**Preferred citation:** A. Isogai and L.A. Berglund. Review: Preparation and applications of nanofibrillar celluloses. In **Advances in Pulp and Paper Research, Cambridge 2013**, *Trans. of the XVth Fund. Res. Symp. Cambridge, 2013*, (S.J. I'Anson, ed.), pp 737–763, FRC, Manchester, 2018. DOI: 10.15376/frc.2013.2.737.

# PREPARATION AND APPLICATIONS OF NANOFIBRILLAR CELLULOSES

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## ABSTRACT

Nanofibrillar celluloses are promising new bio-based nanomaterials that can be prepared from paper-grade chemical pulps and other plant celluloses by mechanical shearing in water, usually after pretreatments. For example, enzymatic hydrolysis, carboxymethylation, addition of cationic polymers, TEMPO-mediated oxidation and others have been applied as wood cellulose pretreatments to reduce the energy consumption of the mechanical shearing process and to improve nanofibrillation level. Nanofibrillated celluloses (NFCs) prepared from wood cellulose by either enzymatic hydrolysis or partial carboxymethylation and subsequent mechanical shearing in water are convertible to nanopaper films and aerogels using a filtration process like that used in papermaking, which is advantageous for efficient removal of water from the strongly swollen NFC/water dispersions. NFCs have high molecular weights and long fibrils and form fibril network structures both in aqueous dispersions and dried nanopaper films/aerogels. This makes them preferable for use as base materials for nanocomposites. Thus, various nanopaper/matrix composites have been prepared, some of which show remarkably high mechanical strength including high ductility. When TEMPO-mediated oxidation is used as the pretreatment, almost completely individualized TEMPO-oxidized cellulose nanofibrils (TOCNs) with homogeneous widths of ~3 nm dispersed in water can be prepared from oxidized wood celluloses with carboxylate contents >1.2 mmol/g by gentle mechanical disintegration treatment. Because TOCN elements form nematic-ordered structures due to their self-assembling behavior in water, TOCNs are able to be converted to dense films with plywood-like layered structures, stiff hydrogels by acid treatment, aerogels with extremely high specific surface areas, and other unique bulk materials. When TOCNs are used to make nanocomposite materials, high mechanical strengths and gas-barrier properties can be achieved even with low TOCN-loading ratios.

## INTRODUCTON

More quantitative and qualitative expansion of plantation wood use would contribute to the acceleration of the immobilization of atmospheric carbon dioxide in materials, and to the establishment of a sustainable society based on reproducible biomass recourses. Pulp and paper industry has been developing environmentally friendly and cost-effective processes to isolate and purify cellulose from wood and non-wood resources using pulping and subsequent multi-step bleaching processes, and to recycle used-paper via many related innovations, technologies, and skills. If paper pulps and recycled fibers produced by cost-effective and environmentally friendly processes could be used not only as conventional paper and board products, but also in the production of high-tech and commodity materials with high performance, partly in place of petroleum-based materials, the pulp and paper industry would assume a large role on the way to a sustainable society. One of the promising new material streams is the production of "nanocelluloses" from wood biomass. Fundamental and application-based research and development in this area have started early this century and have since expanded worldwide. For example, according to Google Scholar the number of nanocellulose-related reports (scientific publications, presentations, and patents) was only 55 in 2001, but has rapidly increased to 2660 in 2012, approximately 48 times as many.

There are several reasons for this greatly increased interest in nanocelluloses: 1) Nanocelluloses can be produced from abundant wood biomass partly using conventional and already established pulping/bleaching technologies; 2) recent advances in nanotechnology-related science and engineering for both inorganic and organic materials have opened up new applications in high-tech material fields; 3) compared with the representative and most attractive nanomaterials developed in recent decades such as carbon nanotubes and graphene nanocelluloses

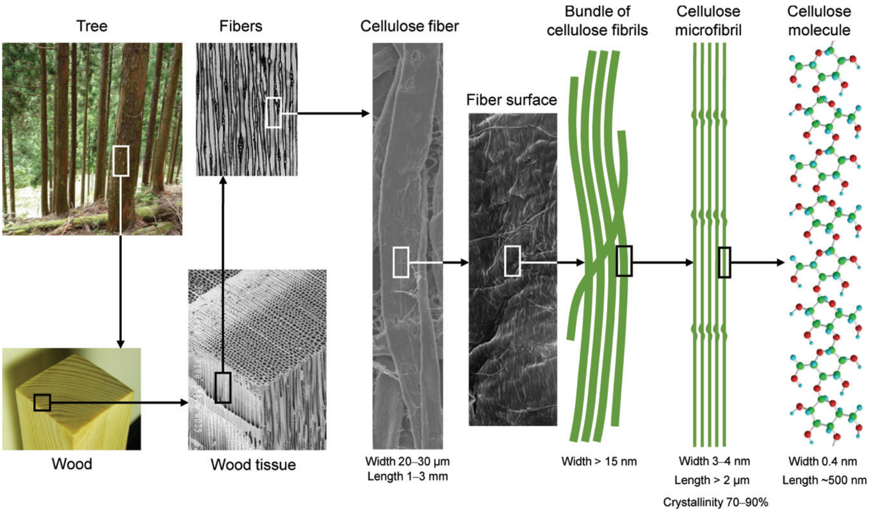

**Figure 1.** Hierarchical structure of wood cellulose, forming crystalline cellulose microfibrils.

originating from reproducible wood biomass are deemed to be much more preferential and beneficial in terms of production process energy consumption and environmental and safety issues; 4) consumption of paper and board products is almost saturated in developed countries, and the paper industry has been looking for new applications of wood fibers, and therefore 5) nanocelluloses have great potential to be used as new bio-based nanomaterials.

In this review paper, nanocellulose-related scientific topics hopefully useful for Pulp and Paper Fundamental Research Society members are reported primarily based on results recently obtained in our two laboratories. It is an impossible task for us to cover all nanocellulose-related and significant topics reported across the world. Several comprehensive review papers concerning various aspects of nanocelluloses, which would be good complementary references, have already been published in scientific journals [1–7].

## HIERARCHICAL STRUCTURE OF WOOD CELLULOSE

Higher plants form highly crystalline cellulose microfibrils, each of which consists of 30–40 fully extended and linear cellulose chains and are the elements with the second smallest width (~3 nm) after single cellulose chains. Plant cell walls are comprised of cellulose microfibrils filled with hemicelluloses and lignin, forming natural nanocomposites that protect their living bodies against biological attack and external stress (Figure 1). The pulp and paper industries have used such wood fiber microfibril structures to effectively control paper properties by controlling their degrees of fibrillation, generally using disk refiners and other mechanical fibrillation apparatuses in stock preparation processes. Because numerous hydrogen bonds are formed and are present between cellulose microfibrils in wood cellulose fibers, it has been difficult to prepare highly fibrillated celluloses from wood cellulose fibers by only mechanical refining in water. In the 1980s, Turbak and his coworkers of ITT Rayonier developed a new method to prepare highly fibrillated celluloses, i.e., microfibrillated celluloses (MFCs), directly from wood cellulose fibers by repeated high-pressure homogenization treatment in water [8]. Moreover, Daicel Company, Japan, commercialized MFCs suspended in water at ~2% solid consistency (CELISH®) during the 1980s [9]. However, the energy required to produce such MFCs is so large that their cost exceeds 2,000 Japanese Yen (~£13 or ~€15) per kg in dry weight. Although some paper companies in Japan were interested in using MFCs and also bacterial cellulose as additives in papermaking to improve filler retention and homogeneous distribution of filler particles in paper in 1990–2000, it has been difficult primarily because of their high cost.

## PROCESSES TO PREPARE NANOFIBRILLAR CELLULOSES

Various pretreatments of wood cellulose fibers have therefore been studied since the early 2000s to reduce the energy consumption of mechanical nanofibrillation processes and to improve the degree of nanofibrillation achievable. A novel route toward exploiting the attractive mechanical properties of cellulose I nanoelements was developed that combines enzymatic hydrolysis and mechanical shearing. This involved the introduction of mild enzymatic hydrolysis combined with mechanical shearing and a high-pressure homogenization, which led to a controlled fibrillation to the nanoscale and a network of long and highly entangled cellulose I elements (Figures 2 and 3). Partial cleavage of cellulose glycoside bonds present on the surface P and S1 layers of wood pulp fibers may also improve nanofibrillation efficiency during mechanical treatment in water. The surface-active properties of enzyme molecules seem to synergistically improve nanofibrillation efficiency during mechanical homogenization.

