The Emergence of Practical Nanocellulose Applications For A More Sustainable Paper/Board Industry

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ABSTRACT

There has been extensive research and development activities in the field of nanofibrillated cellulose (NFC) materials during recent years, although microfibrillated cellulose was developed already during the late 1970s at ITT-Rayonier in USA. A major impediment for the large-scale use of NFC has been the high-energy use (excess of 30000 kWh/ton NFC in energy consumption). This problem has now been alleviated by a series of different pre-treatment procedures of the fibres prior to the subsequent mechanical cell wall delamination.

The focus in practical papermaking applications of NFC is in the reinforcement of paper/board materials (dry strength wet-end additive) and in barrier coating applications.

The driving forces in these applications are resource and energy efficiency in papermaking and the vision of substituting fossil-based films with nanocellulose barriers. Nanocellulose has excellent oil, fat and oxygen barrier properties in the dry state, but the oxygen barrier properties deteriorate at high relative humidities and the approaches to alleviate the moisture sensitivity will be discussed.

Today, there are many companies in the process of commercializing NFC and several of them have pilot plants/pre-commercial operations and are planning for up scaling. A pilot plant for the nominal production of 100 kg/day (dry based NFC) was also taken into operation at Innventia AB in 2010.

The current contribution will highlight critical issues in the production of NFC and discuss various applications and hurdles to be overcome in order to make NFC production for paper/board based end-use applications viable.

Introduction

The growing demand for sustainable products made from natural and renewable materials has propelled the development of new cellulosic materials, among which the development of nanocellulosic materials has come to the forefront in the pulp and paper industry during the past two decades.

There are, at least, three major domains of nanocellulosics: microfibrillar cellulose (MFC), nanocrystalline cellulose (NCC) and bacterial nanocellulose (BNC), Klemm et al(1). The acronym "microfibrillar cellulose" was coined by the original inventors of MFC Herrick et al(2)Turbak et al.(3)in the late 70s and was later renamed to "nanofibrillar cellulose" or "nanofibrillated cellulose" (NFC) at the beginning of the millennium. The nomenclature is not clear in the literature although some publications try to distinguish between nanofibrillated cellulose and microfibrillar cellulose. Here, the acronym for nanofibrillatedcellulose (NFC) will be used for both terms.The materials in the three domains of nanocellulosics all have different characteristics and uses, but in this communication NFC will be the only nanocellulosic material discussed.It should also be recognized that a new nomenclature for nanocellulosics is currently under development. The suggested nomenclature for NFC is about to change to cellulose nanofibrills(CNF), according to the emerging ISO-standard (ISO TC 229), but in this context the old acronyms are used.

The manufacture of NFC from wood was pioneered by Turbak (3) and Herrick(2) at ITT Rayonier in the late 1970s and early 1980s. The forcing of a suspension of wood-based cellulosic fibres through mechanical devices, such as high-pressure homogenizers, produced NFC. This mechanical treatment delaminated the fibres and liberated the nanofibrils (widths from 5-60 nm). The so produced nanofibrils had a high aspect ratio and exhibited gel-like characteristics in water, with pseudo-plastic and thixotropic properties.

The major impediment for commercial success has been the very high energy consumption amounting to over 30,000 kWh/tonne, Lindström and Winter(4)in the production of nanocellulose as a result of the required multiple passes at high pressures through homogenizers. Extensive clogging of homogenizers was also found to be a chronic problem. More recently, there has been a focus on energy-efficient productionof NFC, whereby fibres are pre-treated by various physical, chemical, and enzymatic methods, Klemmet al.(1), before homogenization in order to decrease the energy consumption.

The literature on nanoncellulosic materials is today vast. Some recent reviews are given here to guide the reader;Siró and Plackett(5), Moon et al.(6), Lavoine et al.(7),Dufresne et al.(8), Lindström et al.(9)Most literature is concentrated on high-end applications of nanocellulosics, whereas Innventia, as an organisation, has targeted low to medium-end applications with a focus on low-energy, cost-efficient, production methods of NFC. This communication will briefly discuss some manufacturing methods for NFC and discuss some potential large-scale applications.

