Research needs for nanocellulose commercialization and applications

TOM LINDSTRÖM

INTRODUCTION: This short review deals with some applications and research needs for nanocellulosic (NC) materials; primarily cellulose nanocrystals (CNC), cellulose nanofibers (CNF), and bacterial cellulose (BC). Whereas CNC and BC materials are fairly homogenous, CNF materials represent a wide sector of different materials, often with a high heterogeneity. This is due to different pretreatment methods (mechanical, chemical, enzymatic), wood-based or agricultural-based materials, delignification and bleaching procedures, etc. The purpose of this comprehensive review is not to discuss the various production methods, for which the reader may consult with a selected number of reviews [1-6]; thus, the focus is on practical applications. Practical applications and potential markets were also discussed some years ago by other investigators [7-8]. Upscaling and choice of pretreatment methods, as well as economic considerations and different business models, have also been discussed, along with:

- Toxicity and environmental issues [9-10]
- The complex characterization of cellulose nanomaterials [4]

The reader should also be aware of new contenders to the three classic groups of cellulosic nanomaterials, which are already in a commercial phase. These include cellulose filaments [11-12] and materials from mechanical grinding processes [13], and these materials may be nanostructures or not, depending on our classification.

Finally, as indicated by the editorial on p. 275, scientists are currently taking a deep dive into the fundamental features of nanocellulosic materials [14-15].

NANOCELLULOSE APPLICATIONS AND CHALLENGES

Paper and board applications

The use of nanocellulose as a dry strength additive in papermaking was an obvious application early on, as papermakers have known for many years that fines are beneficial for strength properties of paper and board. This application requires an appropriate use of flocculation agents in order to cope with retention and dewatering issues. The economics require cheap CNF materials, such as enzymatically liberated CNC [16-17], that are commercial and can be considered as a mature technology. StoraEnso has been aggressive in this area, but has had few followers. The effects on paper mechanical properties are also theoretically well known. Likewise, cellulose filaments and grinded fiber materials are being explored for the same purpose (see introduction).

Plastic films

Nanofibrils are stronger than the same material in bulk, and this is particularly true for brittle materials, to which CNF can be categorized. This is due to surface defects, internal stresses, etc. The smaller the material entities, the less likely it is to find a defect of given critical size. For nanocellulose, being a fairly new type of material, there has been little or no consideration of the impact of structural defects. The ultimate strength properties of CNF films have been discussed [18-19] and can be conceived as well-known today, as well as their barrier properties [20]. There is no doubt that such films could find great use in the food packaging sector. The economics are, however, critical when competing with cheap fossil-based film materials such as polyethylene. The processing to make such films in an efficient manner has not yet been successful because of the water removal/drying problem associated with high-viscosity materials. There is a pressing research need to alleviate this problem and the oxygen barrier problem at high relative humidity (RH).

Nanocomposite materials

There has been extensive work going on to make strong nanocomposite materials [21]. The crucial point in making composites is the processing. The wet-processing method (casting/evaporation) is a more efficient method compared to extrusion and injection molding. In the wet-processing method the interactions between the nanofibrils formed during drying will form a strong percolated network, ensuring high mechanical stiffness and strength. Focal research needs in wet processing are that drying is difficult with respect to solvent removal and the development of residual stresses.

Extrusion and injection molding are far more difficult, and research challenges such as nanocellulose-aggregation prior to melt processing, nonuniform dispersion within the polymer melt, and compatibility between the nanocellulose and the polymer used are focal needs in this area. CNF materials are obviously more difficult in processing than CNC materials.

Viscosity modifiers

The use of nanocellulose (then termed microfibrillar cellulose) as a viscosifier in food products was extensively explored already in the late 1970s and in the beginning of the 1980s by Turbak's pioneering group. Turbak's group investigated nanocellulose as a stabilizing agent (oil, water, fats) and as a functional food agent [22-23]. It should be noted that agriculturally produced BNC (Nata de Coco) has long been used in various foods as a viscosity modifier. There is no doubt that CNF/BC materials will be explored as a food and pharmaceutical additive and in other industrial applications, such as paints. Market introduction of food products containing CNF is already beginning. The general rheology of CNF materials is fairly well understood, but details of their complexity still need investigation, particularly in view of the polydispersity of CNF materials used in commercial applications [23]. Many general and difficult chemical engineering issues, such as pumping, mixing, and flow features need to be much better understood.