The strong aqueous nanofibrillated cellulose (NFC) network gels thus obtained exhibited more than 5 orders of magnitude tunable storage modulus G′ upon changing the concentration. Cryo-transmission electron microscopy (Cryo-TEM), atomic force microscopy (AFM), and solid-state $^{13}$C NMR suggested that the cellulose I structural elements obtained were dominated by two fractions, one

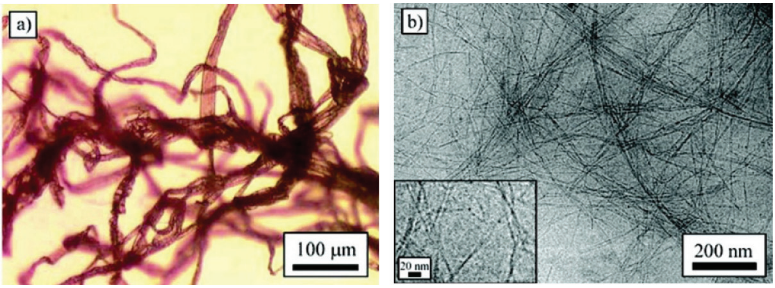

**Figure 2.** (a) Optical micrograph of original sulfite cellulose fibers, and (b) Cryo-TEM of the frozen 2% w/w nanofibrillated cellulose (NFC) gel after refining, enzymatic hydrolysis, and homogenization processes [10].

with lateral dimensions of 5–6 nm and one with lateral dimensions of about 10–20 nm. The thicker diameter regions may have acted as junction zones for the networks. Dynamical rheology showed that the aqueous suspensions behaved as gels within the concentration range 0.125–5.9 wt%, and had G′ ranging from 1.5 Pa to 105 Pa. The described NFC preparation method allows a control over the final properties that opens novel applications in materials science such as reinforcement in composites and as templates for surface modification [10–12].

Minimal carboxymethylation of the hydroxyl groups of wood cellulose with aqueous NaOH and monochloroacetic acid to introduce anionic charges on the surfaces of the cellulose microfibrils was developed in the next stage [13]. Because

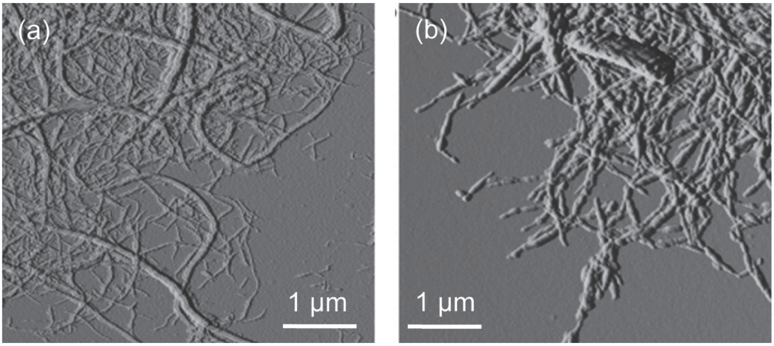

**Figure 3.** AFM images of (a) nanofibrillated cellulose (NFC) prepared from dissolving sulfite pulp (DSP) using cellulase and subsequent mechanical disintegration treatments, and (b) strongly acid hydrolyzed DSP [11].

the production processes of carboxymethyl celluloses (CMCs) from wood cellulose have been established at the industrial level, and because the safety standard issues of CMCs and their production systems have been already satisfied, the conventional industrial scale carboxymethylation process is applicable to the pretreatment, which is advantageous. However, because carboxymethylation itself is a type of competition reaction between cellulose hydroxyl groups and water molecules always present in the reaction media, the reaction efficiency of introducing carboxymethyl groups only on the crystalline cellulose microfibril surfaces may not be so high.

In an opposite manner, introduction of sufficient amounts of cationic charges to wood cellulose microfibril surfaces originally having anionic charges (0.02–0.08 mmol/g) using cationic polymers via paper chemistry technology has also been exploited as a pretreatment [14]. Partial acetylation of cellulose microfibril surfaces has been applied to wood cellulose, in which mechanical disintegration of the partially acetylated cellulose fibers was applied in acetone to reduce energy consumption in the mechanical disintegration stage [15]. Each pretreatment resulted in a remarkable reduction of fibrillation energy to lower than 10% of that without pretreatment.

On the other hand, new methods using 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated oxidation in water have been developed to selectively introduce abundant sodium carboxylate groups on crystalline wood cellulose microfibril surfaces [6,16–18]. TEMPO is a water-soluble and stable nitroxyl radical, and its chemical structure changes to *N*-oxoammonium cation and hydroxyl amine structures upon oxidation and reduction, respectively (Figure 4). de Nooy et

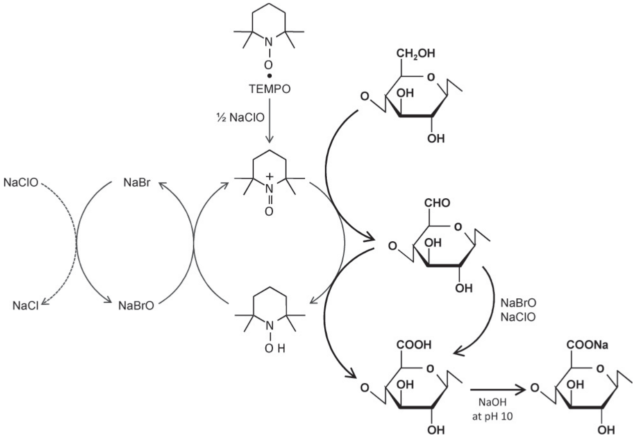

**Figure 4.** TEMPO-mediated oxidation of cellulose glucosyl unit to glucuronosyl using the TEMPO/NaBr/NaClO system in water at pH 10 [6].

al. were the first to succeed in the highly position-selective and efficient conversions of C6-primary hydroxyl groups of water-soluble polysaccharides such as pullulan and amylodextrin to C6-carboxylates by TEMPO/NaBr/NaClO oxidation under aqueous alkaline conditions [19].

When TEMPO-mediated oxidation is applied to bleached wood cellulose fibers, the original fibrous morphologies and the crystal structure, crystallinity, and crystal width of cellulose I are unchanged before and after the oxidation, while significant amounts of sodium carboxylate groups are formed in the oxidized cellulose fibers. Subsequent studies showed that such sodium carboxylate groups are formed selectively on crystalline cellulose microfibril surfaces by TEMPO-mediated oxidation; the C6-primary hydroxyl groups of glucosyl units exposed on the crystalline cellulose microfibril surfaces are selectively oxidized to C6-carboxyl groups of glucuronosyl units [20,21]. Aqueous slurries of TEMPO-oxidized wood celluloses having sufficient C6-carboxylate content (>1.2 mmol/g) are convertible to highly viscous and transparent gels consisting of mostly individualized TEMPO-oxidized cellulose nanofibrils (TOCNs) by gentle mechanical disintegration treatment (Figure 5).

For effective preparation of TOCNs with sufficient amounts of carboxylate groups within a shorter reaction time, printing and writing papermaking grade bleached kraft pulps containing 10–15% hemicelluloses are preferable. In the case of TEMPO-mediated oxidation, oxidized TEMPO molecules or *N*-oxoammonium ions should have covalent bonds with C6-primary hydroxyls present on the crystalline cellulose microfibrils. Hemicellulose fractions present between crystalline cellulose microfibrils in such paper-grade kraft pulps behave like sponges, achieving quite smooth movement of the TEMPO molecules between the fibrils [6]. When highly crystalline cotton linters pulp was used as a starting material in place of wood kraft pulp, the obtained TEMPO-oxidized celluloses had lower carboxylate content and lower nanofibrillation yield after mechanical disintegration treatment in water.

Because completely individualized and long nanofibrils were obtained, the tensile strengths and Young's moduli of individual TOCNs were measured using AFM. TOCN tensile strength was estimated based on a model for the sonication-induced fragmentation of filamentous nanostructures. The resulting strength parameters were then analyzed based on fracture statistics. The thereby obtained mean strength of the wood cellulose nanofibrils ranged from 1.6 to 3 GPa, comparable to those of commercially available multi-walled carbon nanotubes and Kevlar® [22,23].

