USE OF NANOTECHNOLOGY FOR HIGH PERFORMANCE CELLULOSIC AND PAPERMAKING PRODUCTS

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Nanotechnology is of great importance in almost all modern day industries targeting high quality, efficiency and market potential. The large interest in the nano-scale range is due to the fact that nanomaterials can have enhanced properties, as compared to the same material with larger particle size. The modification of cellulose into different types of micro- and nano-structures has been reported in literature. In papermaking, nanotechnological advances were reported about a decade ago, though it could not be commercialized at a large scale. Nanofiber, nanofiller, nanocomposites and nanoscale chemicals to be used in pulp and paper applications are in main focus. Because of the wide abundance, renewable and environmentally benign nature, and outstanding mechanical properties of nano-based cellulosic materials, great attention has been paid to their use in pulp and paper, and other industries. There are a few challenges associated with their efficient use at a commercial scale, such as cost, lack of compatibility among materials and knowledge gap. This review of recent work discusses the manufacturing, application and properties of different nanoparticles and nano-based technological developments reported by researchers worldwide, related to cellulose and paper manufacturing.

Keywords: Cellulose, microcrystalline cellulose, microfibrillated cellulose, nanocomposites, nanofiller, nanofiber

INTRODUCTION

Nanotechnology deals with natural and artificial structures on the nanometer scale, *i.e.* in the range of 1 µm to 10 Å. One nanometer (1 nm) is one-billionth of a meter (1 m); roughly the distance from one end to the other of a line of five neighboring atoms in an ordinary solid.[1] To put this size in perspective, a sheet of writing paper is about 100000 nm thick; 10 hydrogen atoms laid in a row are one nanometer wide.[2]

Nanotechnology is expected to be a critical driver of global economic growth and development in the near future. Already, this broad multi-disciplinary field is providing glimpses of exciting new capabilities, enabling materials, devices and systems that can be examined, engineered and fabricated at the nanoscale. Using nanotechnology to controllably produce nanomaterials with unique properties is expected to revolutionize technology and industry.

The purpose of nanotechnology is to control and manipulate materials to obtain a special function. Nanotechnology is a new tool added in the recent years in a wide range of applications; pulp and paper is one of them. In recent years many research works have been carried out by researchers worldwide on the use of nanotechnology in many areas of technology. Figure 1 indicates the researchers' awareness of the subject and undoubtedly its importance. The number of publications in the area of nanotechnology since 1978 has increased several times. Figure 2 shows the number of publications in different application areas of nanotechnology. Nanotechnogical applications are the highest in the packaging segment, followed by electronics, pharmaceuticals, plastics, cosmetics and others including paper coating.[3]

Paper is a material made of cellulosic fibers, derived mainly from wood, rags, and certain grasses, processed into flexible sheets or rolls by deposit from an aqueous suspension. Cellulose is a high molecular weight, stereoregular and linear polymer of repeating beta-D-glucopyranose units. It is the principal structural element and major constituents of the cell wall of trees and plants. The empirical formula for cellulose is $(C_6H_{10}O_5)_n$, where 'n' is degree of polymerization.

The pulp and paper industries aim to better utilize all the components that are available in wood and wood-based materials. New methods for liberating these materials, including nano-dimensional cellulose fibrils, macromolecules and nanominerals, will be needed in order to use the techniques developed for other nanomaterials as platforms for creating new wood-based materials and products. Nanotechnology holds the promise of changing virtually all of the processes by which wood and paper products are now made, transforming the sector from a resource-based to a knowledge-based industry with much greater prospects for long-term stability.

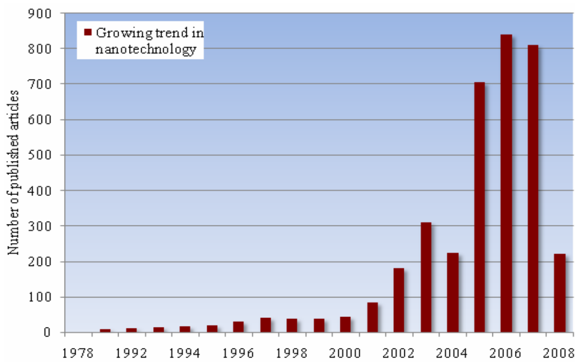

Figure 1: Growing trend in nanotechnology[3]