Drug delivery, medical applications and cosmetics

BNC materials dominate this area, as they are particularly suited for use as scaffolds for cell cultivation and drug delivery, as well as medical implants [5]. Suitable implants for medical applications include the flat form, which is used as a mesh, or a tube for the repair of hollow organs and vessels.

Additional current developments in the BNC field mainly concern novel carrier materials for cell cultivation, encapsulation of enzymes, and coatings for medical devices.

There are basic challenges in upscaling of BNC production and in creating additional control elements for BNC production. Not only is the design of BNC hydrogel shape and dimensions important, but also the surface structure and internal BNC structure [5]. CNC materials also show great potential in biomedical devices. Nanocellulose materials are commercially available as various skin creams and facemasks as well.

Water remediation technologies

Cellulose nanomaterials have also been explored for water purification. These technologies include various water/wastewater treatment processes, such as sorption by surface modified NC materials, membrane filtration, and flocculation [24]. This is an emerging technology, which has not yet arrived at commercial scale. The most investigated area is that of adsorbents, which are beneficial for the removal of dyes, heavy metal ions, pharmaceuticals, etc. Tailoring nanofilters made from NC materials is a difficult exercise, as the balance between entrapment capacity and flow capacity must be tailored. A new class of thin film nanofibrous composite (TFNC) membranes, which contain multilayered fibrous scaffolds that include charged CNF with fiber diameters ranging from nanometers to tens of microns, is, however, a promising approach to achieve high capacity filters [25]. Scientific challenges include wet strengthening and membrane fouling, and more detailed studies are necessary to assess the practical applicability of NC materials in catalytic degradation and disinfection-based water treatment processes.

Aerogels, insulation, and polystyrene foam replacement

Cellulose nanogels have low density, high porosity, and large specific surface area, making them useful for adsorption and thermal insulation, as well as for replacement of fossil-based foams [26]. These materials have large-scale potential in the building and the packaging sector. Again, while they have interesting mechanical properties, the economic processing is crucial. These materials are made from sol-gel processing followed by gel drying, usually vacuum or freeze drying or supercritical drying. These methods are, however, expensive for large quantities of solvent removal, and remain as laboratory scale methods. Hence, there are some important research challenges: Cellulose is prone to self-agglomeration, resulting in collapse of the nanogel, while crosslinking or other methods are necessary to maintain the structural features. Therefore, there is a need for an inexpensive and environmentally-friendly method for solvent removal.

Cement nanocomposites

It has recently been found that small additions (0.2 %) of CNC to a cement paste can increase the flexural strength by 20%. The addition of CNC increases the hydration of the cement, thereby improving the mechanical properties of the cement [27-28]. This research is very interesting, but it is an early development stage. Many variables, such as type of CNC and cement, dosage addition mode, dispersion, matrix type and curing process (to mention a few) affect the end result. It is, however, clear that CNC is more efficient than BC or CNF because dispersion is much simpler with CNC. At this point, when there is only minimal information on how the different variables affect the properties and there is limited information on possible mechanisms (apart from the hydration effect), it is difficult to point to a dedicated research direction, as well as assess the economics.

Oil and gas applications

During recent years, there has been great interest in using CNC materials for various applications, such as drilling, completion and spacer fluids, thickeners, shear thinning agents, proppants, etc. [29-30]. Large drilling companies like Schlumberger and Halliburton are intensively investigating these applications. Hence, Schlumberger announced an investment in Celluforce 2015 in order to enhance the productivity of oil and gas wells. One application is the replacement of hydrolyzed polyacrylamide in chemical flooding applications. The objective is to improve displacement efficiency by increasing viscosity of the aqueous phase in order to reduce viscous fingering effects and change the flow pattern in reservoirs. Among various research efforts, the charge and structure of the CNC materials have been found to be critical and optimization of the CNC is of great importance.

Textile fibers and filaments

There has been growing interest in spinning continuous fibers from biomaterials and also from nanocellulosic materials. Methods such as dry spinning, wet spinning, melt spinning, and electrospinning have been investigated, though most research activities have been in the field of electrospinning [31]. This field is, however, in an embryonic state. The tensile properties of some fibers compare favorably with regenerated cellulose, promising potentially cheap processing methods. It will, however, be necessary to maximize the fibril alignment and bonding and reduce voids in the filaments.

