Present situation and future prospects of Nanocellulose R&D in Japan

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President of Nanocellulose Forum
Quantitative and qualitative expansion of utilization of renewable wood biomass resources is required for establishment of a sustainable society and for prevention of global warming.

Vascular plants consisting of pipe-like fibers in stems containing lignin can efficiently reduce CO$_2$ to carbon-containing plant components, forming O$_2$ during growing.

Creation of a new materials stream with CNFs from forest to high-tech industry is needed for activation of forestry industry.

Ca. 66% of Japanese area is covered with forest, consisting of unutilized wood resources.

The Paris agreement has been concluded in COP21, 2015 (United Nations Framework Convention on Climate Change 21th Conference), and Japan has set a reduction goal, by 2030, of 26% CO$_2$ emission from the 2013 year-level.

The CNF utilization from wood biomass resources is expected to strongly contribute to the reduction of CO$_2$ emission because of their carbon neutrality. The next goal is reduction of 80% CO$_2$ emission by 2050!
Nanocellulose Forum has been established in 2014, supported by Ministry of Economy, Trade and Industry (METI), and National Institute of Advanced Industrial Science and Technology (AIST) to accelerate nanocellulose-related business through all Japan framework.

**Member:** 224 Industries, 84 Researchers, 5 Ministries, and 51 Local governments

**Industries:** Pulp & Paper, Metal, Forestry, Construction, Food, Textile & Fiber, Chemicals & Petroleum, Rubber, Machinery, Precision Machinery, Equipment for transportation, Commerce, Service, etc.

**CNF was described in Japan Revitalization Strategy in 2014**

Accordingly, the Liaison Committee between five Ministries was established.

- Ministry of Economy, Trade and Industry
- Ministry of Agriculture, Forestry and Fisheries
- Ministry of the Environment
- Ministry of Education, Culture, Sports, Science and Technology
- Ministry of Land, Infrastructure, Transport and Tourism
The new market creation strategy of CNF industry

The expected market scale of a cellulose nanofiber reference material in 2030 $10 billion/year

Development of the innovative manufacturing technology

Automobile component
Information electronic material
Packaging material
Building material
Thickening agent for food
High-performance tech filter, etc.

Reported by Ministry of Economy, Trade and Industry (2013)
Production Facilities in Japan

- **Kusano Sakko**
  - Bacteria cellulose 3 t/y

- **Ogata, TEMPO-CNF**
  - 1 t / day

- **Chuetsu Pulp & Paper**
  - Takaoka
  - Sendai 100 t/y
  - Mishima 100 t/y

- **Mishima**
  - Tomioka, Phosphorylated CNF 40 t/y

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  - 40 t/y

- **Kyoto, Ligno-CNF & resin**
  - 1 t/y

- **Fuji**
  - Acetylated CNF-reinforced resin 10 t/y

- **Ryugasaki**
  - 24 t/y

- **Ishinomaki, TEMPO-CNF**
  - 500 t/y

- **Nippon Paper Industries**
  - Nippon Paper Industries
  - Nippon Paper Industries
  - OJI Holdings

- **AsahiKASEI**
  - ASAHI KASEI FIBERS

- **DAIO PAPER CORPORATION**
  - Mishima 100 t/y
Nanocellulose Forum, Japan: Corporate member

Manufacturer
- NIPPON PAPER INDUSTRIES CO., LTD.
- OJI HOLDINGS
- DAIO PAPER CORPORATION
- Asahi KASEI ASahi KASEI FIBERS

Machinery
- SUGINO
- MORI MACHINERY CORP.
- AIKAWA
- ASADA
- JSW

User
- Kao
- DAICEL
- LION IDEMITSU COMPOSITES CO., LTD.
- Mitsubishi Engineering-Plastics Corporation
- C.I. KASEI CO., LTD.
- TAIYO HOLDINGS CO., LTD.
- YUSHIRO CHEMICAL INDUSTRY CO., LTD.
- JSR Corporation

Fabricator
- TOPPAN
- Osaka Sealing Printing Co., Ltd.
- TOYOTA BOSHOKU
- MITSUBISHI PENCIL
- Panasonic
- GUNZE
Nanocellulose Forum, Japan

- Surveys, sharing, information exchange, and information publicizing of technology trends
  - Organizing technical seminars
  - Publishing newsletters
  - Forum for information exchange and interactions

- Proposition for join R&D and promotion of commercialization

- Promotion of nanocellulose standardization

- Provision of information on R&D facilities availability

- Human resource development

- Sample information
Companies challenging nanocellulose productions and applications in Japan

- **Nippon Paper**: TEMPO-CNF, carboxymethylated-CNF
  - Super deodorant diapers for adults, food additives, etc.