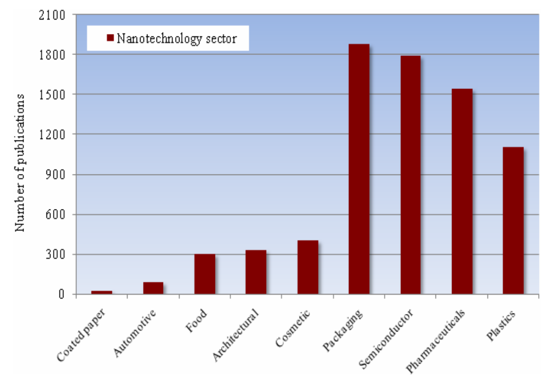

Figure 2: Nanotechnology based on the application in various market segments[3]

Research is showing the way to increase performance and add value in a host of traditional forest-based products. Initiatives to provide greater strength, water resistance, fire-retardancy and new forms of packaging are showing great promises in this area. These contemplations give an insight to envisage the role of nanotechnology-based materials in pulp and paper industry. The aim of this paper was to highlight the recent developments on the role of nanotechnology in pulp and paper industry by reviewing the existing literature, present the authors' perspective and suggest directions for future research.

NANOTECHNOLOGICAL DEVELOPMENTS IN PULP AND PAPER

Nanotechnology may have an unforeseen impact on forest-based paper industry. Many novel materials have been developed and fundamental studies have been carried out in different areas. The examples on nanomaterials and nanostructures of interest or potential in the forest products sector are given below:[4-7]

- Monolayers or multilayers by selective adsorption of polymers and biopolymers
- Exfoliated clays, such as montmorillonite and hectorite for coating and barrier films
- Engineered surfaces with tailored properties by the use of enzymes for selective removal of fiber constituents, such as hemicelluloses or chemo-enzymatic modification
- Topochemical modification by surface selective chemical and physical reactions
- Micro and mesopores in wood and pulp fiber cell walls
- Isolated cellulose fibrils and fibril aggregates, such as microfibrillated cellulose (MFC), microcrystalline cellulose (MCC) and cellulose whiskers
- Inorganic nanoparticles and colloids, and organic nanoparticles, such as dendrimers
- Nanoscale pores in paper coatings

Three types of nanocellulosic materials have been investigated in recent decades. The first is microfibrillated cellulose, which is prepared by mechanical processes that involve very high shear forces to defibrillate cellulose fibers, the second – cellulose nanocrystals, which are prepared by the acid hydrolysis of cellulose fibers, followed by mechanical action, and the third – nanocomposites, which may be the combination of first and second types of nanocellulosic materials, along with polymers or other matrices.

Microfibrilated/microcrystalline cellulose

The fiber wall thickness is roughly between 1 and 5 µm. The fiber wall is composed of defined layers, including the primary wall (P) and several secondary wall layers (S1, S2 and S3) (Figure 3).

Each of these layers is characterized by a specific arrangement of fibrils. Chemical pulp fibers have a surface, which is characterized by a particular pattern created by wrinkles and microfibrils in the outer layers of the fiber wall structure.[8,9] The microfibrils are generally 2-10 nm thick fibrous cellulose structures.[9] The diameter of microfibrils may vary depending upon the origin. In wood, the lateral dimension for microfibrils is around 3-5 nm.[10,11] "Nanofibril" and "nanofiber" are also used as synonyms for "microfibril".[12] Microfibrils are agglomerates of elementary fibrils and always have diameters which are multiples of 3.5 nm.[13]

Microfibrillated cellulose (MFC) was introduced in 1983.[14,15] The MFC could be as small as 3-10 nm in thickness with typically a broad range of 20-40 nm, since it consists of aggregates of cellulose microfibrils.[16] The properties of MFC have been previously reviewed by Siro and Plackett.[12] Researchers have used different terminology for describing MFC. Those mainly include microfibril,[17-20] microfibril aggregates,[21-23] microfibrillar cellulose,[24-26] nanofibril,[27,28] nanofiber[24,29,30] and nanofibrillar cellulose.[24,26,27,31,32]

The acid hydrolysis of cellulose microfibrils followed by sonication gives a rod-like material with a relatively low aspect ratio referred to as cellulose whiskers.[33] The typical diameter and length distribution of cellulose whiskers is around 2-20 and 100-600 nm, respectively.[34] Other terms used for cellulose whiskers include nanowhiskers,[35-40] nanorods[41,42] and rod-like cellulose crystals.[23] Due to the near perfect crystalline arrangement of cellulose whiskers, this form of nanocellulose has a high modulus and therefore significant potential as a reinforcing material.[43]