Acid hydrolysis pretreatment of native celluloses with, for example, 64% $H_2SO_4$ has been well known to prepare nanocrystalline celluloses (NCC, cellulose nanocrystals or cellulose nanowhiskers) which have spindle-like morphologies with low aspect ratios [24]. CelluForce, Canada, has successfully

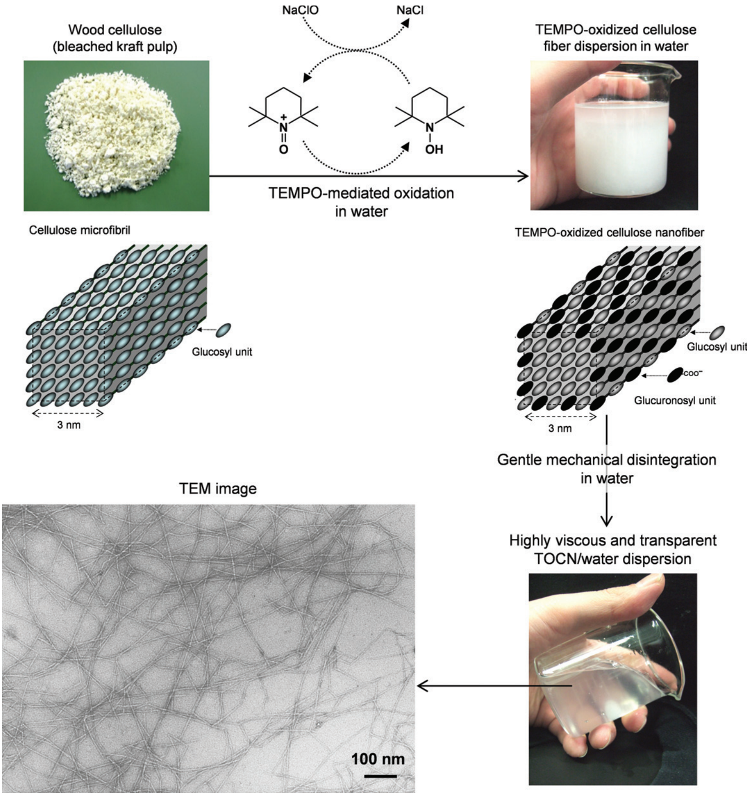

**Figure 5.** Preparation of TEMPO-oxidized cellulose nanofibrils (TOCNs) from wood cellulose, and the corresponding structural model of TOCN.

began production NCC at 1t/d from 2012 for various applications in high-tech fields. In the case of NCC, fully spray-dried and powder-like samples can be delivered, which is advantageous [25] when compared with aqueous MFC, NFC, and TOCN dispersions containing more than 98% water.

## APPARATUSES OF CELLULOSE FIBRILLATION

Ball-milling of cellulose fibers under dry conditions leads to decreases in both crystallinity and molecular weight, converting them into powder-like morphologies with irregular shapes which have been used as disordered cellulose model samples at the laboratory level. When cellulose fibers suspended in water undergo refining or disintegration with strong mechanical shear-forces, micro- and partial nano-fibrillation proceed more efficiently. Various apparatuses, such as high-pressure homogenizers, including microfluidizer-type and aqueous counter-collision-type homogenizers, grindstone-type ultra-fine friction grinder (i.e., Super Masscolloiders®), and twin-screw-type extruders have been applied to prepare highly fibrillated celluloses suspended in water or in thermoplastics in some cases. Each apparatus has both advantageous and disadvantageous points in terms of nanofibrillation efficiency, depending on the targeted nanofibrillation level and also the pretreatments applied to the original wood cellulose.

When TEMPO-oxidized celluloses with sufficient carboxylate contents (>1.2 mmol/g) were subjected to nanofibrillation, the oxidized wood cellulose fibers were convertible to mostly individualized TOCNs dispersed in water which had ultrafine and homogeneous widths of ~3 nm, similar to those of the original wood cellulose microfibrils. In this case, the lengths and length distributions of the TOCNs caused primary variables of the properties, and the viscoelastic characters of diluted TOCN/water dispersions and molecular weights of TOCNs provided some information concerning the above variable factors [26]. On the other hand, when cellulase-pretreated or partially carboxymethylated wood cellulose fibers were converted into NFC/water dispersions using the aforementioned apparatuses, NFCs with much higher molecular weights (than TOCNs) consisting of longer fibril lengths (than TOCNs) partially forming network structures were obtainable. The widths of these NFCs averaged 10–20 nm but ranged widely from 3 nm to ~100 nm, depending on both the pretreatment and fibrillation conditions.

## PROCESSING OF NANOFIBRILLATED CELLULOSE TO BULK MATERIALS

NFCs with various fibrillation levels, width/width distributions, length/length distributions, and surface structures are obtained, as described above, from wood pulps subjected to various pretreatments under different nanofibrillation conditions. The next stage is how to process such promising and new bio-based water-dispersed nanofibers into functional materials using cost-effective and environmentally friendly procedures. Two key requirements are: i) an efficient way to remove abundant water from the highly swollen and nanodispersed NFC/water dispersions while maintaining the unique properties of NFCs, and ii) an effective procedure to add functionalities (such as high mechanical strength, light transparency, gas-barrier properties, efficient nanometal catalysts, electric conductivity, thermal stability, porous structure) to wet or dried bulk materials and composites consisting of NFCs.

## Nanopaper films

Drying of NFC/water dispersions having low solid consistencies cast on a plate to make films or paper-like materials takes a long time. When NFC/water dispersions are filtered using a coarse filter, most of the NFCs move with the filtrate without being trapped. In contrast, when the dispersions are filtered with too fine a filter, the filter becomes clogged with highly swollen NFC gel. However, filtration is one of the most effective ways to remove water from aqueous NFC dispersions and increase their solid content. Moreover, if nanopaper films could be prepared from NFCs using papermaking-like processes, they would be of great interest as a reinforcement in biocomposites, and as gas barriers, membranes, filters, and films for use in high-technology devices, including for biomedical applications. Rapid preparation of large and flat nanopaper films of high surface smoothness and optical transparency is, therefore, important to facilitate the development of such new applications. Furthermore, the hydrocolloid nature of NFC suspensions suggests inclusion of inorganic particles is possible, as has been done by mixing water-soluble polymers with exfoliated nanoscale silicate platelets obtained from montmorillonite.

In this context, a procedure which uses a semiautomatic sheet former to make large and smooth nanopaper films of 200 mm in diameter and 60 μm in thickness from NFC/water dispersions has been developed. Flat nanopaper films can be prepared using this procedure within about 1 h. This procedure is applicable to the preparation of not only cellulose nanopapers but also NFC/inorganic hybrid films (Figures 6 and 7) [27,28]. A total of 80 g NFC/water dispersion was diluted with water, and the final NFC concentration was adjusted to 0.2 wt%. The dispersion was degassed with a water vacuum pump, and filtration of the degassed dispersion was carried out in a semiautomatic sheet former under vacuum (Figure 6, step 1). The dispersion was poured into a hollow cylinder containing a metallic sieve

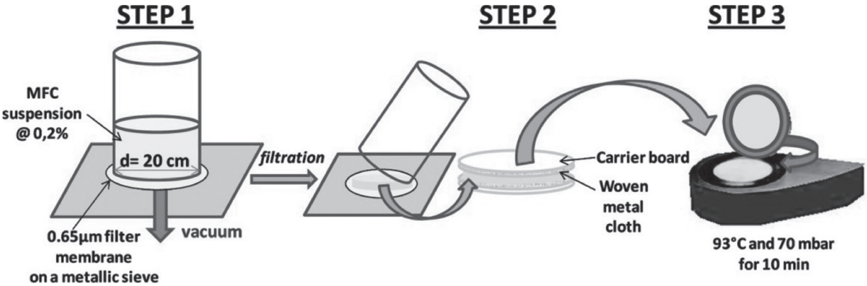

**Figure 6.** Preparation of large and smooth nanopaper films from NFC/water dispersion using a semiautomatic sheet former [27,28].