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Manufacture of nanofibrillated cellulose (NFC)

The original method developed at ITT Rayonier did not invoke any chemical pre-treatments of the pulps, apart from cutting the fibres in order to decrease the fibre length so clogging in the homogenizer could be avoided. Clogging has its origin in fibre flocculation and the higher the fibre concentration and the longer the fibres, the greater the tendency for clogging of the communition devices used to delaminate the fibres. This imposes a general limitation, when delaminating fibres in high-pressure homogenizers or microfluidizers. The ITT Rayonier team found out, however, that the energy consumption was very high and that the NFC produced was subjected to extensive hornification during drying and later abandoned further developments. Japanese groups took up some further developments of wood-based materials during the 90s, but the high energy use was still a major hurdle for further developments. French groups also found out that fibres containing parenchyme cells (e.g. potato tubers) were much easier to delaminate, but it was not until the turn of the millennium that more wide-spread, extensive developments started.

The energy consumption for delamination of wood-basedNFC has now with chemical pre-treatments been reduced by several orders of magnitude, see table 1.

Table 1. Some representative data reported for the energy consumption to make NFC from wooden materials using certain pre-treatments

Pre-treatment	Pulp type	Energy demand (kWh/tonne)	Reference
None	Bleached kraft	12.000-70.000	Eriksenet al (10)
None	Bleached sulphite	30.000	Lindström and Winter (4)
Enzymatic/refining	Bleached sulphite	350-500	Lindström and Ankerfors (11) Pääkköet al. (12)
Carboxymethylation D.S = 0.1	Bleached kraft/dissolving pulp	Less than 350	Wågberget al (14) Lindström et al. unpublished (14)

It was recognized early on by the original inventors that high hemicellulose pulps e.g. sulphite pulps were easier to delaminate than bleached kraft pulps. It should be pointed out that the definition of NFC, and hence the energy consumption, is somewhat arbitrary, but practitioners usually define NFC when the treated pulp has gelled, after homogenization. Basically, the chemical pre-treatments fall into two major groups:

- Electrostatically induced swelling by the introduction of charged groups, induced either by certain pulping and bleaching procedures or by subjecting pulps to derivatization (e.g. carboxymethylation) or oxidative treatments, such as TEMPO-oxidation.
- Mild acid or enzymatic treatments

TEMPO-oxidation (2,2,6,6-tetramethylpyridine-1-oxy radical)(4-H TEMPO) pre-treatments subject the fibres to simultaneous oxidation and hydrolysis and treated fibres scarcely need any homogenization, Saito et al (15), Saito and Isogai (16) and Saito et al.(17).

The mechanical treatments can invoke different communition devices, and have, of course been extensively studied by papermakers for more than 100 years, Page (18).Papermaking fibres swell during refining and become flexibilized, so they can form interfibre bonds during consolidation of the wet fibre mat. The principal design that has emerged is that of disc-refiners fitted with bars and grooves, between which the fibres are subjected to repeated cyclical stresses. It should be noted that high-pressure homogenizers or microfluidizers have not been used in commercial production of paper and board. The original inventors of NFC used high-pressure homogenizers, while other investigators have used microfluidizers. A similar device to disc-refiners that has also been used for production of NFC is known as super-grinding. Ball mills and cryo-crushing are still other methods, which have been employed.

It appears, however, that chemical, physical and enzymatic pre-treatments are the most important technologies to maximize the energy efficiency during delamination of fibres. Interestingly, these pre-treatment methods are not used in commercial paper-making treatments. It is common knowledge among papermakers that fibres having high hemicellulose content and low lignin content (lignin functions as a cross-linker in the cell wall) are easy to beat. Hemicellulose promotes swelling of the fibres and due to their hydrophilic character and the presence of carboxyl groups, the fibres will behave as a polyelectrolytic gel. As such, the highest swelling is obtained when the carboxyl groups are in their ionized state with a monovalent counterion (e.g. Na^+), Lindström(19).