The microcrystalline cellulose (MCC) is formed through strong hydrogen bonding among individual cellulose crystals/whiskers, which promotes reaggregation during spray-drying procedures.[44] Their length is generally greater than 1 μm.[33,45,46] MCC is a commercially available material widely used as a rheology control agent and as a binder in the pharmaceutical industry.[46] Though all of these terms have been used by different investigators for same purpose, they have slight difference in their length and width as shown in Table 1.[12,34,41,45]

The production of MFC into nanoscale elements requires intensive mechanical treatment. However, depending upon the raw material and the degree of processing, chemical treatment may be applied prior to mechanical fibrillation. The enzymatic pretreatment prior to mechanical action has also been tried in the literature, which has shown reduction in energy demand.[22,47] Siro and Plackett[12] have reviewed the production mechanisms and properties of MFC and reported the following routes of treatments for the production of MFC:

Mechanical:

- Refining and high-pressure homogenization
- Cryocrushing
- Grinding

Pretreatments:

- Alkaline pretreatment
- Oxidative pretreatment
- Enzymatic pretreatment

In general terms, the production of homogeneous fibril qualities may require major costs, including costs related to pretreatments and energy consumption during production. The less energy is utilized, the less is the fibrillation of cellulose fibers and the less the amount of produced nanofibrils. Conventional fibrillation (e.g. homogenization without pretreatment) produces a material that is inhomogeneous and may contain a major fraction of poorly fibrillated fibers and fines. MFC *per se* is not necessarily a nanomaterial, but contains nanostructures, *i.e.* nanofibrils.

Table 1
Nanocellulose dimensions[12,34,41,45]

Cellulose structure	Length (nm)	Diameter (nm)	Aspect ratio (L/d)
Microfibril	>10000	2-10	>1000
MFC	>1000	10-40	100-150
Cellulose whisker	100-600	2-20	10-100
MCC	>1000	>1000	~1

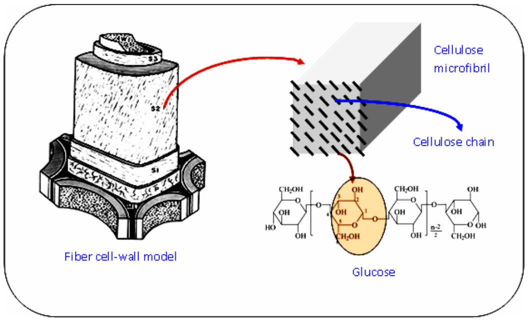

Figure 3: The structure of wood cell and cellulose microfibril[8,11]

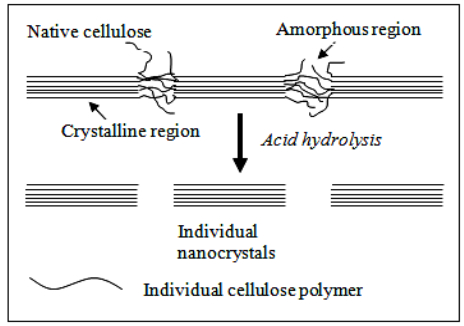

Figure 4: Schematic diagram of acid hydrolysis of cellulose and generation of nanocrystals[50]

To define MFC as a nanostructure, it is necessary to give substantial evidence with respect to (1) the fraction of fibrillated fibers, (2) the fraction of nanofibrils and (3) the morphology of the nanofibrils in a MFC material. Provided that a given MFC is composed of an appropriate fraction of individualized nanofibrils, the MFC will have a positive impact on the rheological, optical, mechanical and barrier properties of the corresponding materials.

MFC has shown many potential achievements at laboratory and pilot scales, but still there are challenges to produce them at a commercial scale. The high need of the mechanical energy in the production of MFC is the major obstacle. The energy consumption could be reduced significantly with selection of an appropriate chemical or enzyme pretreatment process.[12,22,47]

Cellulose nanocrystals

Cellulose is the most abundant biological polymer on the planet and it is found in the cell walls of plant and bacterial cells. Composed of long chains of glucose molecules, cellulose fibers are arranged in an intricate web that provides both structure and support for the cell. Interestingly, within the jungle of fibers there are regions that are very well ordered: chains are aligned parallel and are packed close together. Crystalline is the name given to these unique fiber regions which often measure between micrometers and nanometers in length.[48] Cellulose is one of the most abundant natural biopolymers, which, upon acid hydrolysis, yield highly crystalline rod-like rigid hydrophilic particles having nanoscale dimensions. The yield increases with time, temperature and acid concentration.[49]

Individual cellulose nanocrystals are produced by breaking down the cellulose fibers and isolating the crystalline regions. Strong acid hydrolysis, a process described nearly 60 years ago by Ranby[50] has been used to isolate the cellulose nanocrystals. Figure 4 shows the hydrolysis of native cellulose structure through the use of acid, which breaks down the amorphous region of cellulose and isolates the crystalline region, *i.e.* nanocrystals or nanocrystalline cellulose (NCC).