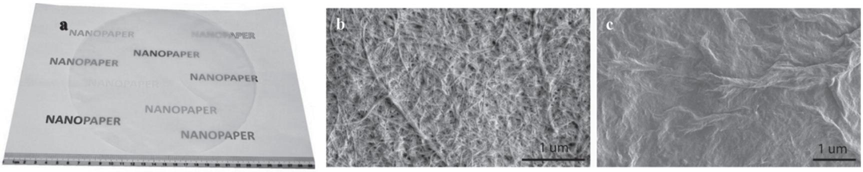

**Figure 7.** (a) Photograph of a 200 nm diameter cellulose nanopaper film on top of A4 copy paper, and SEM images of the surfaces of (b) nanopaper film and (c) hybrid nanopaper film consisting of NFC and montmorillonite [27].

at the bottom (pore size, 110 µm). A nitrocellulose ester filter membrane with 0.65 µm pore size was placed on top of the sieve. The filtration time of the 0.2 wt% dispersion depended on the final thickness of the nanopaper, and was ~45 min for a 60 µm thick nanopaper film. A strong gel formed on top of the filter membrane after filtration. The gel cake was peeled from the membrane and stacked first between two woven metal cloths (aperture width 80 µm; wire diameter 50 µm) and then two paper carrier boards (Figure 6, step 2). This package was placed in the sheet dryer for 10 min at 93ºC under a vacuum of about 70 mbar (Figure 6, step 3) [27]. A similar papermaking process to prepare nanocellulose sheets from MFC/water dispersions was reported by Varanashi and Batchelor [29].

The work of Henriksson et al. [30] showed the potential of nanopaper to provide high tensile strength and high strain to failure (Figure 8a). In these experiments, nanopaper films were prepared by vacuum filtration of a 0.2% aqueous NFC

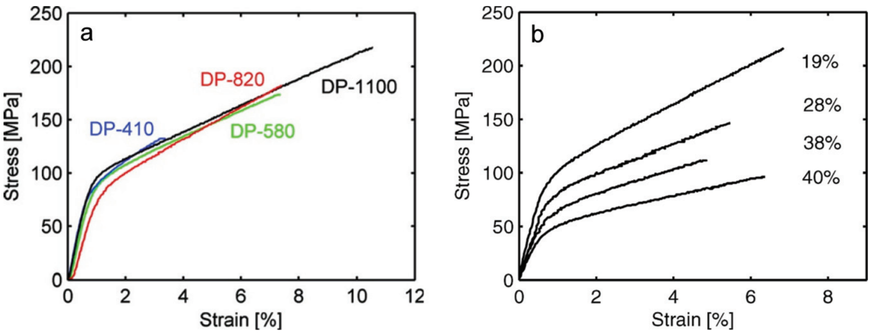

**Figure 8.** (a) Typical stress-strain curves for nanopaper films prepared from aqueous dispersions of NFCs with different DP values, and (b) those of NFC (DP 800) films with different porosities [30].

dispersion. The films were filtrated on a glass filter funnel using filter paper or filter membrane. After filtration, the wet films were stacked between filter papers and then dried at 55ºC for 48 h under an applied pressure of about 10 kPa. This resulted in NFC films with thicknesses in the range 60–80 μm. Porous films were prepared by solvent exchange on the filtered film before drying. After filtration, the wet film was immersed in methanol, ethanol, or acetone for 2 h. The solvent was replaced by fresh solvent and the film was left for another 24 h, after which the film was dried in the same way as described above. This resulted in films of various porosities and thicknesses in the range of 70–90 μm [30].

The strongest nanopaper film prepared above exhibited a strain to failure of around 10% and a strength of above 200 MPa. The film showed yield at a stress level of ~100 MPa much lower than its ultimate strength, which was followed by a plastic deformation region with considerable strain-hardening due to the formation of a nanofibrous network. Yielding is associated with failure at the fibril-fibril interface. In the plastic deformation region, the modulus of the network increased with strain. It is likely that the individual nanofibrils became straightened and better oriented in the direction of loading during plastic deformation. Nanofibrils slide with respect to each other so that their nanofibril network structure is altered during loading. The results in Figure 8a show that the strongest nanopaper films were also the most ductile. Their high degrees of cellulose polymerization (DP) should have a positive effect on tensile strength.

The best nanopaper structures also had carboxylate groups on the fibril surfaces, prepared by TEMPO-mediated oxidation. Because the tensile tests were carried out under conditions of 50% relative humidity (RH), those nanofibrils with carboxylate functionality in aqueous dispersions were surface-hydrated in nanopaper form. This could favor plastic deformation since the hydrated region may serve as a lubricant and thus facilitate the sliding of fibrils with respect to each other.

From a physical mechanism point of view, the density of fibril-fibril bonds and corresponding debonding behavior are important. Moreover, the frictional behavior between fibrils sliding with respect to each other is significant for the strain-hardening behavior of the materials. High strain to failure correlates with a high specific area or porosity of the NFC network, which is possibly correlated with a low density of weak fibril-fibril bonds (Figure 8b) [31]. The nanopaper films with different pore structures were those prepared with the solvent-exchange and filtration method.

Nanopaper films with preferred orientation of TOCNs have been prepared by cold-drawing [32]. The preparation route is papermaking-like and includes vacuum filtration of the TOCN/water dispersion, drawing in a set state, and drying. At a high draw-ratio, the degree of TOCN orientation is as high as 82%, and the Young's modulus is 33 GPa. The highest average strength reported is

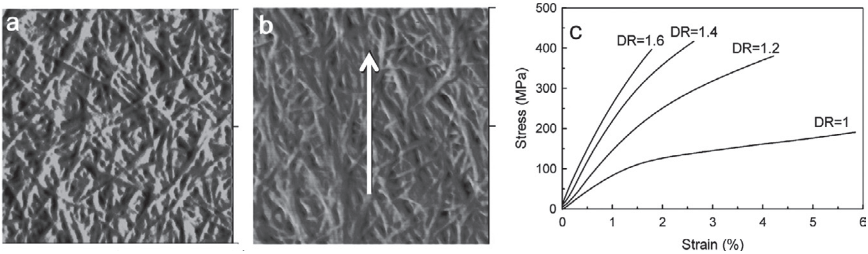

**Figure 9.** AFM micrographs of the surfaces of (a) a reference non-drawn TOCN nanopaper sample (DR = 1), (b) a drawn TOCN nanopaper at DR = 1.4, (c) tensile stress-strain curves of TOCN nanopaper films at different draw ratios [32].

430 MPa (Figure 9). This is much higher than the mechanical properties of isotropic nanopaper made of the same TOCNs, where the typical modulus is 15 GPa and the tensile strength is ~220 MPa. However, the strain to failure of the oriented sample is only 2%, because TOCNs do not reorient and slide when they are in parallel orientation. The cold drawing method can also be applied to TOCN/hydroxyethyl cellulose (HEC) nanocomposites [32].

## Nanopaper aerogels

Aqueous NFC and TOCN dispersions can be converted into nanopaper aerogels using new drying methods [31,33]. Very porous aerogels were prepared by solvent exchange from water to *t*-butanol followed by drying [31]. This resulted in much higher specific surface areas of the aerogels (150–280 $m^2/g$) compared with those of freeze-dried aerogels prepared from water. The resulting aerogels showed a fine NFC network structure and much lower modulus and yield strength compared with those of cellular structured freeze-dried foams. Fitting of modulus data to a theoretical fiber network model resulted in estimated NFC segment lengths between fibril-fibril joints of 300–480 nm in agreement with the structures observed in FE-SEM images.