- **Oji Holdings**: Phosphorylated-CNF
  - Electronics, cosmetics, etc.

- **Asahi Kasei Chemicals**: Mechanically fibrillated CNF sheets
  - Non-woven fabrics for composite sheets, separator for Li-ion secondary battery, etc.

- **Chuetsu Pulp & Paper**: Mechanically fibrillated CNF from bamboo KP
  - Speaker corn paper, paintings, etc.
Companies challenging nanocellulose productions and applications in Japan

- **Daio Paper**: Mechanically fibrillated CNF from KP $O_2$-barrier sheets, etc.
- **Hokuetsu-Cooperation**: TEMPO-CN, CNC, ZnCl$_2$-treated CNF Air-filter, composites, etc.
- **Rengo**: Xanthate-CN
- **Tokushu-Tokai Paper**: Mechanically fibrillated CNF, etc. Separator for Li-ion secondary battery, etc.
- **Daiichi Kogyo Seiyaku**: TEMPO-CN Thickeners, cosmetics, etc
Companies challenging nanocellulose productions and applications in Japan

- **Toppan Printing**: TEMPO-CNF films
  O₂-barrier packaging, color filters, etc.

- **Kao**: Chemically modified TEMPO-CNF
  Composites for electronic circuit board, etc.

- **SEIKO-PMC**: ASA-treated CNF
  CNF/plastic composites

- **Kyoto University**: Mechanically fibrillated and acetylated lignin-containing CNF
  Plastic/CNF composites for automobile

- **Forestry and Forest Products Institute**: Enzyme-treated and mechanically fibrillated CNF
  Food additives, etc.

- **National Institute of Advanced Industrial Science and Technology (AIST)**: Mechanically fibrillated
  agricultural wastes, Plastic/CNF composites

- **Academia**: University of Tokyo, Kyoto University, Osaka University, Kobe University, Kyushu University,
  Shinshu University, Tohoku University, Hokkaido University, Sophia University, Kyoto Institute of Technology,
  Shizuoka University, etc.
Commercial production and applications of TEMPO-CNF, carboxymethylated-CNF and acetylated LCNF-reinforced plastics

**TEMPO-CNF**
- Width: 2-4 nm
- Capacities: 30 and 500 tons/year
- Started: November 2013 and April 2017

**CM-CNF**
- Width: 2-15 nm
- Capacities: 30-100 tons/year
- Started: September 2017

**Acetylated LCNF/plastics**
- Capacities: 10 tons/year
- Started: June 2017

NIPPON PAPER INDUSTRIES CO., LTD.
Commercial production and applications of TEMPO-CNF and carboxymethyl-CNF

SEM image of CNF from never-dried state

SEM image of re-dispersed CNF from dried state

Drying
Nippon Paper Industries, Inc. has manufactured TEMPO-CNFS mass production facility at 500–1500 ton per year in Ishinomaki Mill, Sendai, Tohoku

April 25th, 2017
Nippon Paper Industries, Inc.
Phosphorylated CNF for hydrogels and transparent films

Pulp sheet (10 g)

Water (15 g)
Urea (12 g)
NH₄H₂PO₄ (4.5 g)

Heating at 165°C for 200 s

Washing with water

Addition of dil. NaOH

with water

High-pressure homogenization in water

Aqueous phosphorylated CNF-Na dispersion

Noguchi et al., Cellulose (2017)
Phosphorylated CNF for hydrogels and transparent films

AUROVISCO CNF dispersion

High transparency, viscosity
thixotropic properties

Favorable for cosmetics, inks, paints
and other chemical application

Demonstration facility

Project overview

Capacity: 40 tonnes (dry) / year
Location: Tokushima, Japan

Oji Holdings
Phosphorylated CNF for hydrogels and transparent films

AUROVISCO CNF dispersion

High transparency and flexibility

Continuous film making process

Very low coefficient of thermal expansion

Transparent phosphorylated CNF film production started from 2017 with capacity of 250,000 m²/ year.
Chuetsu Pulp & Paper Co. announced in January 2015 a successful preparation of miscible nanocomposites between ACC-nanocellulose and poly(propylene).
Cellulose nanofiber nonwoven fabrics: CNF-$nw$

Very thin CNF-$nw$ layer with thicknesses of 3–80 µm can be formed on substrate fabric layer.
Cellulose nanofiber nonwoven fabrics: CNF-nw

Applications

- Low thermal expansion and high storage modulus of 100 nm-CNF-nw epoxy resin composite film.