The production of cellulose nanocrystals involves chemical treatment. Strong acids, such as sulfuric, nitric and hydrochloric acid, have been shown to successfully degrade cellulose fibers. The reaction with sulfuric acid has been extensively investigated and it appears that the latter is the most effective. The current accepted explanation depicts this process of acid hydrolysis as a heterogeneous process that involves the diffusion of acid into the cellulose fibers, followed by the cleavage of glycosidic bonds.[51,52]

The type, concentration of acid, time and temperature during hydrolysis are the factors that affect the quality of cellulose nanocrystals produced through the hydrolysis process. It is believed that acid interacts mainly with the amorphous regions of cellulose, as they are the most easily accessible and have the greatest surface area. Therefore, the amorphous regions are the first to be targeted by the strong acid, followed by regions of increased crystallinity. A controlled hydrolysis can, therefore, extract regions of a specific crystallinity from a cellulose sample.

Bai *et al.*[52] used sulfuric acid hydrolysis process for the production of NCC. The aspect ratio of NCC produced in different fractions of differential centrifugation technique had a relatively narrow range. This was an easy process to produce NCC whiskers with a narrow size distribution. Bondeson *et al.*[53] also used sulfuric acid hydrolysis process using microcrystalline cellulose as the initial reagent, and performed a systematic analysis of nanocrystals. With a sulfuric acid concentration of 63.5% (w/w) and a hydrolysis time of approximately 2 hours, it was possible to produce cellulose nanocrystals with lengths between 200 and 400 nm, and widths less than 10 nm. The overall yield of NCC was approximately 30% of the initial biomass. When sulfuric acid is used as a hydrolyzing agent, it reacts with the surface hydroxyl groups of cellulose to yield charged surface sulfate esters that promote dispersion of the NCC in water. However, the introduction of charged sulfate groups compromises the thermostability of the nanocrystals. The prolongation of the hydrolysis time induced a decrease in the length of nanocrystals and an increase in surface charge.[53-55]

Zimmermann *et al*.[56] separated nanofibrillated cellulose (NFC) at the greatest possible lengths and diameters below 100 nm from different starting cellulose materials. In addition, the suitability of the obtained NFC, together with two commercial fibrillar-fibrous cellulose products for the reinforcement of polymers, was determined by tensile testing. They found that cellulose fibrils with diameters below 100 nm and lengths in the micrometer range could be isolated out of different raw materials using mechanical dispersion and high-pressure homogenization processes, resulting in nanoscaled fibril networks.

The tensile strength, modulus of elasticity and density of cellulose nanocrystals and other metallic and polymeric materials is shown in Table 2. The tensile strength of cellulose nanocrystals is almost double of glass wire.[57]

Figure 5 shows a pictorial view taken with an AFM by Roman and Gray[58] of the formation of cellulose nanocrystals through the hydrolysis process. Nanocrystals are mainly used in the electronics, catalysis, energy and biomedical fields, and a number of other applications, of which the following:[58]

- Security features to prevent counterfeiting, such as iridescent strips/patches and color shifting inks
- Decorative coatings, such as nail or car polishes
- Selectively reflecting films, such as car windows, optical information storage devices, optics for laser systems

Literature shows the importance of cellulose nanocrystals as their strength properties are much higher than those of various metallic and polymeric products available commercially. They may add distinguished properties to the end-product. However, their use in pulp and paper products is not extensively researched. This area needs to be explored in a broader manner.

Cellulose nanocomposites

The cellulosic nanofibrillar structures have recently come into focus to be used as components in nanocomposites because of their wide abundance, renewable and environmentally benign nature, and outstanding mechanical properties. The major challenge has been to find efficient ways to liberate cellulosic fibrils from different source materials, including wood, agricultural residues, or bacterial cellulose. The recent work carried out by worldwide researchers shows that considerable progress has been achieved in addressing these issues and that there is potential to use cellulosic nanocomponents in a wide range of high-tech applications.[34]

The composite interconnection can be based on a secondary force or physical entanglement; for example a polymer/nanofiller-hybrid, in turn, is formed when the polymer and the nanoparticle are covalently bonded. The covalent bond can be formed during the *in-situ* polymerization, or during the composite processing. Nanocomposites are mainly the blends of two or more materials.