Oxidation of cellulosic fibres through TEMPO-oxidation provides a very interesting way to introduce carboxyl groups in aqueous systems. The 4-H TEMPO is a nitroxy radical, which selectively oxidizes the C-6 primary hydroxyl into carboxyl groups. If a sufficient number of hydroxyl groups are introduced, a very slight post-delamination treatment is necessary. The most widely reported procedure in this context is the TEMPO/NaBr/NaClO system. The TEMPO oxidation treatment has been extensively investigated by Isogai´s group in Japan;Isogaiet al.(20).There are opportunities and limitations with the various methods, which also have been discussed in the literature,Aspler and Bouchard.(21).

Enzymatic means to facilitate delamination procedures have primarily been investigated at Innventia/KTH,Henriksson et al. (22),Pääkköet al. (12).

Enzymatic pre-treatments with small endoglucanase have been the focus at Innventia/KTH. Cellulases can be subdivided into two types, A and B, termed cellohydrolases, which attack the crystalline structure of cellulose, whereas Cand D types (endoglucanases) require some disorder of the cellulose structure, and the latter type has been employed in our laboratory for delamination of wood fibres; Henriksso net al. (23), Henrikssonet al(24). Enzymatic pre-treatments also require some general refining treatment both before the enzymatic treatment (in order to enhance the accessibility of the enzyme) and some post-refining, which shorten the fibres and are advantageous in order to decrease the clogging of interaction chambers during homogenization.

A wide range of raw materials can be used to make NFC-fibres. Apart from various common papermaking pulps, a range of different raw materials have been used to produce NFC and some examples are given in table 1. There are, however, indications that the choice of raw materials is not that important for the quality of NFC-fibres. It has, for instance, been found that NFCs made from rice, wood or potato tuber have very similar properties, Abe and Yano (25). It is rather more likely that the required processing set-up, material logistics and economy will determine the NFC-raw material choice.

Table 2. Examples of NFC raw materials other than common papermaking pulps

CNF produced from various materials	References
Sugar beet pulp	Dinandet al. (26) Dufresneet al. (27) Dinandet al. (28)
Potato tuber pulp	Dufresne and Vignon (29) Dufresneet al. (30)
Bagasse	Bhattachayaet al. (31)
Wheat straw	Alemdar and Sain (32)
Kenaf	Jonoobiet al (33)
Rubberwood	Jonoobiet al.(34)
Sisal	Siquieraet al (35)
Flax bast fibres	Bhatnagar and Sain(36)
Bamboo	Abe and Yano (37)Zhanget al. (38)
Rice	Abe and Yano (25)
Banana rachis	Zuluagaet al. (39)
Palm tree	Bendahouet al. (40)
Hemp	Bhatnagar and Sain(41)Daiet al (42)Puangsin, et al (43)

Paper and board applications of nanocellulosic materials.

There are numerous applications of NFC. A recent publication, Aspler et al(21) lists about 30 specific applications for NFC and NFC materials and discusses the likelihood of their commercial applications. The major potential markets for nanocellulosics range from large-scale use of nanocellulose as a strength adjuvant in paper/board and applications for surface strength and barrier coating,to high-tech applications in the medical/electronics markets.

In the EU paper/board market, the anticipated uses for nanocellulose is to reinforce paper/board materials for fibre reduction, enhanced energy efficiency (wet-end additive) and to produce coatings/laminations for applications in the food packaging sector as a replacement for aluminium foils and fossil-based laminations. These applications are currently a major driver for the installation of larger scale pre-commercial/pilot plant production facilities for nanocellulosic materials. Approximately a dozen such plants have been announced globally and there are probably another dozen plants, the operations of which have not yet been disclosed. These are large-scale, low-end applications that, when up-scaled, are likely to have a large economic, environmental and societal impact. Often new materials initially find an inroad to the high-end of the market, but NFC materials have been around for many years and it is only recent pre-commercial operations and larger pilots have started up with applications in the low and medium end of the markets rather than at the high-end.

