MWP

16 March 2015

The 2015 MWP Award – Full motivation

Citation

The 2015 Marcus Wallenberg Prize is awarded to Prof. Akira Isogai and Associate Prof. Tsuguyuki Saito from Japan, and Dr. Yoshiharu Nishiyama from France, for their ground-breaking research on TEMPO-mediated oxidation of cellulose fibre and further exploitation of this oxidation as a tool to produce nanofibrillated cellulose from wood pulp in an energy-efficient way. Their innovative work has strongly intensified the interest for industrially attractive production of nanofibrillated cellulose (NFC) and the development of commercial applications throughout the world. Production of nanofibrillated cellulose and development of new NFC-based value chains is opening up considerable future business opportunities to the global forest-based sector.

Background and Prize motivation

Wood cellulose is composed of both crystalline and amorphous regions. The generalized term nano-cellulose refers to both nanofibrillated celluloses (NFCs) and to cellulose nanocrystals (CNCs) (Fig. 1). Despite their similar chemical compositions, cellulose nanocrystals and nanofibrillated celluloses have different macro-level properties (size, physical properties) and different end-uses. CNC has unique liquid crystal properties and outstanding mechanical strength. NFC has high mechanical strength, surface area, aspect ratio and molecular weight and has potential applications in areas such as composites, construction materials, porous materials, paper and board additives, self-standing films, and as a rheology modifier. Nano-celluloses can be made from wood cellulose by disintegrating the fibre structure to its nano-scale cellulosic building blocks by either acid hydrolysis (yielding the crystalline CNC) or by mechanical disintegration (yielding the nanofibril NFC). The former process results in low product yields, whereas the latter process consumes high amounts of energy.

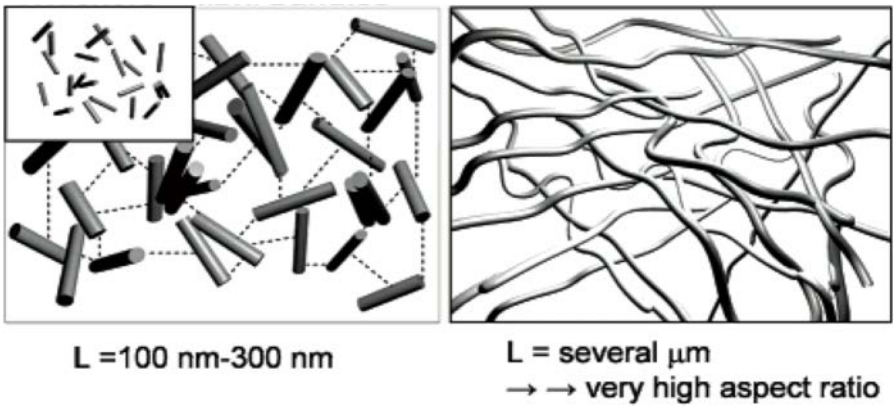

Fig. 1. Cellulose nanocrystals CNC (left) and nanofibrillated cellulose (right).[1]

Two years ago, Prof. Derek Gray received the Marcus Wallenberg Prize for his fundamental discoveries relating to the unique optical properties of cellulose nanocrystals. This year's prize goes to an invention concerning the production of cellulose nanofibrils (NFC) using the TEMPO-mediated oxidation of the cellulosic raw material. Despite the intriguing and potentially useful properties of NFC, until quite recently, industrial interest was largely subdued due primarily to the high energy demand needed to effectively mechanically disintegrate the material for NFC production, resulting in high production costs. When working during 2005-2008, Assistant Professor Tsuguyuki Saito, Dr. Yoshiharu Nishiyama together with

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

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Professor Akira Isogai discovered that wood cellulose can be selectively oxidized by TEMPO.[2] The TEMPO-oxidized wood fibres could be subsequently disintegrated into individual cellulose nanofibrils after relatively mild mechanical treatments.[3] By using TEMPO-mediated oxidation the subsequent defibrillation step became more selective, requiring substantially less energy without compromising the properties of the NFC and yielding a much more homogeneous material. The energy required to produce mechanically-derived NFC can be as high as 30 000 kWh/ton of NFC whereas TEMPO-mediated production can reduce the energy demand to 100-500 kWh/ton. The selectivity of the process has paved the way for subsequent, more intensive research into NFC production and its applications to industrial developments around the world, particularly in Japan, Finland and Sweden (Fig. 2).