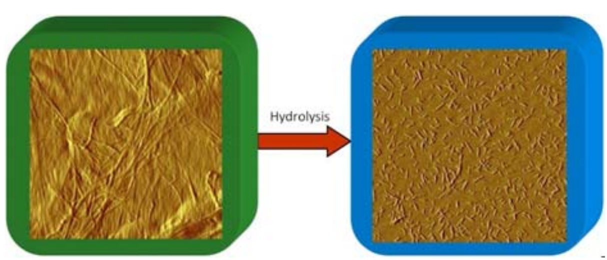

Figure 5: Micrographs showing formation of cellulose nanocrystals through hydrolysis[58]

Table 2
Properties of cellulose nanocrystals relative to metallic and polymeric materials[57]

Material	Tensile strength (MPa)	Elasticity modulus (GPa)	Density (g/cc)
Cellulose nanocrystals	7500	120-143	1.50
Glass fiber	4800	86	2.50
Steel wire	4100	207	7.85
Graphite whisker	21	410	1.80
Carbon nanotubes	11-63	270-970	1.33
Kevlar	3.5	124	1.40

Cai *et al*.[59] used melamine-urea-formaldehyde (MUF) for the preparation of cellulose nanocomposites. The nanofiller/MUF treated wood exhibits a significant improvement in water repellency, dimensional stability and antiswelling efficiency (from 63.4 to 125.6%). The introduction of MUF and nanofillers into the wood could be attributed for the significant improvement in physical properties, dimensional stability and water resistance of the resulting wood polymer.

Lonnberg *et al*.[60] grafted MFC with poly(e-caprolactone) or PCL of different molecular weights in order to improve compatibility with a PCL matrix. The laminates consisting of PCL-grafted MFC films showed a significant improvement in interfacial adhesion when compared with laminates incorporating ungrafted MFC films. The grafted MFC-reinforced PCL composites possessed higher modulus and lower elongation at break at a given loading level, compared to cellulose whisker-reinforced nanocomposites.

Several approaches have been proposed for improving polylactic acid (PLA) properties, including blending[61-65] and copolymerization.[66,67] Preparation of nanocomposites has also been considered as a promising method for PLA property improvement.[39,68,69]

Iwatake *et al*.[70] premixed MFC with PLA using acetone and the mixture was kneaded after the removal of the solvent to attain uniform dispersion. Young's modulus and tensile strength of PLA increased by 40 and 25%, respectively, without a reduction in yield strain at a fiber content of 10% (w/w). Suryanegara *et al*.[71] applied the same method, but replaced acetone with dichloromethane, and showed that the resulting MFC-PLA nanocomposites had improved storage modulus when compared with PLA only. Okubo *et al*.[68,72] mixed MFC, PLA and bamboo fibers in water and the dispersion was vacuum-filtered. Composites were fabricated by hot pressing to the dried filtered sheets. The mechanical properties of the composites were significantly enhanced even at low MFC loadings.

Chakraborty *et al*.[73] used a twin-screw Brabender mixer to disperse MFC in water solution in a PLA matrix and the resulting compound was then hot-pressed at 190 °C. Microscopic images showed uniform dispersion of MFC in the PLA matrix. On the contrary, Mathew *et al*.[74] reported a non-uniform dispersion of cellulose fillers in the PLA matrix, when nanocomposites of PLA with 5% (w/w) cellulose nanowhiskers and MFC were prepared by twin-screw extrusion.

The potential use of chemically coated hemp nanofibers as reinforcing agents for biocomposites (BC) was explored by Wang *et al*.[75] Bio-nanocomposites were prepared from PLA and poly-β-hydroxybutyrate as matrices. Nanofibers were only partially dispersed in the polymers. Mechanical properties were lower than those predicted by theoretical calculations. Positively charged amine-functionalized MFC was reported to be antimicrobially active in biomedical applications.[76]

Hosokawa et al.[77,78] reported a novel and biodegradable composite film derived from chitosan and MFC that had a high oxygen-gas barrier capacity and was hydrophilic but insoluble in water. The composite films had a maximum wet strength (60 MPa) and dry strength (more than 100 MPa) at 10-20% chitosan on cellulose. Recently a new route to enhance the wet properties of chitosan-acetic-acid-salt films by adding MFC at 5% (w/w) loading has been presented by Nordqvist *et al*.[79] Ciechanska[80] presented a manufacturing technique for BC/chitosan nanocomposite materials suitable for medical applications. In particular, the modification of the BC occurred during microbiological synthesis by introducing selected bioactive polysaccharides, such as various chitosan forms and their derivatives, into the culture medium. As a result several advantageous features of a composite were achieved, including good mechanical properties in the wet state and improved water holding capacity.

