvinyl alcohol-based polymer composition. JP2010242063A, 2010.
[171] Lindström T, Ankerfors M, Henriksson G. Method for the manufacturing of microfibrillated cellulose. WO2007091942A1, 2007.
[172] Henriksson M, Berglund L, Zhou Q, Bulone V. Method of producing and the use of microfibrillated paper. US20100065236A1, 2010.
[173] Shibuya H, Hayashi N. Cellulose nano-fiber and method for producing the same. JP2008150719A, 2008.
[174] Wichmann J-U, Haugen Ø. Method for producing microfibrillated cellulose. EP2196579A1, 2010.
[175] Miyawaki S, Katsukawa S, Abe H, Iijima Y, Isogai A. Process for producing cellulose nanofibers. WO2010116826A1, 2010.
[176] Miyawaki S, Katsukawa S, Abe H, Iijima Y, Isogai A. Method for manufacturing cellulose nano-fiber. JP2010235679A, 2010.
[177] Jin H, Pääkkö M, Ikkala O, Ras RH. Liquid-repellent material. WO2011001036A1, 2011.
[178] Castro C, Zuluaga R, Putaux J-L, Caroa G, Mondragon I, Gañan P. Structural characterization of bacterial cellulose produced by *Gluconacetobacter swingsii sp*. from Colombian agroindustrial wastes. Carbohyd Polym 2011; 84: 96-102.
[179] Putra A, Kakugo A, Furukawa H, Gong JP, Osada Y. Tubular bacterial cellulose gel with oriented fibrils on the curved surface. Polymer 2008; 49: 1885-91.
[180] Chawla PR, Bajaj IB, Shrikant AS, Singhal RS. Fermentative production of microbial cellulose. Food Technol Biotechnol 2009; 47: 107-24.
[181] El-Saied H, Basta AH, Gobran RH. Research progress in friendly environmental technology for the production of cellulose products (bacterial cellulose and its application). Polym Plast Technol Eng 2004; 43: 797–820.
[182] Yamada Y, Hoshino K, Ishikawa T. The phylogeny of acetic acid bacteria based on the partial sequences of 16S ribosomal RNA: the elevation of the subgenus *Gluconoacetobacter* to the generic level. Biosci Biotechnol Biochem 1997; 61: 1244-51.
[183] Yamada Y. Transfer of *Acetobacter oboediens* and *Acetobacter intermedius* to the genus *Gluconacetobacter* as *Gluconacetobacter oboediens* comb. nov. and *Gluconacetobacter intermedius* comb. nov. Int J Syst Evol Microbiol 2000; 50: 2225-7.
[184] Valla S, Kjosbakken J. Cellulose-negative mutants of *Acetobacter xylinum*. J Gen Microbiol 1982; 128: 1401-8.
[185] William WS, Cannon RE. Alternative environmental roles for cellulose produced by *Acetobacter xylinum*. Appl Environ Microbiol 1989; 55: 2448–52.
[186] Brown AJ. On an acetic ferment which forms cellulose. J Chem Soc 1886; 49: 172–86.
[187] Brown AJ. An acetic ferment which forms cellulose. J Chem Soc 1886; 49: 432-9.
[188] Hestrin S, Aschnerm M, Mager J. Synthesis of cellulose by resting cells of *Acetobacter xylinum*. Nature 1947; 159: 64-5.
[189] Hestrin S, Schramm M. Synthesis of cellulose by *Acetobacter xylinum*. II. Preparation of freeze-dried cells capable of polymerizing glucose to cellulose. Biochem J 1954; 58: 345-52.
[190] Colvin JR. Formation of cellulose micro-fibrils in a homogenate of *Acetobacter xylinum.* Arch Biochem Biophys 1957; 70: 294-5.
[191] Bicerano J, Brewbaker JL. Reinforcement of polyurethane elastomers with microfibres having varying aspect ratios. J Chem Soc Faraday Trans 1995; 91: 2507-13.