The most easily accessible market is probably the use of NFC as a wet-end additive.

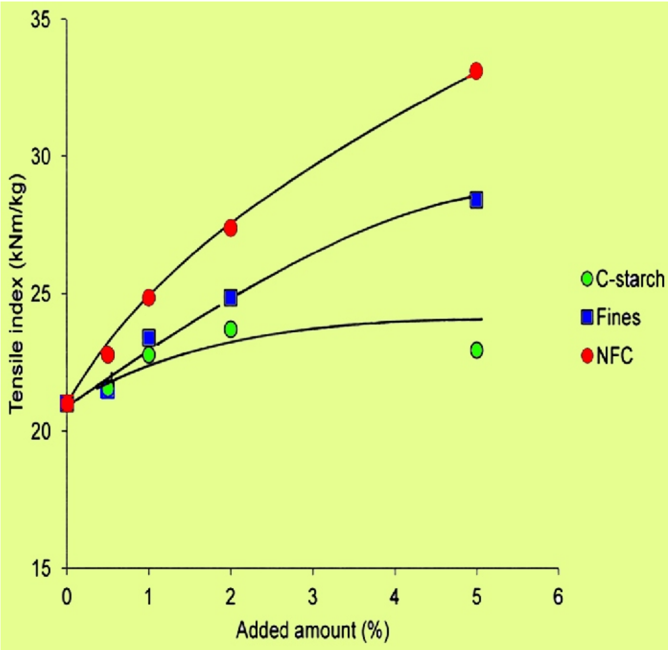

Fig 1 The effects of C-starch, fines and nanocellulose on the tensile index of CTMP , Lindström and Winter, (4).

It has for a long time been known that fines materials created during beating/refining of pulps improve the strength properties of papermaking furnishes, Page (18). Whereas the width of nanocellulose materials are in the order of 5-20 nm, the width of fines materials are thicker by an order of magnitude, so these materials are very different in nature.

There are relatively few accounts of the effects of nanocellulose on reinforcement of paper/board in the literature; Ahola et al. (44), Erikse net al. (10), Schlosser (45), Tailpale et al. (46), Johansson et al. (47), although it has been known for along time that nanocellulose/microfibrillar cellulose has better strength reinforcement effects than fines materials (see e.g. fig 1).

Fig 2 shows how the addition of NFC affects the general strength properties when added to an unrefined bleached softwood kraft furnish.

As a rule, dry strength additives have the largest effects on unrefined pulps and as the relative magnitude of the strength increase diminishes, the more the pulp is refined. The choice between refining and addition of NFC to papermaking furnishes will be determined by the energy demand to make NFC vs. refining energy of the pulp. Dewatering will always be a critical factor when applying NFC to paper furnishes and a prerequisite for a successful application of NFC is that the chemical dewatering/retention systems should always be optimized.

Relevant applications are as a z-strength enhancer in paperboard materials, particularly when bulky fibres, such as CTMP or bulking fibres are used. High-filler content papers have also come into fashion again and nanocelluloses have a specific advantage compared to starches in that they also give an enhanced wet web strength, van de Ven (49).

The manufacture of totally biodegradable packaging materials has been the subject of intensive research over the years, but few commercial materials have surfaced.

A major driving force has been the problem of plastic waste and particularly plastic waste in the oceans,European Commission (50), Rochman et al. (51) Firstly, Ocean plastic waste can damage marine life,Browne (52); Uhrin and Schellinger, (53), through ingestion of micro-pieces of plastics. Secondly, plastic marine debris contains highly toxic substances such as PCBs/DDT in concentrations that are 10^3 to 10^4 higher than in those in the ocean waters Hirai et al. (54) A major problem is that when the plastic debris are worn down into smaller pieces they will enter the food chain and finally into humans, the effect of which is largely unknown.

