Special issue on nanocellulose- Editorial

Monika Österberg and Emily D. Cranston

This special issue contains a mixture of novel research papers on CNFs, CNCs and bacterial cellulose, as well as review papers focusing on topical issues for industrial applications of nanocellulose. As a result, we envision that it will be of interest not only to the existing nanocellulose community, but also to potential end users and scientists not yet familiar with nanocellulose.

ADDRESSES OF THE AUTHORS: Monika Österberg (monika.osterberg@aalto.fi): Aalto University, School of Chemical Technology, Department of Forest Products Technology, P.O. Box 16300, FI-00076 Aalto, Finland and **Emily D. Cranston** (ecranst@mcmaster.ca): Department of Chemical Engineering, McMaster University, 1280 Main Street West, Hamilton, Ontario, Canada L8S 4L7.

Interest in nanocellulose research has increased dramatically during recent years, though the materials themselves are not new. The first paper on colloidal cellulose, now called cellulose nanocrystals (CNCs), was published by Rånby in 1949 (Rånby, 1949), and in 1983, Turbak published the first paper on mechanical disintegration of cellulose fibers into microfibrillated cellulose (Turbak et al. 1983). Despite these early publications, research into these materials did not become popular until the early 2000's.

The main reason for this renewed interest was likely societal. The rise of digital technology negatively impacted the market for paper in Europe and North America such that the forest products industry was forced to rethink and find new products to sell. The same was true for the research institutes; it became increasingly difficult to get financing for research on "classical" papermaking. Along with the societal need to find novel uses for wood, a key reason for the renewed interest in cellulose nanofibrils (CNFs) was the development of chemical (Saito et al. 2007, Wågberg et al. 2008) and enzymatic (Pääkkö et al. 2007) pretreatments that substantially decreased the energy consumption during production, and attracted industrial attention. Interest in CNCs took off after the pioneering work by Derek Gray and his co-workers (see e.g. Revol et al. 1992, 1994) for which Professor Gray was awarded the 2013 Marcus Wallenberg Prize. New CNC research was also driven by industrial interest and subsequent success in scaling up the production of this unique nanomaterial, which had previously been primarily an academic curiosity.

Applications

Currently, interest in all forms of nanocellulose (bacterial cellulose, CNCs and CNFs) continues to grow due to the exciting properties of these materials along with the diversity of potential applications which have been proposed. Both "nano-enhanced" and completely new "nano-enabled" products have been envisioned ranging from bulk applications like rheological modifiers, composite reinforcement or paper additives, to high-end applications such as tissue engineering, drug delivery and functional materials. In this special issue, some of these applications are addressed. Brodin et al. (2014) discuss the possibilities and challenges of using CNFs as paper additives and coating materials while Korhonen and Laine (2014) consider the use of various CNF grades for flocculation and retention of fillers. A concise review of nanocellulose for drug delivery is presented by Plackett et al. (2014), and suggests wound dressings with controlled drug release as a logical first application. Their review also addresses the need for further *in vivo* studies in order to fully understand the biomedical potential of nanocellulose. In terms of composite reinforcement, Goodsell et al. (2014) develop a hierarchical analytical model to predict the strengthening potential of nanocellulose in a matrix and two specific composites are investigated; CNC-reinforced hydrogels (Atifi et al. 2014), and CNF-reinforced thermoplastic starch biofilms (Karimi et al. 2014). In the lone paper dealing with bacterial cellulose, Bizot and Cathala (2014) suggest a new method to obtain highly oriented ribbons of bacterial cellulose nanocrystals using an isomalt sacrificial template.

Energy consumption of the production process

Despite the vast application possibilities for nano-cellulose, one key issue for large scale production, particularly for CNFs, remains in reducing the energy consumption of the fibrillation process. It has been shown that introducing surface charge by chemical pretreatment considerably decreases the energy consumption during preparation (Saito et al. 2007, Wågberg et al. 2008). But can the fibrillation efficiency be affected by the choice of raw material? In an earlier paper by Pääkkö et al. (2007), hemicellulose rich sulfite pulp was chosen as the raw material for CNFs, but the effect of the raw material was not explicitly discussed. In this issue, Fall et al. (2014) compare eucalyptus, acacia and pine fibers and conclude that the raw material does affect the fibrillation efficiency, but that the charge density of the pulp remains the most important factor. From this perspective, it is also interesting to note that storage may affect the surface charge density of nanocelluloses, as addressed by Beck et al. (2014). Reducing the overall energy consumption of CNF production can also be done by using waste materials, like wheat straw and recycled newspaper, as raw material, which is proposed by Josset et al. (2014).