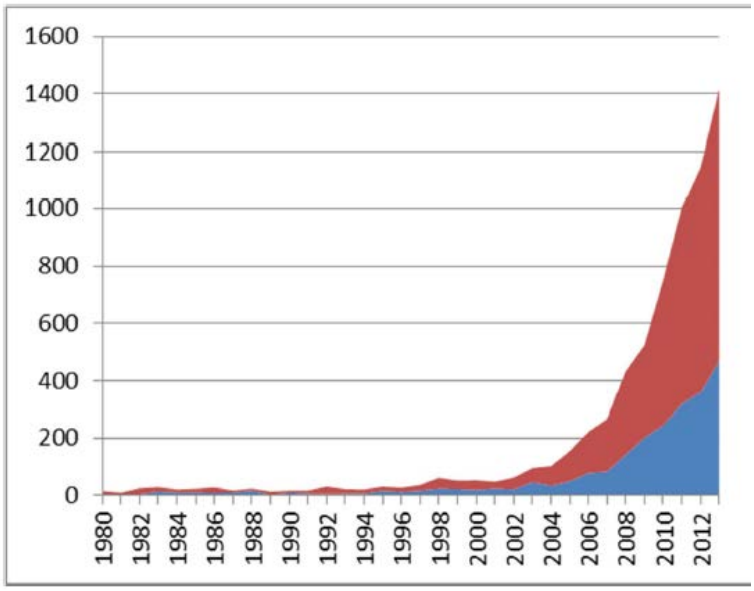

Fig. 2. Nanocellulose patents (blue) and publications (red) during years 1980-2013. [Source: Chemical abstracts, 18/6/2014 (Figure by VTT)].

The first papers on TEMPO-mediated oxidation of insoluble cellulose were published by Chang and Robyt (1996) and Isogai and Kato (1998).[4] T. Saito, as part of his PhD work under the supervision of Prof. Isogai, applied this catalyst to the heterogeneous oxidation of native cellulose. He discovered that significant amounts of carboxylates could be introduced to the surface of cellulose nanocrystals without destroying the crystallinity.[5] The analysis of the morphological details of this TEMPO-oxidized material was initiated in collaboration with Prof. Sugiyama (University of Kyoto)[6] and carried out in more detail with Dr. Nishiyama at CERMAV, France. Inspired by previous attempts to isolate cellulose nano-elements by the introduction of charged functionalities onto the nanofibrillar surfaces, working at CERMAV, Saito and Nishiyama under the supervision of Isogai, discovered that native TEMPO-oxidized cellulose could be disintegrated into well-defined nanofibrils by means of mild mechanical treatment, e.g., mild homogenization, stirring or

[2]TEMPO is a water-soluble and stable nitroxyl radical (2,2,6,6-tetramethylpiperidine-1-oxyl) that can be used for catalytic and selective oxidation of the primary alcohol groups of polysaccharides under aqueous conditions to corresponding carboxylates.[4]

[3]T. Saito, Y. Okita, T.T. Nge, J. Sugiyama, A. Isogai. (2006) TEMPO-mediated oxidation of native cellulose: Microscopic analysis of fibrous fractions in the oxidized products. *Carbohydrate Polymers* **65** 435-440; T. Saito, Y. Nishiyama, J.-L. Putaux, M. Vignon and A. Isogai. (2006) Homogeneous suspensions of individualized microfibrils from TEMPO-catalyzed oxidation of native cellulose. *Biomacromolecules* **7**, 1687-1691; T. Saito; S. Kimura; Y. Nishiyama; A. Isogai (2007) Cellulose nanofibres prepared by TEMPO-mediated oxidation of native cellulose. *Biomacromolecules* **8**, 2485-2491; Pat publ. JP2008001728 A2 (Saito, Nishiyama, Vignon, Pateux, and Isogai); Pat Publ. JP 2008308802 A2 (Saito, Okita, Isogai).