The aerogel study inspired work on nanopaper structures dried by different routes. The stress-strain curves of such nanopaper structures having high specific surface area showed high ductility. Drying from supercritical carbon dioxide resulted in a specific surface area of 480 $m^2/g$. The strain to failure of this supercritical $CO_2$-dried nanopaper was 17% at 56% porosity and 50% RH, the modulus was 1.4 GPa, and the strength in tension was 84 MPa. In the context of a fiber network model, a higher specific surface area of the nanopaper may be related to increased length of fibril segments between fibril-fibril joints, which would explain the lowered modulus and yield strength obtained. The increased strain

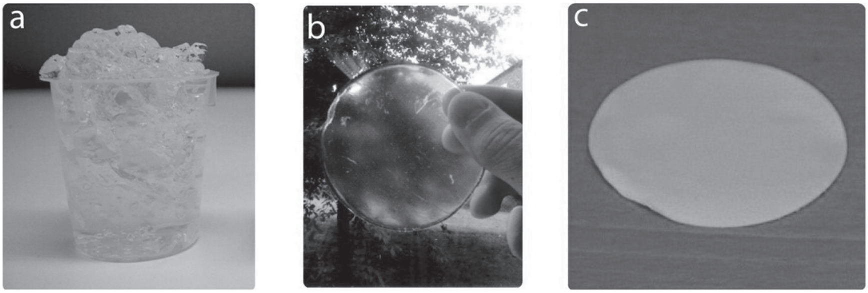

**Figure 10.** Images of (a) TOCN dispersion, (b) a TOCN nanopaper hydrogel, and (c) a typical NFC nanopaper [31].

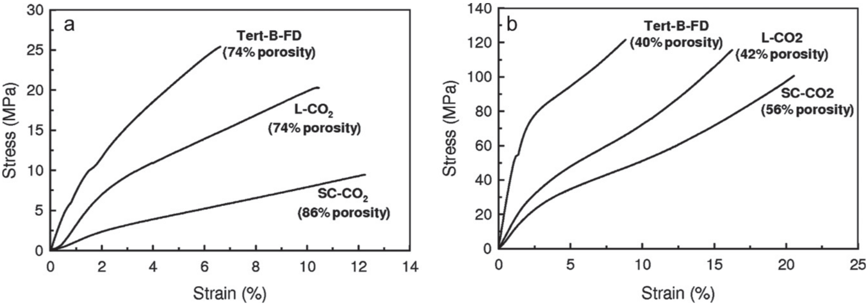

**Figure 11.** Tensile stress-strain curves for porous nanopaper aerogels prepared from (a) NFCs and (b) TOCNs. The different preparation methods and the corresponding porosities are shown [31]. Tert-B-FD: freeze-dying from *t*-butanol, L-$CO_2$: liquid $CO_2$-drying, SC-$CO_2$: super-critical $CO_2$-drying.

to failure indicated that sliding and reorientation of the NFCs with respect to neighboring fibrils were facilitated (Figures 10 and 11) [31].

## NANOPAPER COMPOSITES

Based on the aforementioned preparation techniques of nanopaper films and aerogels and their specific properties, various NFC-containing composites have been prepared in the expectation of high mechanical properties and unique functionalities. For example, homogeneous films with an NFC content in the range of 10–70 wt% were successfully prepared by casting and drying dispersions of

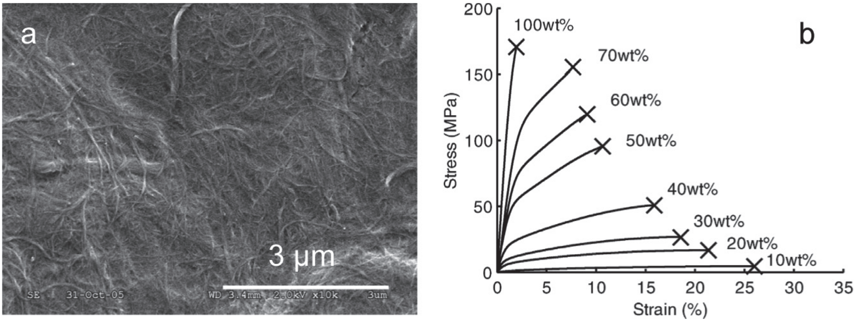

**Figure 12.** (a) FE-SEM image of a cellulose nanocomposite film surface (50 wt% NFC, 50/50 amylopectin/glycerol matrix), and (b) typical tensile curves for NFC-amylopectin-glycerol composites with varied NFC content and fixed matrix composition: 50 wt% glycerol and 50 wt% amylopectin. The NFC contents are indicated in the figure [34].

nanostructured cellulose network combined with an almost viscous polysaccharide matrix in the form of a 50/50 amylopectin-glycerol blend. The NFCs were well dispersed and predominantly oriented randomly in-plane. High tensile strength was combined with high modulus and very high work of fracture in the nanocomposite with 70 wt% NFC. The reasons for this interesting combination of properties include the properties of the nanofibrils and matrix, favorable nanofibril-matrix interaction, good dispersion, and the ability of the NFC network to maintain its integrity to a strain of at least 8% (Figure 12) [34,35].

Nacre-mimicking hybrids having high inorganic content (>50 wt%) tend to show low strain-to-failure. Therefore, clay nanopaper hybrid composites consisting of montmorillonite platelets in a continuous NFC matrix have been prepared with the aim of harnessing the intrinsic toughness of fibrillar networks. Hydrocolloid mixtures were used in a filtration approach akin to paper processing. Measurement of their uniaxial stress-strain curves under tension with thermal analysis were carried out by dynamic mechanical thermal analysis (DMTA) and thermogravimetric analysis (TGA). Their fire retardancy and oxygen permeability characteristics were also measured. The continuous NFC matrix is a new concept and provides unusual ductility to the nanocomposite, allowing inorganic contents as high as 90 wt%. Clay nanopaper extends the property range of cellulose nanopaper, and is of interest in self-extinguishing composites and in oxygen barrier layers [34].

Moreover, NFC/HEC biocomposites show unique nanostructural toughening effects. HEC is an amorphous cellulose derivative of high molar mass and toughness and is prepared using a previously developed route inspired by papermaking which is green, scalable, and allows high reinforcement content. Nanostructural control of polymer matrix distribution is exercised as the polymer associates with the reinforcement. This results in nanocomposites of a soft HEC matrix surrounding NFC forming a laminated structure at the submicron scale, as observed by FE-SEM. The effect of NFC volume fraction on the tensile properties, thermomechanical stability, creep properties, and moisture sorption of these nanocomposites has been studied. The results showed strong property improvements with increasing NFC content due to the load-carrying ability of the fibril network. At an NFC volume fraction of 45%, the toughness was more than doubled compared with that of NFC nanopaper. This nanocomposite is located in previously unoccupied space in a strength versus strain-to-failure property chart, outside the regions occupied by microscale composites and engineering polymers. These results therefore emphasize the potential for the extended mechanical property range offered by nanostructured biocomposites based on high volume fraction nanofibril networks (Figure 13) [35].

NFC-reinforced starch-based foams, prepared by the freezing/freeze-drying route, are interesting porous materials due to strong NFC reinforcement of the cell wall itself. However, both cell wall composition and cell structure must be controlled to fully realize the potential of these nanocomposite biofoams. NMR-analysis of bound water content, DSC and freezing experiments in combination with freeze-drying experiments and FE-SEM microscopy were used to determine a suitable freeze-drying temperature. The freeze-drying temperature was found to be critical in avoiding cell structure collapse. Improved preparation conditions enabled the successful creation of foams with mixed open and closed cell structures and as much as 70 wt% NFC in the cell wall (Figure 14) [36].

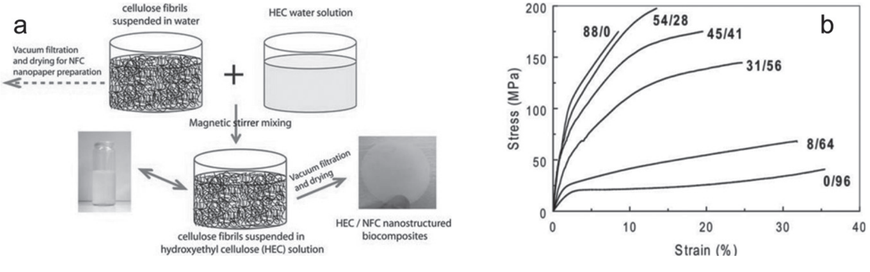

**Figure 13.** (a) Preparation scheme for NFC nanopaper and its HEC biocomposites. A beaker of NFC hydrocolloid is combined with an HEC solution and mixed. The mixture is then filtered and dried to produce a biocomposite film. (b) Stress-strain curves of NFC/HEC nanocomposites with different NFC/HEC volume fractions under uniaxial tensile loading, where 0/96 represents neat HEC and 88/0 represents nanopaper with 100 wt% NFC and an estimated porosity of 12% [35].