The replacement of fossil-based materials with biodegradable materials is, however, not a perfect solution as there are several

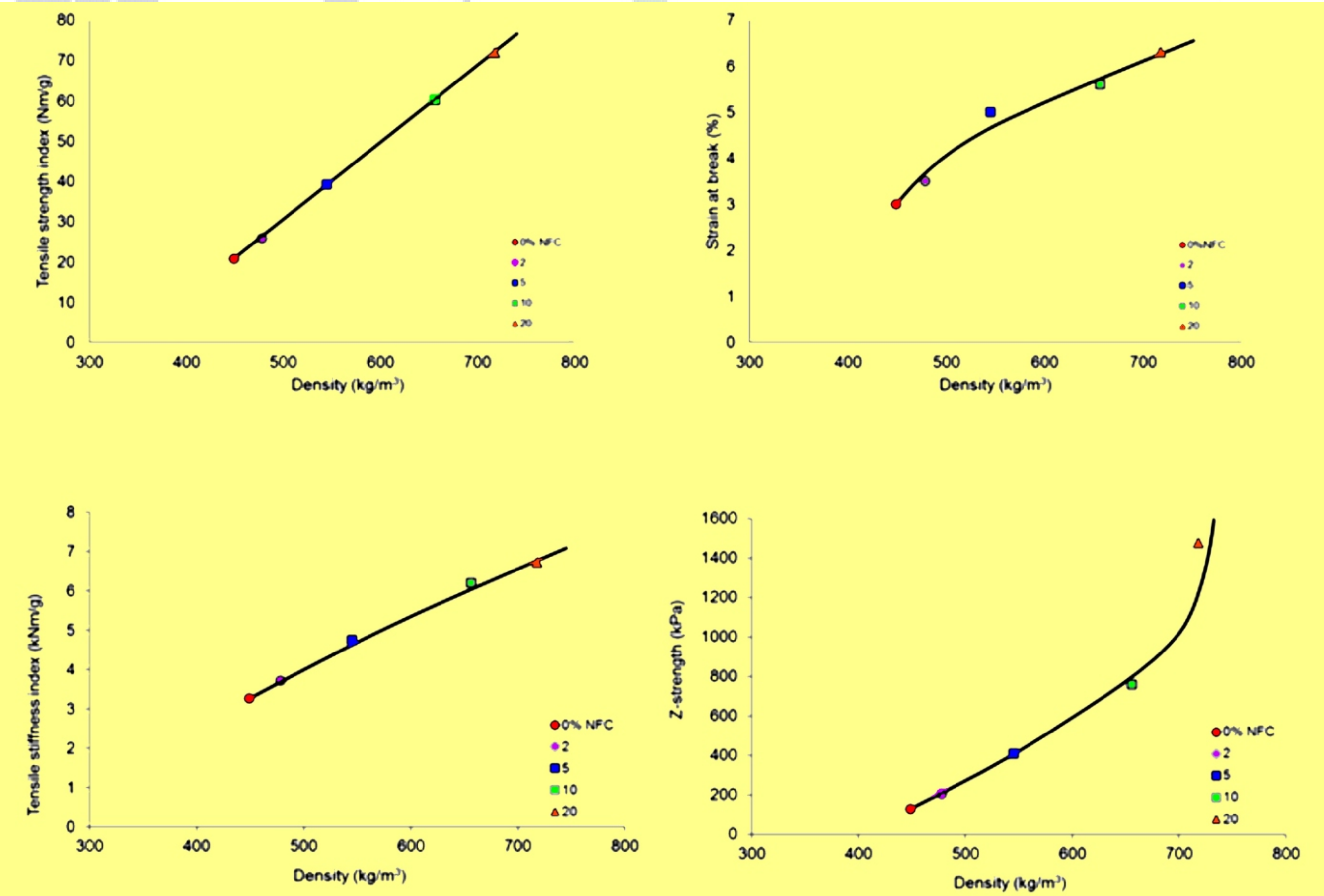

Fig 2 The effects of adding nanocellulose (enzymatically liberated CNF) on the general strength properties of an unrefined softwood bleached kraft pulp, Lindström et al. (48)

remedies for the elimination of plastic waste in different countries. In some countries, like Sweden, incineration of plastics for energy generation is the preferred solution, whereas other countries prefer composting, both of which require an efficient infra-structure to alleviate the problem.