[4]P.S. Chang, J.F. Robyt. (1996) Oxidation of primary alcohol groups of naturally occurring polysaccharides with 2,2,6,6-tetramethyl-1-piperidine oxoammonium ion. *Carbohydrate Chemistry* **15**, 819-830.; A. Isogai and Y. Kato (1998) Preparation of polyuronic acid from cellulose by TEMPO-mediated oxidation. *Cellulose* **5**, 153-164.

[5]T. Saito and A. Isogai (2004) TEMPO-mediated oxidation of native cellulose. The effect of oxidation conditions on chemical and crystal structures of the water-insoluble fractions. *Biomacromolecules* **5**, 1983-1989.

[6]T. Saito, Y. Okita, T.T. Nge, J. Sugiyama, A. Isogai (2006) TEMPO-mediated oxidation of native cellulose: Microscopic analysis of fibrous fractions in the oxidized products. *Carbohydrate Polymers* **65**, 435-440.

ultrasound treatment.[7] The formation of the anionic groups on the nanofibril surfaces resulted in repulsive electrostatic forces between the individual nanofibrils, subsequently decreasing the energy demand required for disintegration (Fig. 3). This discovery by Saito, Nishiyama and Isogai provided the fundamental insight that is the basis for much of the ongoing research into nanofibrillar cellulose (NFC).