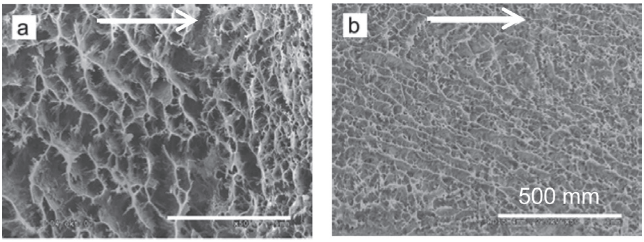

**Figure 14.** Starch-based foams with 60 wt% NFC in the cell wall, freeze-dried at a chamber pressure of (a) 0.19 mbar and (b) 0.008 mbar. The sections are at half the height of the original foams. The samples were obtained from the vicinity of the middle parts of the foams. The arrows show the direction of the cylinder axis in the foams [36].

Meanwhile, a starch-based biofoam was able to reach mechanical properties (E = 32 MPa, compressive yield strength, 630 kPa) comparable to those of expanded poly(styrene) (PS) of similar relative density at 50% relative humidity. This result was attributed to the nanocomposite concept in the form of a NFC network reinforcing the hygroscopic amylopectin starch matrix in the cell wall. The biofoams were prepared by the freezing/freeze-drying technique and subjected to compressive loading. The cell structure was characterized by cross-sectional FE-SEM. The mechanical properties observed were related to the cell structure and nanocomposite composition of the cell wall (Figure 15) [37].

Consequently, NFCs can be combined with low yield stress polymers to form cellulose biocomposites with a unique combination of high strength, modulus, and strain to failure explained by their mechanism of plastic deformation. Papermaking-type processes can be used, and materials with high volume fraction

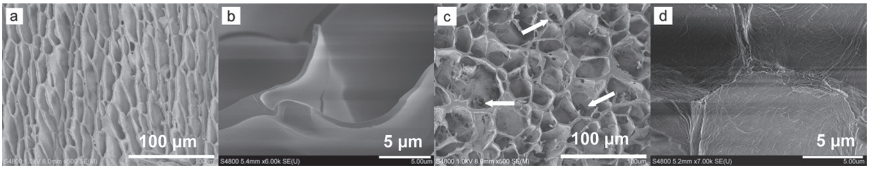

**Figure 15.** FE-SEM images of (a, b) neat amylopectin starch foam and (c, d) a composite foam with 40 wt% NFC in the cell wall. Images show (a, c) the cell structure and (b, d) the structure of the cell wall. Holes present in the cell walls of the composite foam are indicated by white arrows, showing the hierarchical structure of the composite foam [37].

of the reinforcement phase can be formed. Clay platelets have also been added to the hydrocolloidal mixture to obtain high-performance nanocomposites with good flame and fire-retardant properties [31].

## PREPARATION OF BULK MATERIALS FROM TOCN/WATER DISPERSIONS

When TEMPO-oxidized wood celluloses have sufficient amounts of carboxylate groups (>1.2 mmol/g), transparent and highly viscous TOCN/water dispersion gels consisting of completely individualized cellulose nanofibrils can be obtained by mild mechanical disintegration treatment in water. For such TOCNs, filtration is not suitable for making dried films, although complete filtration takes long time due to clogging, some of the TOCNs pass through a fine pore-sized membrane. Thus, casting of the TOCN/water dispersions on a plate and drying is used. The TOCN films thereby obtained are transparent and self-standing with plywood-like nanolayered structures originating from nematic-ordered domains consisting of self-aligned structures of TOCN elements, good oxygen-barrier properties under dry conditions, and high mechanical strengths [38–41].

In addition, careful adjustment of the pH and solvent evaporation in TOCN dispersions produce a wide range of artificial bulk materials with outstanding properties. Examples include unprecedentedly stiff freestanding hydrogels with a water content of 99.9% and ultralow-density, and tough aerogels with large surface areas. These materials are expected to be further developed as robust frameworks for polymer nanocomposites or high-capacity supports for catalysts and the other functional materials [39].

On the other hand, porous TOCN networks, similar in appearance to spider ‘webs, have been prepared by direct air-drying of TOCN/surfactant dispersions using support materials containing micrometer- or submicrometer-sized pores. These porous TOCN networks were composed of a mixture of single TOCNs with widths smaller than 10 nm and TOCN bundles, and approximately 90% of the open pores in the networks were 10–100 nm in size. These network structures can be categorized as nanoporous materials. Laser scanning microscopy was used for progressive observations of the formation of porous TOCN networks, and showed that wet thin films of the TOCN/surfactant dispersion were first formed, followed by the gradual appearance of submicrometer-sized pores in the films as water evaporated. In all cases examined, a single TOCN network with a two-dimensional structure was formed in the pore of the support [42]. The conversion systems used to from bulk materials from TOCN/water dispersions containing self-aligned TOCN elements are summarized in Figure 16.

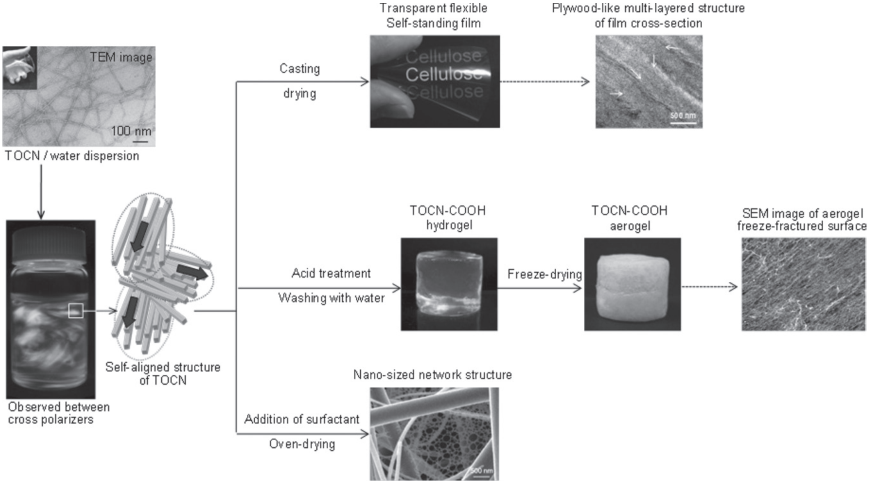

**Figure 16.** Conversion from TOCN/water dispersion to diverse bulk materials.

## TOCN COMPOSITE MATERIALS

Because TOCN elements form dense films with plywood-like nanolayered structures [39], not only TOCN-self standing films but also TOCN-coated poly(L-lactide) (PLLA) and poly(ethylene) (PE) films have high oxygen-barrier properties under dry conditions (Figure 17a). Positron-annihilation lifetime-spectroscopy (PALS) analysis showed that such TOCN layers had quite small and similar pore sizes of ~0.47 nm from the film surface to inside, which is slightly greater than the kinetic diameter of oxygen (0.34 nm). However, the pores were present independently without any structures connecting them [40]. These close-packed structures of TOCN elements in the layers likely originate from strong electrostatic repulsion between anionically charged TOCN elements, which may work efficiently not only in the aqueous dispersion state but also during the drying process of water evaporation. In fact, when the counter ions of TOCN-COONa were changed to protons (TOCN-COOH), the TOCN-COOH thin layer did not have as high oxygen-barrier properties as those of the TOCN-COONa layer [43]. However, the low oxygen permeabilities of the TOCN-COONa films and layers remarkably increase with RH due to the hydrophilic nature of TOCN-COONa type structures, which is one of the shortcomings of TOCN films and layers used as gas-barrier materials [40].