Dufresne and Vignon[81] and Dufresne *et al*.[82] aimed to improve the thermomechanical properties and reduce the water sensitivity of potato starch-based nanocomposites, while preserving the biodegradability of the material through addition of MFC. The tensile modulus was found to be 7 GPa at 50 wt% cellulose content compared to 2 GPa for unreinforced samples (0% MFC).

Nanocomposites from wheat straw nanofibers and thermoplastic starch from modified potato starch were prepared by the solution casting method. The modulus of the thermoplastic starch increased from 111 to 271 MPa with maximum (10% w/w) nanofiber filling.[83]

Polyvinyl alcohol (PVOH) is an ideal candidate for biomedical applications, including tissue reconstruction and replacement, cell entrapment and drug delivery, soft contact lens materials, and wound covering bandages for burn victims.[84,85] Zimmermann *et al*.[86] dispersed MFC into PVOH and generated fibril-reinforced PVOH nanocomposites (fibril content – 20% w/w) with up to three times higher Young's modulus and up to five times higher tensile strength when compared to the reference polymer.

A blend containing 10% cellulose nanofibers obtained from various sources, such as flax bast fibers, hemp fibers, kraft pulp or rutabaga and 90% PVOH, was used for making nanofiber-reinforced composite material by a solution casting procedure.[29] Both tensile strength and Young's modulus were improved as compared to PVOH film only, with a pronounced four to five fold increase in Young's modulus observed. Such improvement in mechanical properties can be explained by strong interfacial bonding between the cellulose nanofibers and PVOH.

Nakagaito and Yano[87,88] impregnated MFC from kraft pulp with a phenol formaldehyde resin and then compressed the resulting material under high pressure to produce high strength cellulose nanocomposites. It was found that fibrillation that only influences the fiber surfaces is not effective in improving composite strength, but that a complete fibrillation of the bulk of the fibers is required. Nakagaito and Yano[87] achieved the same by 16-30 passes through a refiner followed by high pressure homogenization.

Henriksson *et al*.[21] produced nanocomposite films of MFC and melamine formaldehyde (MF) resin as a potential material for use in loudspeaker membranes, where a high Young's modulus and low density are required. The MF-MFC nanocomposites showed average Young's modulus as high as 16.6 GPa and average tensile strength as high as 142 MPa, while the density of the composite was higher than that of conventional paper prepared from pulp fibers. The combination of properties attainable with MFC films and composites, including high mechanical damping, demonstrates that these materials have the potential to be used as loudspeaker membranes.

The specific interactions between cellulose nanofibrils in polymer composites involve the development of strong hydrogen bonds between cellulose nanofibrils, which can be simulated in the context of percolation theories.[89,90] The interaction and bonding of cellulose nanofibrils induce mechanical percolation of nanofibrils, which differs from geometrical percolation. Cellulose nanofibrils thus act as those exposed on the surface of cellulose fibers (by fibrillation) in paper sheets during water evaporation. Surface modification/treatment is primarily responsible for the stabilization of the cellulose nanocrystalline aqueous suspension, and as such, the entanglement between flexible fibrils may play a crucial part in the mechanical behavior of the nanocomposite, mainly in the nonlinear range.

The composites developed in laboratory show superior properties but there is no assurance that they can be achieved at a commercial scale. It can be anticipated from the literature that the most successful applications of cellulosic nanocrystals, as composites, ought to be formulated from water-miscible matrix materials, such as latex, polyvinyl alcohol, starch products, etc. The use of cellulosic nanoelements in such applications is analogous to using hydrophilic cellulose fibers for the manufacture of paper, a product that is formed in the presence of water and then dried.

Nanofillers/pigments

Paper consists not only of cellulosic fibers, but also of considerable amounts of mineral fillers which are added prior to sheet formation. Fillers are highly desirable in printing papers because they increase the opacity and brightness, and generally improve printing properties. The main types of mineral filler for papermaking are talc, ground calcium carbonate (GCC), precipitated calcium carbonate (PCC), hydrous kaolin, calcined kaolin, precipitated silica and silicate, and titanium dioxide. The finer proportions of GCC and kaolin are also used for the coating of paper surface. The use of fillers is important when opacity is needed at a low-basis weight; they are invaluable in packaging grades where low permeability is combined with opacity to protect food from light. The presence of fillers, however, affects fiber-to-fiber contact and reduces paper strength. Other properties are improved rendering the paper useful for special purposes.