One very interesting technology is fiber spinning using a process combining hydrodynamic alignment with dispersion–gel transition (through coagulation) that produces homogeneous and smooth filaments from a low-concentration dispersion of cellulose nanofibrils in water. The alignment can be controlled by processing and was found to produce very strong cellulose filaments [32].

Electroactive polymers and composites

The use of nanocellulose in electroactive polymers is today one of the largest fields of nanocellulose research exploitation [33-37]. Applications include energy storage (solar cells, supercapacitors, etc.) actuators, sensors for foods, food active and intelligent packaging applications, electronic nanodevices, and various biomedical applications. All types of cellulosic nanonomaterials are studied, and the focus is on hybrids with conductive materials and nanocarbons. Electronic conductive polymers (ECP) have disadvantages, such as poor cycling stability, high self-discharge rate, low attainable doping degrees, and mass-transport limitations due to thick polymer layers. Nanostructuring with nanocellulosic materials have solved several of these problems by utilizing high surface area nanomaterials resulting in thinner films. Also, by using strong nanomaterials like CNF, the internal strain caused by redox reactions (volume changes) and thin films, the stability problem can be alleviated. Apart from challenges of upscaling, there is a need for appropriate surface/interface engineering: tunable nano-, microstructures with excellent conductivity, flexibility, strength, stability and high-energy storage capacity. Pore engineering is critical; for example, hierarchical micro/mesoporous structures for electrodes to improve contact with the electrolyte and shorten diffusion length is needed. **TJ**

LITERATURE CITED

1. Isogai, A., Saito, T., and Fukuzumi, H., *Nanoscale* 3(1): 71(2011). https://doi.org/10.1039/C0NR00583E.
2. Klemm, D., Kramer, F. Moritz, S., et al., *Angew. Chemie, Int. Edn.* 50(24): 5438(2011). https://doi.org/10.1002/anie.201001273.
3. Moon, R.J., Martini, A., Nairn, J., et al., *Chem. Soc. Rev.* 401: 3941(2011). https://doi.org/10.1039/c0cs00108b.
4. Foster, E.J., Moon, R.J., Agarwal, U.P., et al., *Chem. Soc. Rev.* 47(8): 2511(2018). https://doi.org/10.1039/C8CS90043D.
5. Klemm, D., Cranston, E.D., Fischer, D., et al., *Mater. Today* 21(7): 720(2018). https://doi.org/10.1016/j.mattod.2018.02.001.
6. Bejoy, T., Midhun, C.R., Athira, K.B., et al., *Chem. Rev.* 118(24): 1157(2018).
7. Cowie, J., Bilek, E.M., Wegner, T.H., et al., *TAPPI J.* 13(6): 57(2014).
8. Shatkin, J.A., Wegner, T.H., Bilek, W.E., et al., *TAPPI J.* 13(5): 9(2014).
9. Shatkin, J.A., Ong, K.J., Ede, J.D., et al., *TAPPI J.* 15(6): 425(2016).
10. Shatkin, J.A., Ong, K.J. and James, E., "Minimizing risk: An overview of risk assessment and risk management of nanomaterials," in *Metrology and Standardization of Nanotechnology: Protocols and Industrial Innovations* (D.E. Mansfield, D.D.L. Kaiser, P.D. Fujita, and P.M. Van de Voorde, Eds.) Wiley-VCH Verlag GmbH & Co. KgaA, Weinheim, Germany, 2017, pp. 381-408. https://doi.org/10.1002/9783527800308.ch24.
11. Hua, X., Laleg, M., Miles, K., et al., (FP Innovations) U.S. patent US 2013/0017394 A1 (Jan. 17, 2013).
12. Hiltunen, J., Kemppainen, K., and Pere J., Int. patent WO 2015/092146 A1 (June 25, 2015).
13. Svending, P., Phipps, J.S., Kitzinger, J., et al., (FiberLean Technologies Ltd.) U.S. patent US 2017/0284030 A1 (Mar. 31, 2017).
14. Su, Y., Burger, C., Ma, H., et al., *Biomacromolecules* 16(4): 1201(2015). https://doi.org/10.1021/bm501897z.
15. Usov, I., Nyström, G., Adamcik, J., et al., *Nature Comm.* 6: 7564(2015). https://doi.org/10.1038/ncomms8564.
16. Henriksson, M., Henriksson, G., Berglund, L.A., et al., *Eur. Polym. J.* 43(8): 3434(2007). https://doi.org/10.1016/j.eurpolymj.2007.05.038.
17. Pääkkö, M., Ankerfors, M., Kosonen, H., et al., *Biomacromolecules* 8(6): 1934(2007). https://doi.org/10.1021/bm061215p.
18. Benítez, A.J. and Walther, A., *J. Mater. Chem. A* 5(31): 16003(2017). https://doi.org/10.1039/C7TA02006F.
19. Lindström, T., *Curr. Opin. Colloid Interface Sci.* 29: 68(2017). https://doi.org/10.1016/j.cocis.2017.02.005.
20. Aulin, C., Gällstedt, M., and Lindström, T., *Cellulose* 17: 559(2010). https://doi.org/10.1007/s10570-009-9393-y.
21. Dufresne, A., *Philos. Trans. R. Soc., A* 25 Dec. 2017. https://doi.org/10.1098/rsta.2017.0040.
22. Gómez, C., Serpa, A., Velásquez-Cock, J., et al., *Food Hydrocolloids* 57: 178(2016). https://doi.org/10.1016/j.foodhyd.2016.01.023.
23. Hubbe, M.A., Tayeb, P., Joyce, M., et al., *BioResources* 12(4): 955(2017). https://doi.org/10.15376/biores.12.2.2252-2253.
24. Mohammed, N., Grishkewich, N., and Tam, K.-C., *Environ. Sci.: Nano* 5(3): 623(2018). https://doi.org/10.1039/C7EN01029J.
25. Ma, H., Burger, C. Hsiao, C., et al., *J. Mater. Chem.* 21(21): 7507(2011). https://doi.org/10.1039/c0jm04308g.
26. Long, L.-Y., Weng, Y.-X. and Wang, Y.-Z., *Polymers (Basel, Switz.)* 10(6): 623(2018). https://doi.org/10.3390/polym10060623.
27. Fu, T., Moon, R.J., Youngblood, J., et al., in *Cellulose-Reinforced Nanofiber Composites: Production, Properties and Applications*, Woodhead Publishing, Cambridge, U.K., 2017, pp. 445-482.
28. Balea, A., Fuente, E., Blanco, A., et al., *Polymers (Basel, Switz.)* 11(3): 518(2019). https://doi.org/10.3390/polym11030518.
29. Lafitte, V., "Application of cellulose nanocrystals in oilfield gravel packing fluid," *TAPPI Int. Conf. Nanotechnol. Renewable Mater.*, TAPPI Press, Peachtree Corners, GA, USA, 2017.