Poly(vinyl alcohol)/TOCN composite fiber with a weight ratio of 100:1 was prepared from a mixture of aqueous poly(vinyl alcohol) (PVA) solution and

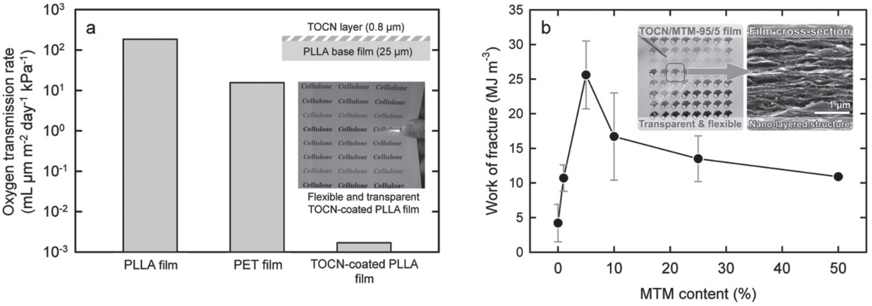

**Figure 17.** (a) Oxygen permeability of PLLA, poly(ethylene terephthalate) (PET) and TOCN-coated PLLA films at 0% RH. (b) Transparent, flexible and ultrastrong TOCN/montmorillonite (MTM) composite films [44].

aqueous TOCN dispersion using spinning, drawing, and drying processes. The as-spun PVA/TOCN composite fiber was further drawn up to a draw ratio of 20 by heating at up to 230ºC. The maximum tensile modulus of this PVA/TOCN composite drawn fiber reached 57 GPa, remarkably higher than that of commercial PVA drawn fibers. In addition, the PVA/TOCN composite drawn fiber had higher storage modulus than that of the PVA drawn fiber at each temperature in the range 28 to 239ºC. Structural analyses showed that amorphous PVA regions in the composite drawn fiber were more oriented than those in neat PVA fiber after the addition of the small amount of TOCN used. These results indicate that TOCN elements were individually dispersed in the PVA matrix without aggregation and formed hydrogen bonds with amorphous PVA molecules in the composite drawn fiber [45].

TOCN/montmorillonite (MTM) composite films were prepared from TOCN with an aspect ratio of >200 dispersed in water with MTM nanoplatelets. The composite films were transparent and flexible and showed ultrahigh mechanical and oxygen barrier properties through their nanolayered structures, which were formed by compositing the anionic MTM nanoplatelet filler in anionic and highly crystalline TOCN matrix. A composite film with 5% MTM content had a Young's modulus of 18 GPa, tensile strength of 509 MPa, work of fracture of 25.6 MJ/$m^3$, and oxygen permeability of 0.006 mL µm $m^{-2}$ $day^{-1}$ $kPa^{-1}$ at 0% RH, respectively, despite having a low density of 1.99 g/$cm^3$ (Figure 17b) [44].

Because TOCN has abundant sodium carboxylate groups densely present on the surface of each nanofibril, sodium counter ions can be replaced with protons and other metal ions by simple ion-exchange. Thus, metal nanoparticles were prepared using TOCN elements as template and their catalytic reaction rate for reduction from 4-nitrophenol to 4-aminophenol with $NaBH_4$ were found to be

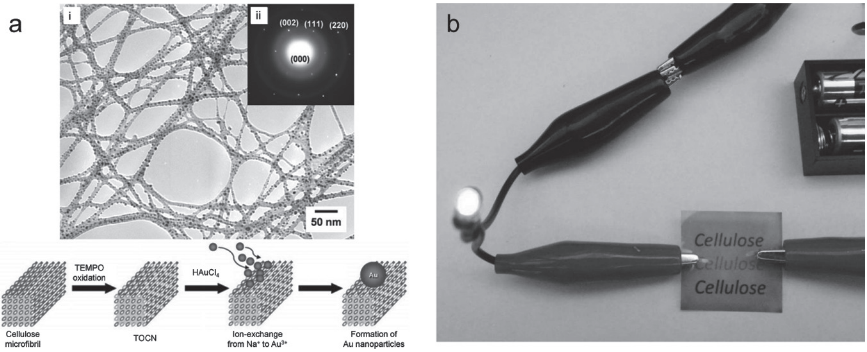

**Figure 18.** (a) TEM image of gold nanoparticles present on TOCN elements, and scheme to prepare gold nanoparticles on TOCN template [46]. (b) TOCN/carbon nanotubue-coated PET film having transparency and conductivity [48].

1000 times that of reference [46,47]. A TEM image showed the formation of gold nanoparticles along the TOCN elements (Figure 18a). When an aqueous dispersion of 6% single-walled carbon nanotubes containing carboxyl groups was mixed with a TOCN/water dispersion and the mixture was cast on a hydrophilized PE film, transparent, flexible and conductive composite films were obtained (Figure 18b) [48,49].

Although TOCNs with sodium carboxylate groups are nanodispersible only in an aqueous medium, TOCN-COOH prepared by ion-exchange with acid becomes nanodispersible in some high boiling point polar aprotic organic solvents such as DMF, DMAc, and NMP [50]. Because PS is soluble in DMF, TOCN-COOH/PS composite films were obtained by mixing TOCN-COOH/DMF dispersion and PS/DMF solution at various ratios followed by casting and vacuum-drying. The obtained composite films exhibited high optical transparencies and their tensile strengths, elastic moduli, and thermal dimensional stabilities were found to increase with TOCN content. Dynamic mechanical analysis showed that the storage modulus of the obtained TOCN/PS films increased significantly with TOCN content above the glass-transition temperature of PS due to the formation of an interfibrillar network structure of TOCNs in the polymer matrix, based on percolation theory. The outstanding and effective polymer reinforcement by TOCNs results from their high aspect ratio, high crystallinity, and nanodispersibility in the polymer matrix (Figure 19a) [51].

When primary amine compounds having long hydrophobic chains were introduced into the abundant carboxyl groups of TOCN to form amine/carboxyl salt structures, the surface-hydrophobized TOCNs become nanodispersible in

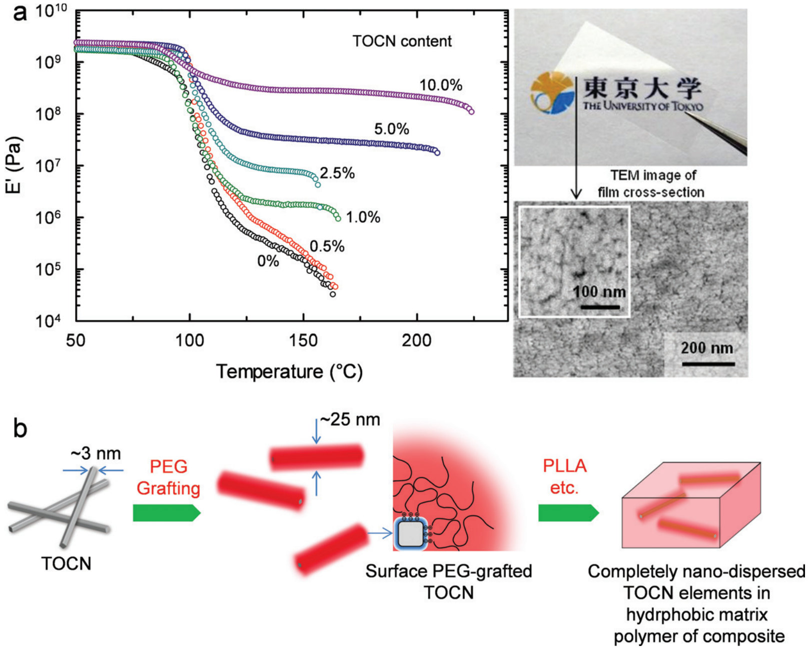

**Figure 19.** (a) Thermal properties of TOCN/PS composite films, and TEM image of a cross section of the composite film, showing the nanodispersibility of TOCN elements in PS matrix [51]. (b) Surface PEG-grafting on TOCN elements and TOCN/PLLA composite films using chloroform as a common medium [52].

*i*-propanol, chloroform, toluene, tetrahydrofuran, and other conventional low boiling point organic solvents [51–53]. For example, surface-grafting of crystalline and ultrafine TOCNs with poly(ethylene glycol) (PEG) chains via ionic bonds was achieved by a simple ion-exchange treatment. The PEG-grafted TOCNs/chloroform dispersion and PLLA/chloroform solution were mixed in various ratios, and PEG-grafted TOCNs/PLLA composite films with various blend ratios were prepared by casting the mixtures on a plate and drying. The tensile strength, Young's modulus, and work of fracture of these composite films were remarkably improved, despite low cellulose addition levels (<1 wt%). This highly efficient nanocomposite effect was explained in terms of achievement of nanodispersion of the PEG-grafted TOCNs in the PLLA matrix. Moreover, some attractive interactions mediated by the PEG chains were likely to have formed between the TOCNs and PLLA molecules in the composites, additionally enhancing the efficient nanocomposite effect [52]. Similar work using PLLA oligomer-grafted NFC/PLLA has been reported [54].