Nanoparticles can add new functionalities to uncoated and coated papers. The main parameters of the fillers/pigments are particle size and size distribution, aspect ratio, stabilization and surface modification. Yan *et al.*[5] studied the photocatalytic degradation of xylene with nano-titanium dioxide (TiO_2), and a combination of nano-TiO_2 and beta-cyclodextrin (beta-CD) coated papers. Paper coated with a combination of nano-TiO_2 and beta-CD had a better effect on degradation than paper coated only with nano-TiO_2, and beta-CD and nano-TiO_2 had a significant synergistic effect on the degradation of xylene.

Fukugaichi *et al.*[6] carried out research on sludge recovered from paper ash containing nanosized TiO_2, which was obtained *via* acid treatment after the alkali hydrothermal reaction of paper sludge ash. They showed that the crystal structure of TiO_2 in the paper sludge ash was of the anatase type and the crystal size was of 10-20 nm. The photocatalytic activity of nanosized TiO_2 in the paper sludge was evaluated by gaseous acetaldehyde removal. It was found that the obtained nanosized titanium dioxide was capable of completely decomposing acetaldehyde to carbon dioxide under UV radiation.

The surface properties of nano-TiO_2 with hexadecanoic acid were investigated by Li *et al.*[7] The wetting and dispersion of the mixture were improved greatly. The coatings containing modified nano-TiO_2 had higher dynamic elastic modulus and viscosity modulus than coatings containing unmodified nano-TiO_2.

In a recent study by Huang *et al.*[91] a new type of paper with superhydrophobic surface was prepared with the addition of modified nano-TiO_2 to cellulosic fibers. Nano-TiO_2 powder was first dispersed with a high-speed homogenizer, followed by surface modification with the coupling agent, 3-(trimethoxysilyl) propyl methacrylate (MPS). The results show that the water contact angles for the modified paper ranged from 126.5 to 154.2°. Moreover, many well-dispersed nano-TiO_2 protuberances were observed on the surface of the paper, which further confirmed that the obtained paper was superhydrophobic on account of its nanostructure. Comparative optical studies performed on the paper handsheets revealed a much higher opacity for the sample with the MPS-modified-TiO_2 nanoparticles.

TOPCHIM nv, Belgium has developed an organic nanomaterial to create a glossier paper for use in color laser printers and has been working with Mondi Business Paper to develop this technology to launch Neox. NanoTope 26 is a nanopigment based on polystyrene maleimide that comes as a mono disperse liquid of spherical nanoparticles. The average diameter is of 50 nm and the application of the nanoparticles on a non-sized base paper results in no film forming properties after drying, lower required pressure and temperature at calendaring, higher whiteness, and much higher specific surface area at the level of toner resin. After extensive research to attach the nanoparticles in a selection of filler pigment particles, three varieties of hybrids were produced; nanoparticles precipitated on kaolin pigments, nanoparticles precipitated on aluminum hydroxide pigments, and nanoparticles precipitated on a 50:50 mix of kaolin and aluminum hydroxide pigments.[92]

Juuti *et al.*[93] examined the light scattering of precipitated calcium carbonate (PCC) fillers coated with novel silicate and zinc sulfide nanoparticle. The PCC was modified by aluminum-magnesium-silicate and zinc sulfide nanostructures. They showed an enhancement in the light scattering from a pigment coating of a paper using nanoparticles.

Wild *et al.*[94] conducted lab studies, pilot and mill trials on the nanoparticle coating to compare its characteristics with those of existing silica-based coatings. The results showed that nanoparticle coating has good print quality, optical density, color gamut, water permanence, color performance and dimensional stability.

Zinc oxide nanoparticles can also be used on a paper surface without use of binders. Zinc oxide nanoparticles can be coated onto paper, which can be achieved first by ammonia and heat treatment of zinc oxide and cellulose, followed by ultrasound treatment. Paper products coated with zinc oxide nanoparticles exhibit antibacterial activity against *Escherichia coli*. The new nano-silver powder ensures the elimination of odor-causing bacteria and the neutralization of ammonia.[95] The latest work of Prasad *et al*.[96] demonstrates that the brightness, whiteness, smoothness, print density, print uniformity, picking velocity and oil absorbency of nano-ZnO coated paper showed significant improvement, compared to bulk-ZnO coated paper. In addition, the nano-ZnO coated paper showed excellent anti-fungal and UV-protecting properties, essential in enhancing paper life.

Johnston *et al*.[97] produced nanostructured silica with an open network structure by controlled precipitation from geothermal water. It was used as filler in newsprint. The technology was developed on a laboratory scale and progressed to a pilot plant with full-scale paper mill manufacturing and commercial printing trials. Print through reductions of 30% for newsprint and 40% for yellow directory grade paper was achieved. Nanostructured calcium silicate with an open framework structure was also formed from sodium silicate solution. When it was tested as a filler in newsprint on a laboratory scale, a reduced print by about 40 and 53% for 55 and 45 g/m^2 newsprint, respectively, was achieved.