30. Aadland, R.C., Dziuba, C.J., Heggeset, E.B., et al., *Nanomaterials* (Basel, Switz.) 8(7): 547(2018). https://doi.org/10.3390/nano8070547.
31. Clemons, C., *J. Renewable Mater.* 4(5): 327(2016). https://doi.org/10.7569/JRM.2016.634112.
32. Håkansson, K.M., Fall, A.B., Lundell, F., et al., *Nat. Commun.* 5: 4018(2014). https://doi.org/10.1038/ncomms5018.
33. Shi, Y., Peng, L., Ding, Y., et al., *Chem. Soc. Rev.* 44(19): 6684(2015). https://doi.org/10.1039/C5CS00362H.
34. Chen, C. and Hu, L., "Nanocellulose toward advanced energy storage devices: Structure and electrochemistry." *Acc. Chem. Res.* (in press), 2018. https://doi.org/10.1021/acs.accounts.8b00391.
35. Chen, W., Yu, H., Lee, S.-Y., et al., *Chem. Soc. Rev.* 47: 2837(2018). https://doi.org/10.1039/C7CS00790F.
36. Edberg, J., Inganäs,O., Engquist, I., et al., *J. Mater. Chem. A* 6(1): 145(2018). https://doi.org/10.1039/C7TA06810G.
37. Hassan, S.H., Voon, L.W., Velyuthan, T.S., et al., *J. Renewable Mater.* 6(1): 1(2018).

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ABOUT THE AUTHOR

Lindström is professor in the Department of Solid Mechanics at the Royal Institute of Technology (KTH), Stockholm, Sweden and visiting scientist in the Department of Chemistry, SUNY-Stony Brook, Stony Brook, NY, USA. Email Lindström at toml@kth.se.

Lindström