Current situation of Nanocellulose in Japan

Hiroyuki Yano
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At the beginning, we, attendees from Japan, would like to express our sincere appreciation for your heartfelt sympathy which you have shown to us, Japanese, for the terrible earthquakes and Tsunami.
There are many activities on nanocellulose in Japan, ranging from fundamental research to commercial products.

Many Japanese companies have a great interest in standardization in nanocellulose, especially, EHS.
Key players

University:
Univ. of Tokyo (Prof. Isogai group), Kyoto Univ. (Prof. Yano group),
Kyushu Univ (Prof. Kondo group),
+5-10 group

Public research organizations:
Advanced Industrial Sci. & Techol. (AIST, Dr. Endo & Dr. Lee group)
Kyoto Municipal Research Institute (Dr. Kitagawa group)
+3-5 group

Company:
Oji Paper, Nippon Paper Industry, Sugino Machine, Masuko Sangyo,
Mitsubishi Paper, Daicel Chemical, Asahi Kasei Fibers, Mitsubishi
Chemical, DIC, Sumitomo Rubber, Kao, Toppan
+5-10 companies
RISH, Kyoto Univ.
Extraction of nanofibers from wood/plant fibers

Cost and Performance
Facilities for fibrillation

- High speed blender
- High pressure homogenizer
- Ultra high pressure homogenizer
- Grinder
- Batch-type beads mill
- Continuous beads mill
- Twin screw extruder
Grinder treatment

Never-dried pulp

1% conc. suspension of Radiata pine pulp

Set of grindstones

Grindstone
Cellulose nanofibers isolated from wood

Nanofibers observed in wood cell wall
Cellulose Nanofiber Sources

Wood (including pulps), Bamboo, Wheat straw, Rice straw, Potato tuber (pulp), Sugar beet (pulp), Sugarcane bagasse, Water weed, Hemp, Flax, Ramie, Cotton, etc

K.Abe, 2007
Comparison of Nanofibers

K. Abe, 2007

Wood

Sea weed

Rice straw

Potato tuber

Water weed

Cassava

Sugarcane

Sugar beet

Sweet potato
Nanofibrillation using High-speed Blender

Never-dried pulp (NaClO$_2$ treated)

0.7wt% water slurry

Blender, 37000rpm

Uetani and Yano, 2008
Agitation for 1 min by high speed blender

Uetani and Yano, 2008
Kneading using twin screw extruder

Wood Pulp (KP) → Disk Refiner → Kneading

Solid content: 30-50%
Cationized Pulp, Extruder fibrillated (Productivity rate: 600g/hr), 2010
Bacterial Cellulose

Acetobacter

50 nm wide: one-tenth the size of the optical wavelength
Applications
1) Light weight and High strength Cellulose NF-based Composites

- Soft Steel: SS400, ρ: 7.8
- PF, ρ: 1.4
- Mg alloy: AZ91, ρ: 1.8
- GFRP, Chopped, ρ: 1.2
- Polycarbonate, ρ: 1.2
- Starch
- PLA
- Cellulose NF-based Composites
Development of high performance cellulose nanofibers reinforced plastics for automotive parts

Organizations: Kyoto University, Kyoto Municipal Institute, Oji Paper, Mitsubishi Chemical, DIC
Advisers: Toyota Autobody, Nissan, Suzuki, Denso, Japan Steel Works

The project consists of three parts as follows:
1) development of the technology for the chemical modification of cellulose nanofibers
2) development of the technology for the living radical polymerization on the surface of cellulose nanofibers
3) development of the compatibilizer for interphase control
In parallel, CNF-reinforced plastic compounds are supplied to automotive companies, who joined in this project as advisers and supply their evaluations.
Nanofibrillation using twin screw extruder

Refiner treated Pulp
Preparation of Cellulose NF/PP composites: Injection molding

Refiner treated Pulp:NBKP + Polypropylene:PP + additives

PP: ca 60% of plastics used for automotive parts

Twin Screw Extruder

Nanofibrillation & Compounding

Allowing nanofibrillation and well-mixed compounds

Injection Molding
Optically transparent composite reinforced with cellulose nanofiber (left). Organic EL (OLED) emitted on the transparent composite (right).