Compatibility

Major challenges in using nanocellulose in commercial products include the ability to disperse the nanoparticles in various materials (both liquids and solids), and how to characterize the base materials and new products. Surface functionalization offers one solution to the issue of compatibility, and various routes are described in the literature. In this issue, three new approaches are presented. Abitbol et al. (2014) demonstrate a straight-forward surface modification of CNCs with surfactant to increase the nanoparticle's hydrophobicity, Atifi et al. (2014) attach crosslinking groups to CNCs to tailor mechanical properties of CNC hydrogels, and Tian et al. (2014) optimize the grafting of poly(ε-caprolactone) to CNCs using a surface response methodology. Changes in the surface chemistry of CNFs from different raw materials are examined by Tsuboi et al. (2014). They study CNF behavior in different media using materials derived by aqueous counter collision from bamboo and hardwood. Furthermore, the solvation structure and interactions of native and modified CNCs in liquid media are modelled by Stoyanov et al. (2014), who highlight how to choose the best surface functionalization for a given material system. An alternate approach to dispersing nanocellulose in a matrix is to layer it with other materials of interest; a comprehensive review of polyelectrolyte multilayer films with CNCs and CNFs is provided by Martin and Jean (2014).

Characterization

Improving the characterization of nanocellulose materials is critical to commercialization. Currently, strong efforts to standardize terminology and test methods for nanocellulose are being undertaken by ISO, TAPPI, and the Canadian Standards Association. In scientific papers, high resolution transmission or scanning electron microscopy and atomic force microscopy are commonly used to characterize nanocellulose dimensions. However, these techniques are expensive, and obtaining statistically relevant size distributions is challenging. Kangas et al. (2014) discuss the characterization of CNFs, focusing on simple alternatives to high resolution microscopy, while Fraschini et al. (2014) critically compare light scattering and microscopy techniques for determining CNC length and aspect ratio. They also offer advice on choosing the best “online” particle size monitoring method, and stress that electron microscopy is not trouble-free and misinterpretation may occur if samples are not handled with care. To help in this regard, Kaushik et al. (2014) propose that the best way to prepare artefact-free CNC specimens for transmission electron microscopy analysis is to deposit CNCs from acidic solution onto hydrophilic grids and avoid the use of contrast stains.

Literature

Abitbol, T., Marway, H., Cranston, E.D. (2014): Surface modification of cellulose nanocrystals with cetyltrimethylammonium bromide, Nord. Pulp Pap. Res. J. 29(1), 46-57.

Atifi, S., Su, S., and Hamad W.Y. (2014): Mechanically tunable nanocomposite hydrogels based on functionalized cellulose nanocrystals, Nord. Pulp Pap. Res. J. 29(1) 95-104.

Beck, S., Bouchard, J. (2014): Auto-catalyzed acidic desulfation of cellulose nanocrystals, Nord. Pulp Pap. Res. J. 29(1) 6-14.

Bizot, H., Cathala, B. (2014): A route to uniaxially oriented ribbons of bacterial cellulose nanocrystals based on isomalt spun sacrificial template, Nord. Pulp Pap. Res. J. 29(1) 15-18.

Brodin, F.W., Gregersen Ø.W., Syverud, K. (2014): Cellulose nanofibrils: Challenges and possibilities as a paper additive or coating material – a review, Nord. Pulp Pap. Res. J. 29(1) 156-166.

Fall, A.B., Burman, A., Wågberg, L. (2014): Cellulosic Nanofibrils from Eucalyptus, Acacia and Pine Fibers, Nord. Pulp Pap. Res. J. 29(1) 176-184.

Fraschini, C., Chauve, G., Le Berre, J., Ellis, S., Méthot, M., O'Connor, B., Bouchard, J. (2014): Critical discussion of light scattering and microscopy techniques for CNC particle sizing, Nord. Pulp Pap. Res. J. 29(1), 31-40.

Goodsell, J. E., Moon, R. J., Huizar, A., Pipes, R.B. (2014): A strategy for prediction of the elastic properties of epoxy-cellulose nanocrystal-reinforced fiber networks, 29(1)85-95.