[192] Bourne EJ, Stacey M, Tatlow JC. Improvements relating to the esterification of hydroxy-compounds. GB684754A, 1952.
[193] Unger E, Riessner O, Merkel U, Correns E, Purz H-J, Schwarz H-H. Verfahren zur herstellung von elektrischem isoliermaterial. DD132512A1, 1978.
[194] Ring DF, Nashed W, Dow T. Foer medicinska aendamaol avsedd vaetskeimpregnerad saordyna. FI198304623A, 1984.
[195] Iguchi M, Mitsuhashi S, Ichimura K, *et al.* Moulded material comprising bacteria-produced cellulose - Formmasse auf basis von bakteriell hergestellter cellulose - Matériel moulu comprenant de la cellulose préparée par des bactéries. EP200409A2, 1986.
[196] Fiedler S, Sattler K, Verfahren zur immobilisierung von biologischem material. DD242822A1, 1987.
[197] Ben Bassat A, Bruner R, Shoemaker SP *et al*. Reticulated cellulose product, sheets formed therefrom, methods and microorganisms for their production. Produkt auf basis von vernetzter zellulose, daraus geformte filme, verfahren und mikroorganismen zu dessen herstellung. Produit à base de cellulose. EP228779A2, 1987.
[198] Kitamura N, Yamaya E. Glass fiber sheet. JP1014399A, 1989.
[199] Yamashita S, Takehara M. Plaster for oral cavity application. JP1050815A, 1989.
[200] Takai M, Nonomura F, Hayashi J, Fukaya M, Okumura H. Filter membrane containing bacterized cellulose. JP1199604A, 1989.
[201] Saka S. Speaker diaphragm. JP1231599A, 1989.

[202] Stephens RS, Westland JA, Neogi AN. Method of using bacterial cellulose as a dietary fiber component. US4960763A, 1990.
[203] Kurosawa K, Watabe O, Goto Y. Water retaining agent-containing microcapsule. JP2241537A, 1990.
[204] Penny GS, Stephens RS, Winslow AR. Method of supporting fractures in geologic formations and hydraulic fluid composition for same. US5009797A, 1991.
[205] Yamanaka S, Ono E, Watanabe K, Kusakabe M, Suzuki Y. Hollow microbial cellulose, process for preparation thereof, and artificial blood vessel formed of said cellulose - Hohle mikrobielle zellulose, verfahren zur herstellung und kuenstliches blutgefaess, hergestellt aus dieser zellulose - Cellulose microbien. EP396344A2, 1990.
[206] Ono E, Yamanaka S, Rubber compounding composition. JP5301994A, 1993.
[207] Kaneko K, Morinaga Y, Yoshinaga F. Artificial soil composition. JP7298777A, 1995.
[208] Fujita M, Katsura T. Packaging paper. JP9195193A, 1997.
[209] Kaneko K, Watabe O. Edible bacterial cellulose composition. JP10117705A, 1998.
[210] Hioki S, Azuma Y. Adsorptive photocatalytic sheet. JP10263411A, 1998.
[211] Suzuki M, Kitamura N, Matsumoto R. Highly absorbing composite material. JP11172115A, 1999.
[212] Klemm D, Marsch S, Schumann D, Udhardt U. Method and device for producing shaped microbial cellulose for use as biomaterial, especially for microsurgery - Procede et dispositif de production de cellulose microbienne moulee destinee a servir de biomateriau, notamment pour la microchirurgie, verfa. WO2001061026A1, 2001.
[213] Ogiya H. Coagulant, coagulant, flocculant. JP2002355505A, 2002.
[214] Evans BR, O'Neill HM, Jansen VM, Woodward J. Metallization of bacterial cellulose for electrical and electronic device manufacture. US20030113610A1, 2003.
[215] Seliktar D, Almany L. Matrix comprising naturally-occurring protein backbone - Matrice comprenant un squelette proteique reticule naturel. WO2005061018A1, 2005.