The replacement of fossil based barrier coatings/films with nanocellulose, is, however, a new idea, but constitutes a major technical challenge. There are a variety of technological applications ranging from food and beverage packaging to flexible electronics and fuel cells, which require highly flexible and inexpensive high performance gas barrier materials. High oxygen and water vapour barrier protection and aroma and oil/grease resistance, Yang 2013 (55), as well as mechanical strength and flexibility, are examples of important target properties for food packaging film laminates and/or coatings, in order to prevent food/liquid degradation and to increase the shelf life of these products.

Nanocellulosic materials, like most bio-based polymers, have been known for some time to exhibit excellent oxygen barrier properties; Syverud and Stenius (56)Aulin,et al.(57) Fukuzimi et al. (58), rendering them interesting for packaging applications Miller and Krochta (59) Lange and Wyser (60). Nanocellulose is an excellent oxygen barrier due to its high crystallinity and high cohesive energy density, Auli net al.(57). Fig 3 shows the oxygen and water permeability of various film materials, Lindström et al. (61). Nanocellulose has, in the dry state, the lowest oxygen permeability of all investigated organic materials. Its performance is, however, severely limited by its hygroscopic properties and corresponding moisture sorption, deteriorating the barriers at higher relative humidities, Aulin et al. (57)

Moisture sorption is an inherent property of all biodegradable materials and this constitutes a major challenge for all biodegradable film materials. Several strategies have been used to alleviate these problems including the incorporation of nano-sized high aspect clays, cross-linking of polymer films or by adding

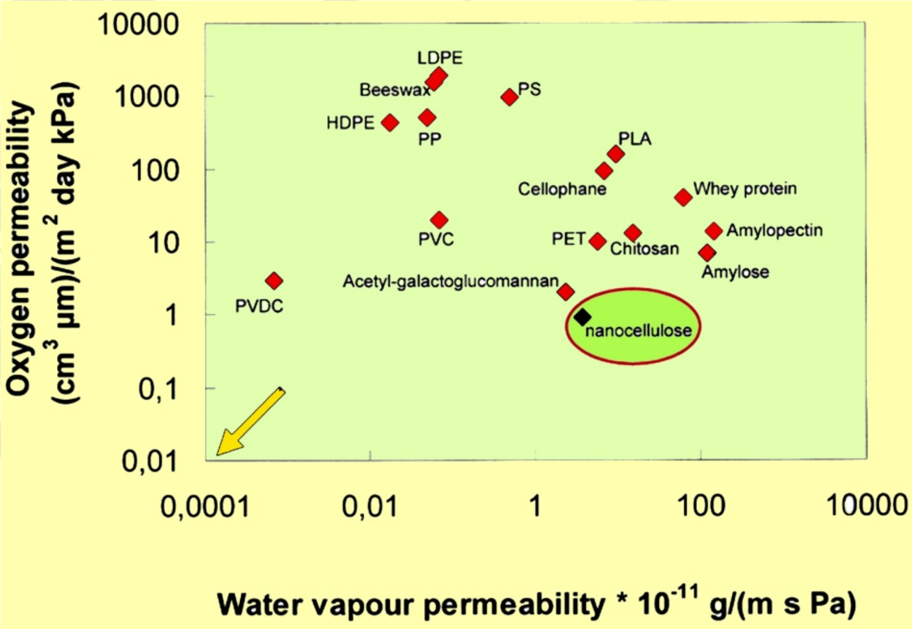

Fig 3. Oxygen and water vapour permeability of various organic films at 50% RH.Aulinet al. (57).