Josset S., Orsolini, P., Siqueira, G., Tejado, A., Tingaut, P., Zimmermann; T. (2014): Energy consumption of the nanofibrillation of bleached pulp, wheat straw and recycled newspaper through a grinding process, Nord. Pulp Pap. Res. J. 29(1) 167-175.

Kangas, H.,Lahtinen, P. Sneck, A., Saariaho, A-M., Laitinen O., Hellén, E. (2014): Characterization of fibrillated celluloses. A short review and evaluation of characteristics with a combination of methods, Nord. Pulp Pap. Res. J. 29(1) 129-143.

Karimi, S. Tahir,Md., Dufresne, A., Karimi, A., Abdulkhani, A (2014): A comparative study on characteristics of nanocellulose reinforced thermoplastic starch biofilms prepared with different techniques, Nord. Pulp Pap. Res. J. 29(1), 41-45.

Kaushik, M., Chen, W. C., van de Ven, T. G. M., Moores A. (2014): An improved methodology for imaging cellulose nanocrystals by transmission electron microscopy, Nord. Pulp Pap. Res. J. 29(1), 77-84.

Korhonen, M., Laine, J. (2014) Flocculation and retention of fillers with nanocelluloses, Nord. Pulp Pap. Res. J. 29(1), 119-128.

Martin, C., Jean, B. (2014): Nanocellulose/polymer multilayered thin films: tunable architectures towards tailored physical properties, Nord. Pulp Pap. Res. J. 29(1) 19-30.

Plackett, D.V., Letchford, K., Jackson, J.K, Burt, H.M. (2014): A review of nanocellulose as a novel vehicle for drug delivery, Nord. Pulp Pap. Res. J. 29(1) 105-118.

Pääkkö M., Ankerfors M., Kosonen H., Nykänen A., Ahola S., Österberg M., Ruokolainen J., Laine J., Larsson PT, Ikkala O, Lindström T (2007): Enzymatic hydrolysis combined with mechanical shearing and high-pressure homogenization for nanoscale cellulose fibrils and strong gels, Biomacromolecules 8(6) 1934-1941.

Revol J.F., Bradford H., Giasson J., Marchessault R.H. and Gray D.G. (1992): Helicoidal self-ordering of cellulose microfibrils in aqueous suspension, Int J Biol Macromol, 14(3), 170-172.

Revol J.F., Godbout L., Dong X.M., Gray D., Chanzy H. and Maret G. (1994): Chiral nematic suspensions of cellulose crystallites; phase separation and magnetic field orientation, Liq. Cryst, 16(1), 127-134.

Rånby, B. G. (1949): Aqueous colloidal solutions of cellulose micelles, Acta Chem. Scand., 3, 649-650.

Saito, T., Kimura, S., Nishiyama, Y., Isogai, A. (2007): Cellulose nanofibers prepared by TEMPO-mediated oxidation of native cellulose, Biomacromolecules 8(8), 2485-2491.

Stoyanov, S., Lyubimova, O., Gusarov, S., and Kovalenko, A. (2014): Computational Modeling of the Structure Relaxation and Dispersion Thermodynamics of Pristine and Modified Cellulose Nanocrystals in Solution, Nord. Pulp Pap. Res. J. 29(1) 144-155.

Tian, C., Fu, S., Chen, J., Meng, Q., Lucia L.A. (2014) Graft polymerization of ε-caprolactone to cellulose nanocrystals and optimization of grafting conditions utilizing a response surface methodology, Nord. Pulp Pap. Res. J. 29(1) 58-68.

Turbak, A.F., Snyder, F.W., Sandberg, K. R. (1983): J. Appl. Polym. Sci. Appl. Polym. Symp., 37, 815-827.

Tsuboi, K., Yokota, S., Kondo, T. (2014) Difference between bamboo- and wood-derived cellulose nanofibers prepared by the aqueous counter collision method, Nord. Pulp Pap. Res. J. 29(1), 69-76.

Wågberg, L., Decher, G., Norgren, M., Lindström, T., Ankerfors, M., Axnäs, K. (2008): The build-Up of polyelectrolyte multilayers of microfibrillated cellulose and cationic polyelectrolytes, Langmuir 24(3), 784-795.