## SUMMARY

Both NFCs and TOCNs prepared from wood cellulose have unique and promising properties, such as high crystallinities, aspect ratios, Young's moduli, and tensile strengths, which originate from the properties of natural wood cellulose microfibrils. NFCs are less damaged than TOCNs in terms of molecular weight and fibril length, and form nanofibril network structures having fibril-fibril joints in both aqueous dispersion and dried films and aerogels. These are useful in making light-weight NFC/matrix nanocomposite materials with high mechanical strengths including high ductility. Nanopaper films and aerogels can be prepared efficiently from aqueous NFC dispersions using filtration processes like those used during papermaking, which are expected to widen the practical applications of NFCs. One of the characteristics of TOCNs, on the other hand, is their nanodispersibility in both water and some organic solvents by modification of the abundant carboxyl groups present on their crystalline surfaces with hydrophobic compounds through ion-exchange. If such completely nanodispersed states of TOCNs can also be achieved in hydrophilic and hydrophobic polymer matrices, increased mechanical and thermal properties are expected to be achieved for TOCN-containing composite materials even at low TOCN loading ratios. The oxygen-barrier properties of TOCN films and coating layers are also promising for application in high-performance packaging materials, although the hydrophilic nature of the TOCNs must first be effectively controlled.

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## Transcription of Discussion

# PREPARATION AND APPLICATIONS OF NANOFIBRILLAR CELLULOSES

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First of all, thank you very much for a very nice presentation. Just a general remark about TEMPO oxidation, because of course, the purpose is to have biomaterial. On the other hand, TEMPO oxidation is not so environmentally friendly, especially because you use bleach. So, are you looking at different ways to oxidize your cellulose, to generate the bonds?

*Akira Isogai*

Yes, well as far as I know, the TEMPO method is the best in terms of oxidation selectivity at crystalline cellulose microfibril surfaces, keeping the high crystallinity and high nanofibrillation yields. Of course, you are right that the safety issue of TEMPO is very important, even though the addition level is very small. Nippon Paper are developing a method to recycle TEMPO from the effluent, so as not to cause pollution. It is an aqueous system, with no organic solvent, at room temperature and atmospheric pressure as well as giving the best results.

The way to use and manage bleach has been well controlled by the pulp and paper industry. Therefore, I do not think that the use of bleach is serious, and also bleach is one of the most inexpensive oxidants. As long as bleach is used to fully bleach paper pulps, no dioxins and related toxic compounds are formed. I think it is possible for companies to use bleach in TEMPO-mediated oxidation.

*Discussion*

*Gil Garnier* Monash University

Two short questions. First, do you depolymerise cellulose with the TEMPO process? The second, what is the yield from the pulp?

*Akira Isogai*

Very good questions. Unfortunately, during the TEMPO oxidation process, the molecular weight of the oxidised cellulose decreases to some extent. For example, when the original pulp has a DP of 1200, the oxidized pulp prepared under alkaline conditions, which has a sufficient amount of carboxyl groups to be convertible to nanofibrillar cellulose during mechanical disintegration in water, has a DP as low as 600–800. However, when TEMPO-mediated oxidation under neutral conditions is adopted, which needs a longer reaction time and heating the mixture to 30–60 °C, the DP of oxidized celluloses can be controlled to be as high as around 1000. In some cases, you have to use TEMPO-oxidized cellulose nanofibrils with high aspect ratios and high molecular weights. In these cases, the alternative TEMPO-mediated oxidation under neutral conditions may be preferable rather than that at pH 10.

*Asaf Oko* SP Technical Research Institute of Sweden

Do you know how much nanofibrillated cellulose, approximately, has to be added to a normal pulp in order to enhance the strength of a cardboard product?

*Akira Isogai*

It depends on the matrix polymers to be composited with TEMPO-oxidized cellulose nanofibrils. When poly(lactic acid) is used as a matrix, only 0.2–0.3% addition of nanofibrils is sufficient to achieve 20–30% improvement of mechanical properties. Even though cellulose is an environmentally friendly material, its hydrophilic nature can be a disadvantage for cellulose-containing nanocomposites with high cellulose contents. So, it is better to add small amounts of nanocelluloses as much as possible to polymer matrices. Because TEMPO-oxidized cellulose nanofibrils have potential to be nano-dispersed in polymer matrices, small amounts of addition level are expected for sufficient mechanical improvement of polymer materials.

*Asaf Oko*

One more question: if you do functionalise the surface of the cellulose with some fatty components, do you reduce the hydroscopic nature or does it stay the same?

*Akira Isogai*

Yes; for example, water-contact angles of the hydrophobized TEMPO-oxidised cellulose nanofibrils (TOCN) films can increase to about 100 degrees. The hydrophobic/hydrophilic nature of TOCNs is, therefore, controllable to some extent by controlling alkyl chain lengths introduced to TOCN surfaces. However, gas-barrier properties of such surface-modified TOCN films clearly decrease owing to long and bulky alkyl chains introduced. So, hydrophobisation and gas-barrier properties of TOCN films are a kind of trade-off relationship.

*Roger Gaudreault* Cascades

Assuming that you would be using a sodium periodate process to do the oxidation, instead of TEMPO, and that you would be able to recycle the periodate stream process, can you comment on the fibre characteristics that you would get, and the cost? Would the TEMPO process still be "the best" if you could use the sodium periodate process with a closed loop (the process stream / chemistry is regenerated and recycled)?

*Akira Isogai*

I am not sure exactly, because the work on the establishment of the TEMPO recycling system has been done at Nippon Paper. But they said that you can recycle TEMPO at least 10–15 times to obtain TEMPO-oxidized celluloses with similar carboxylate contents, molecular weights and yields to those at the first time. However, I have no idea about periodate oxidation of cellulose to be converted to nanocelluloses.

*Torbjörn Wahlström* Stora Enso

What is your view on the patent situation in this area?

*Akira Isogai*

We made a very big mistake concerning patents. We had a partner in Japan, but we did not apply for PCT. So you can make as much TEMPO-oxidized cellulose nanofibre as you like! But I think Nippon Paper has been trying to get various surrounding patents concerning recovery systems of chemicals and improvement of the oxidation process, and the company did a very good job. We have carried out a National Project on TEMPO-oxidized cellulose nanofibres from 2007, and Nippon Paper has already acquired many related patents. But the original patent is available in Japan only.

*Discussion*

*Juha Salmela* VTT

When you add TEMPO-oxidised cellulose nanofibrils to a paper matrix, how do you make sure that they are retained?

*Akira Isogai*

We have never applied TOCN as a paper additive. Some company researchers have used TEMPO-oxidized cellulose nanofibres as retention aids of filler-like particles in papermaking. However, addition levels of TOCN are so small that it might be difficult to determine accurate TOCN contents retained in paper sheets. It may be possible that contents of carboxyl groups in paper sheets indicate retained amounts of TOCNs in paper sheets. This is because TOCNs have high amounts of carboxyl groups.

*Harshad Pande* Domtar

Can you comment on the drying of these nanofibrils, the cost effectiveness?

*Akira Isogai*

Yes, drying of nanocellulose/water dispersions to make films and other materials is a big problem in terms of both cost and process. As I mentioned previously, the KTH group has developed a method to prepare nanocellulose sheets using a process similar to the paper making process, but in the case of TOCNs, which are completely nanofibrillated in water, almost all TOCNs will go to drainage fraction, when the filtration process is applied. So as long as we know, casting and drying of TOCN/water dispersions is the only the way to efficiently dry the dispersions to make films. Of course, in this case, a large amount of energy to remove water from the dispersions is needed. Some researchers have tried adding some alcohol to the aqueous TOCN dispersions to reduce drying energy, but I am not sure whether or not it went well. Because at present the highest TOCN solid content in the dispersions is only 5%, or still 95% of the dispersion is water, the application fields of TOCNs may be limited to some high value-added materials.

*Wolfgang Bauer* Graz University of Technology (from the chair)

You mention the increasing amount of literature regarding nanofibrillated cellulose (NFC) and cellulose nanocrystals (CNC), do you know from which fields these publications mainly come? Which fields of science are publishing on this subject?

*Akira Isogai*

Some papers dealing with cellulose nanofibres or cellulose nanocrystals have been published in high-ranked journals such as Nature and Science. However, most of nanocellulose-related papers have been published in good scientific journals such as Biomacromolecules (ACS), Cellulose (Springer), Carbohydrate Polymers (Elsevier) and others. Some of my students tried to submit papers to Nature or Science, but most of them were rejected and returned within 3 days. So, publication of nanocellulose-related papers in such journals is quite difficult.