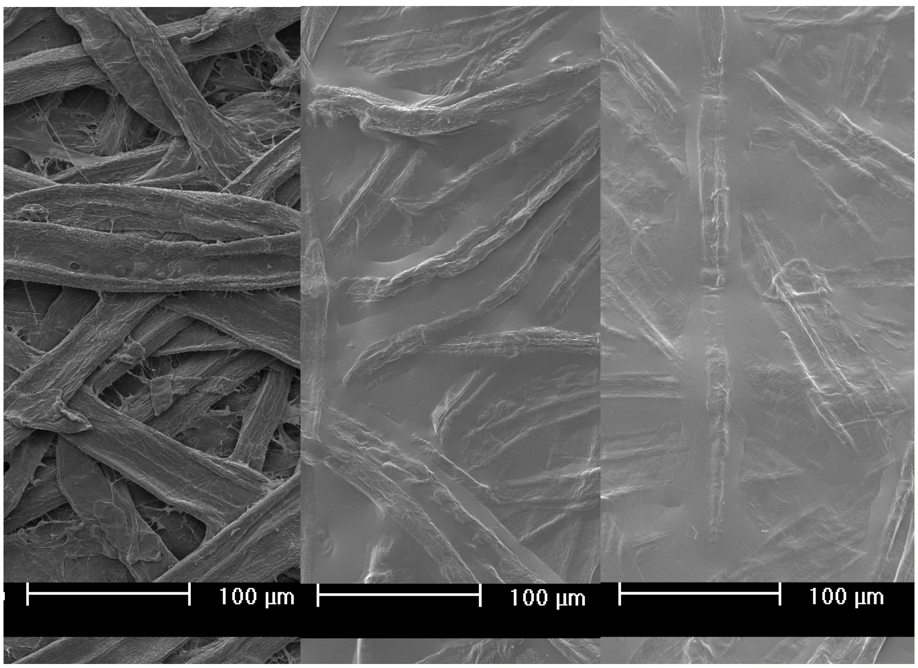

Fig 4.NFC coatings on paper board (a) reference paper. (b) 1 g/m^2 NFC-coat(c) 1.8 g/m^2 NFC-coat, Aulin et al. (57)

hydrophobic additives to the coating/film; Miller and Krochta (59), Lange and Wyser (60), Lindström et al. (61)

Apart from the moisture sorption interference with the gas barrier properties, the application of NFC onto paper/board materials constitutes several challenges.

Freestanding films can, of course, be laminated directly to paper/board packaging materials, but the real challenge is to apply them in coating applications. The base sheet properties of paper/board materials are of paramount importance in terms of coating quality. A base sheet of paper is a highly porous material withvariable smoothness and porosity and these properties are dependent on a multitude of variables, such as fibre type and treatment, filler content, forming conditions, wetpressing, and pre-calendering. The coating hold-out properties and the final coating properties will vary, depending on the base-sheet properties, rheological characteristics of the coating colour and the colour application method. The coating holdout for NFC applications on paper/board is usually excellent as shown in fig 4, where a softwood unbleached kraft pulp sheet was coated with various amounts of NFC.

Another major challenge is the high viscosity of NFC materials. When dealing with NFC coatings with solids contents below 10%, a considerable amount of water has to be removed in subsequent drying operations. No large-scale successful coating applications of nanocellulose as a barrier material has, to the best knowledge of the authors, yet been demonstrated.

Outlook

Nanofibrillar cellulose (NFC) can today be produced efficiently in pilot and pre-commercial operations at more than a dozen installations. Innventia inaugurated a pilot-scale production facility in 2011 (see fig 5) and can make non-ionic, anionic and cationic NFC for various end-use applications. Together with the nanopilot, Innventia harbours a first-class experimental papermachine with various types of forming units and a closed white water system designed to run wet-end chemistries to a chemical equilibrium situation.

Fig 5. Left: The Innventia pilot nanocellulose production unit with a capacity of 100 kg/day. Right: The Innventia experimental paper machine running up to 2000 m/min and suitable for nanocellulose trials, with closed paper machine white waters and technologies for optimizing chemical adjuvants necessary for retention/dewatering/formation studies.

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