[216] Koshobu N, Matsuura T, Kurihara T, Maruno T, Yano H, Atagi M. Low thermal expansion optical waveguide film , low thermally-expansible optical-waveguide film. JP2006208982A, 2006.
[217] Uraki Y, Ubukata M, Yabu H, Tanaka M, Shimomura M. Honeycomb porous body of bacterial cellulose and method for producing the honeycomb porous body, the honeycomb porous body which consists of a microorganisms cellulose, and a method of manufacturing the same. JP2006325534A, 2006.
[218] Zhong CY, Zhong YG. Edible food packaging film. CN102145779A, 2011.
[219] Wan Y-Z, Zhang Y-S, He F, Huang Y, Luo HL. Bacterial cellulose and polymethacrylic acid beta hydroxy ethyl transparent compound material and preparation . CN101274107A, 2008.
[220] Bielecki S, Kolodziejczyk M, Kowalska K, Krystynowicz A, Pankiewicz T. A method of production of a cartilage-like biomaterial designed for reconstructive surgery - Eine Methode zur Produktion von Knorpel-ahnlichem Material für die rekonstruktive Chirurgie - La methode de la formation de biomateriel avec la specificite de car. EP2371401A2, 2011.
[221] Serafica G, Ace C, Donlin J, Wang J. Supporting material for cell sheet. US20110287079A1, 2011.
[222] Mori R, Nakai T, Yoshino K. Bone cement - Ciment osseux. WO2011086788A1, 2011.
[223] Ring DF, Nashed W, Dow T. Liquid loaded pad for medical applications. US4588400A, 1986.
[224] Baldwin SD, Gautam N, Houghton KS, Rogers RM, Ryder JL. Smoking article wrapper for controlling burn rate and method for making same. US5417228A, 1995.
[224] Iguchi M, Mihashi S, Ichimura K, *et al.* Bacterial cellulose-containing molding material having high mechanical strength. JP62036467A, 1987.
[225] Baldwin SD, Gautam N, Houghton KS, Rogers RM, Ryder JL. Smoking article wrapper for controlling burn rate and method for making same. US5263999A, 1993.
[226] Johnson DC, Neogi AN. Sheeted products formed from reticulated microbial cellulose. US4863565A, 1989.
[227] Hoff RE, Cribbs LV. Polymerization catalyst and method. US5198399A, 1993.
[228] Iguchi M, Mitsuhashi S, Ichimura K, *et al.* Bacterial cellulose-containing molding material having high dynamic strength. US4742164A, 1988.
[229] Westland JA, Stephens RS, Johnston JWC, Rosenkrans HJ. Bacterial cellulose binding agent. US5207826A, 1993.
[230] Ring DF, Nashed W, Dow T. Liquid loaded pad for medical applications. GB2131701A, 1984.
[231] Ring DF, Nashed W, Dow T. Microbial polysaccharide articles and methods of production. US4655758A, 1987.
[232] Brown RM. Microbial cellulose modified during synthesis. US4942128A, 1990.
[233] Technology Roadmap. Applications of Nanotechnology in the Paper Industry. Available at: https://www.jyu.fi/science/muut_yksikot/nsc/en/pdf/nanopap (Accessed on: March 21, 2012).
[234] Rani MU, Navin KR, Anu Appaiah KA. Statistical optimization of medium composition for bacterial cellulose production by *Gluconacetobacter hansenii* UAC09 using coffee cherry husk extract – an agro-industry waste. J Microbiol Biotechnol 2011; 21: 739–745.
[235] Moosavi-Nasab M, Yousefi A. Biotechnological production of cellulose by *Gluconacetobacter xylinus* from agricultural waste. Iranian Journal of Biotechnology 2011; 9: 94-101.
[236] Da Silva Perez D, Dufresne A. Overview of cellulose nanocrystals and nanofibres: the science and technology – A European perspective. *OECD Conference on Potential Environmental Benefits of Nanotechnology: Fostering Safe Innovation-Led Growth OECD Conference Centre*. Paris, France, July 15-17, 2009.