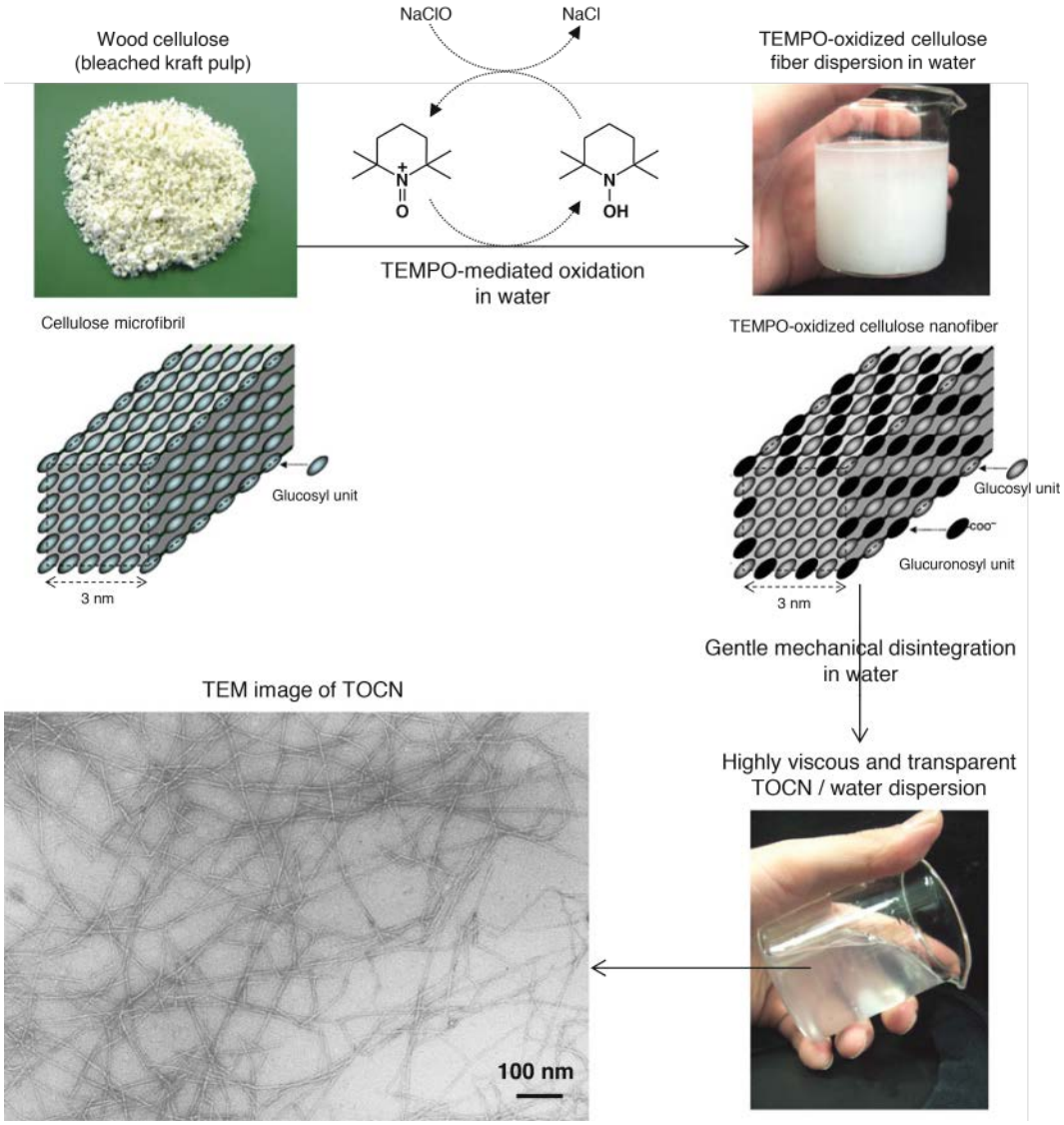

Fig. 3. Preparation of TEMPO-oxidized cellulose nanofibrils (TOCN) from wood cellulose.[8]

[7] T. Saito, Y. Nishiyama, J.-L. Putaux, M. Vignon and A. Isogai. (2006) Homogeneous suspensions of individualized microfibrils from TEMPO-catalyzed oxidation of native cellulose. *Biomacromolecules* **7**, 1687-1691; T. Saito; S. Kimura; Y. Nishiyama; A. Isogai. (2007) Cellulose nanofibres prepared by TEMPO-mediated oxidation of native cellulose. *Biomacromolecules* **8**, 2485-2491.

[8] A. Isogai. (2013) Wood nanocelluloses: fundamentals and applications as new bio-based nanomaterials. Review. *J Wood Sci*, **59**, 449–459.

Akira Isogai

Professor Akira Isogai was born in 1954. He graduated from The University of Tokyo's Faculty of Agriculture in 1980 and obtained his PhD from the same university in 1985. (PhD thesis: Preparation of Cellulose Derivatives using Non-Aqueous Cellulose Solvents). He then worked as a Postdoctoral Fellow at the Institute of Paper Chemistry in Appleton, WI, USA, and later as a Research Associate and Visiting Scientist at the U.S. Forest Products Laboratory, USDA, Madison, USA. In 1994 he was appointed as an Associate Professor at the University of Tokyo and in 2003 he was promoted to full Professor. Since year 2000 professor Isogai has authored and co-authored more the 180 publications.

Yoshiharu Nishiyama

Dr. Yoshiharu Nishiyama was born in 1972. He graduated in Agriculture from the University of Tokyo in 1995, got his master's degree in 1997 and obtained his PhD from the same university in 2000 (Thesis: The Crystal Structure of Cellulose and the Mechanism of Mercerization). During 2000-2004 he worked as Assistant Professor at the Department of Biomaterials Science, School of Agricultural and Life Sciences, the University of Tokyo. From 2004 onwards he has been affiliated with the Centre de Recherches sur les Macromolécules Végétales (CERMAV), France, in the position of 1st class CNRS Researcher. He has authored or co-authored 81 scientific articles in refereed journals.

Tsuguyuki Saito

Dr. Tsuguyuki Saito was born in 1978. He graduated from the University of Tokyo in 2003, got his master's degree in 2005 and obtained his PhD from the same university in 2008 (Thesis: TEMPO-Mediated Oxidation of Native Cellulose). During his PhD studies he was awarded a Marie-Curie Fellowship, which supported his work with Dr. Yoshiharu Nishiyama at the Centre de Recherches sur les Macromolécules Végétales (CERMAV), France, during 2005-2006. After completing his Japan Society for the Promotion of Science (JSPS) Postdoctoral Fellowship at the University of Tokyo he continued to work there, first as an Assistant Professor and currently as an Associate Professor. He also worked as Visiting Scientist with Prof. Lars A. Berglund at the Department of Fiber and Polymer Technology, Royal Institute of Technology, Sweden, during 2012–2013. Dr. Saito has worked on TEMPO-mediated oxidation and nanocellulose with Prof. Isogai for many years and authored or co-authored more than 90 scientific papers in refereed journals.