Functional filter

Substrate for FRP with low thermal expansion

Separator for battery and capacitor

Epoxy/CNF-nw composite

Transparent film

Coefficient of thermal expansion (ppm/K)

Storage modulus $E'$ (GPa)

Temp (°C)

Temp (°C)
Xanthate CNF

Cellulose fiber-OH → Cellulose fiber-OCSSNa → Cellulose dissolution as viscose solution

Degree of substitution: 0.1−0.4

Degree of substitution: 0.3−0.6

TEM image

Disintegration in water

Highly viscous, transparent gel

Cellulose fiber-OCSSNa/ water dispersion

100nm

Width: 3−7 nm

Xanthate CNF with cellulose I crystal structure
A chemically modified dry-pulp with an improved heat resistance and will be easy to fibrillate under melt compounding is developed.

An integrated production process that simultaneously nanofibrillates the dry-pulp and uniformly disperses the CNF in the resins is established.
This test plant with a production capacity of one ton/year of thermoplastic resins with 10 wt% CNF has started from softwood chips (2016).
**Kyoto Process**

- **Goal:** 10% light weight body attaining reduction of CO$_2$ emission by 7%

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**Nanocellulose Vehicle in 2020**

**Leader:** Prof. H. Yano, Kyoto University
Nanoclay/TOCN composite film have high O$_2$-barrier properties up to 80% RH better than aluminum-spattered film.
TEMPO-CNF/ plastic composite films for electronics

Surface hydrophobization using dual grafting system

Small amount of long chains improves individual nano-dispersibility of TOCN elements

Large amount of short aromatic groups improves affinity to organic solvents

Surface-modified TOCN efficiently improves Young’s modulus and coefficient of thermal expansion of composite films.
Acid-free preparation of cellulose nanocrystals from TEMPO-CNF

Softwood bleached kraft pulp for papermaking

TEMPO-mediated oxidation in water

Fibrous TEMPO-oxidized cellulose

Gentle mechanical disintegration in water

High-shear disintegration or long-time disintegration in water

TEMPO-oxidized cellulose nanofibers

~ 3 nm

TEMPO-oxidized cellulose nanocrystals

~ 3 nm

Needle-like cellulose nanocrystals homogeneous ~3 nm in width are prepared from SBKP

Yields of TEMPO-CNCs are ~94% from SBKP

TEMPO-CNCs have carboxylate contents of ~1.7 mmol/g.

Zhou et al., Biomacromolecules (2018)
Concept of wood biomass utilization as CNF for establishment of a sustainable society

Wood biomass resources

Pulping / bleaching technology

Biomass power generation (energy recycling)

Effluent recovering / reductive incineration

Creation of new material stream from wood biomass resources to high-tech and commodity materials through TEMPO-oxidized cellulose nanofibers for establishment of a sustainable society

Surface modification / compositing / processing

Automotive parts
Bio-based fibers
Gas-barrier packaging films
Electronic devices
Health care materials
High-performance separators
Catalyst supports
Housing materials
Insulators
Cosmetics
Capacitor/separator for battery

Wood cellulose fiber

TEMPO-oxidation Nanofibrillation

Carbon neutral

Completely nano-dispersed TEMPO-oxidized cellulose nanofiber
2019 TAPPI International Conference on Nanotechnology for Renewable Materials will be held in Tokyo, Japan

Save the date!

June 3 - 7, 2019, Chiba (Tokyo bay area), Japan

✓ The venue is within 40 mins from major international airports.
✓ TAPPI Nano Division cooperates with Nanocellulose Forum, Japan
✓ Nanocellulose Exhibition will be held at the same time.

Makuhari Messe International Conference Hall

Houryuji temple tower (the world oldest wooden building)