Being lower in particle size, nanofillers could provide better performance than traditional fillers in applications such as adsorption, which can benefit from a high surface area; in such applications they may confer certain unique attributes and functionalities to papers, which is also one of the major concerns of papermakers. The nanofilled paper could also have such attributes as high smoothness, good appearance, or other previously unimagined functions. The benefits associated with the use of nanofillers can be expected to encourage worldwide papermakers to pay attention to this potentially promising research area and to make every effort to create positive breakthroughs.

Nanomaterials for packaging

Packaging is an important application, and unexpected and valuable properties have emerged from materials made using nanotechnology. Low gas permeability is one of the most interesting property enhancements from clay nanocomposites, particularly for the packaging industry with nylon nanocomposites claimed to supply a hundred-fold lessening of oxygen permeation and provide a carbon dioxide barrier giving improved shelf life. Potential applications for nanoclay composites are barrier layers in multilayer polyethylene terephthalate (PET) bottles, meat and cheese containers, multilayer flexible films for ketchup and potato crisps, replacement of ethylene vinyl alcohol copolymer (EVOH) in food packaging and high-density polyethylene (HDPE) containers.[98]

Anon[99] used a nanotechnology-based stainable product entirely manufactured from vegetable materials. The product when applied to a paper surface provided a waterproof barrier. It offered a more sustainable alternative to the conventional polyethylene (PE) and acrylic resins that are commonly used. This paper was fully recyclable, since the product was derived from a vegetable source.

The Packaging Development Center, International Paper, has recently revealed their new technology for gas and moisture barrier for beverage packaging. The technology employs a nanoclay composite coating; similar nanocomposite coatings have also been used by International Paper in inkjet and digital printing paper, which have been marketed under the brand Jet Print Photo paper.[89,100-102]

Cellulose nanocrystals function similar to nanoclays or carbon nanotubes, except that they are readily available from renewable, recyclable natural resources. Rapidly biodegradable hydrophobic material film coatings made of cellulose-latex nanocomposites have recently been commercialized for use in packaging to improve the dimensional stability, hygroexpansivity and toughness of sack paper, with potential application in food packaging.[98,103]

Nanomaterials for other paper-based applications

Papermaking involves the use of wet-end chemicals for effective retention, drainage, formation and machine runnability. The microparticle-based retention aid systems are effectively used for a long time. The fact that nanodimensional fibrils and fines are present in the papermaking process has resulted in the development of retention and drainage aid systems comprised of nanodimensional components.[3]

Chen *et al*.[104] studied the effect of nanosized TiO_2 on the effective removal and control of surface and colloid materials (DCS) in deinking applications. Nanosized TiO_2 colloidal particles were synthesized by the hydrolysis of titanyl organic compounds at low temperature and normal pressure. Anionic polyacrylamide (APAM) and cationic polyacrylamide (CPAM) were used together with amphoteric starch (AmS) and nanosized silicon dioxide. The results indicated that the dual-component retention aids system containing nanosized TiO_2, nano-TiO_2/APAM and nano-TiO_2/AmS were suitable for the removal and control of DCS in deinked paper mills with whitewater closure. The removal of DCS appeared to be due to the bridging flocculation mechanism rather than charge neutralization.

CONCLUSIONS

Nanotechnology has been advancing rapidly in recent years. The enhancement of knowledge in nanotechnology and its applications in pulp and paper industry opens up new insights for the researchers. The nanostructure of cellulose can play a significant part in papermaking and manufacture of high-quality nanocomposites. Various preparation methods to produce cellulose-based nanofibers have been reported. The applications of cellulose nanofibers in various fields have been reported, especially as a reinforcing agent in a composite structure. The use of nanocellulose and its derivatives in health care seem to be highly promising due to their biocompatibility and some other unique properties. Nanotechnology-based developments can provide incremental and evolutionary changes. Dry coating is perhaps one of the most promising technologies offering incremental improvements in mainly paper print quality. The fact that nanodimensional fibrils and fines are present in the papermaking process has resulted in the development of retention and drainage aid systems comprised of nanodimensional components. Nanoscale filler and pigments can also be used for the production of uncoated and coated paper. Due to their lower particle size they need special attention so that they could be retained in the fiber matrix during the papermaking process. Papermakers can select an appropriate nanoproduct and the process for the development or enhancement of desired paper properties or making a new product.

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