As strong as steel, as thermally stable as glass, and as bendable as plastics
2010-2012 Collaborative Research for the Commercialization of Nano Fiber Cellulose Composite Sheet for Plastic Substrate
Development for mill scale Manufacturing

Wood powder → Removal of resin → Removal of lignin → Removal of hemicellulose → Wood powder pulp slurry

Fibrillation → Dewatering → Sheet Making → Drying

Nanofiber wet sheet → Monomer substitution → Polymerization by light or heat → Transparent plastic composite

Nanofiber dry sheet → Monomer soaking → Polymerization by light or heat → Transparent plastic device

Surface treatment → Coating → Transparent plastic device
Prof. A. Isogai, Univ. of Tokyo
TEMPO-oxidized cellulose nanofibers (TOCNs) as new bio-based materials from abundant wood biomass resource

Plants (tree):

- CH₂OH

Hemicellulose region:

- COO⁻ Na⁺

Wood fiber:

- Cellulose microfibrils: 4-5 nm
- Anhydroglucose unit

TEMPO-mediated oxidation in water:

- TEMPO-oxidized cellulose fibers suspended in water
- TEMPO-oxidized cellulose nanofibers (TOCNs) as new bio-based materials from abundant wood biomass resource

Electrostatic repulsion:

- Disintegration in water

TEM image of TOCN:

- TEMPO-oxidized cellulose nanofibers suspended in water
- 100 nm

Disintegration in water:

- Cellulose nanofiber dispersion in water

20~30 µm

Wood fiber

: -CH₂OH

: Hemicellulose region
NEDO Nanotech Challenge Programs
Stages I and II from 2007 to 2013

NEDO: New Energy and Industrial Technology Development Organization of Japan, and is an affiliated organization of Ministry of Economy, Trade and Industry

Project Title

Development of environment compliant high-gas-barrier & highly functionalized packaging materials using TEMPO-oxidized cellulose nanofibers

Organizations: Nippon Paper Ind., Kao Corp., TOPPAN Printing. Co. Ltd., and The University of Tokyo
Total concept of wood biomass refinery, utilizing TEMPO-oxidized cellulose nanofibers

TEMPO-oxidized cellulose nanofibers are New bio-based nanomaterials with high strengths, high transparency, low CTE, high gas-barrier properties, possibly supporting sustainable society, secure / safe society, information technology etc.

Forest biomass resources

Wood cellulose

TEMPO-oxidation Disintegration in water

Carbon neutral

Pulping / bleaching

Modification Compositing Processing

Bio filters

Medical & healthcare

Bio-fibers for industrial use

Metal catalyst support

Electronics devices

High-performance packaging materials

Total concept of wood biomass refinery, utilizing TEMPO-oxidized cellulose nanofibers
Research activities in
Biomass Technology Research Center (BTRC),
National Institute of Advanced Industrial Science and Technology (AIST)

Dr Endo & Dr Lee
Nanofibrillation and Nanocomposites

1. Hot-water treatment and mechanical grinding

- Material: wood powder, non-bleached pulp, etc.
- Temperature 130-200°C, Pressure 1Mpa-5Mpa
- Mainly hemicellulose extraction
- Producing porous structure
- Wide range of fiber diameter can be obtained.
- Increase of surface area to enhance enzymatic degradation
- Application for improving mechanical properties of conventional wood-plastic composite
2. Ozone treatment to loosen cell wall before and after mechanical grinding

- Lignin degradation is effective to improve mechanical fibrillation efficiency
- Can be combined with hot-water treatment
- Surface oxidation and surface charge change
- Reduction of filtration time for preparing nanopaper
- Control of molecular weight (degree of polymerization)
- Treating ozone amount can be adjusted, depending on raw materials

Nanofiber after disk-milling of nut-pine treated by ozone

Increase of surface area by hot-water and ozone treatment

Reduction of filtration time for preparing nanofiber sheets
Other Companies
Cellulose Nanofiber non woven Fabrics (CNF)

Cellulose Nanofiber non woven Fabrics (CNF) is a new sheet material made by cellulose nanofibers below 100 nm in diameter. CNF has large surface area and high porosity, and will be applicable in various fields.

< Features of CNF >

1) Large surface area and high porosity
2) Possible to add a new functionality by a surface modification technique
3) High resistance for general organic solvents (insoluble and non-swollen)
4) High heat resistance properties (showing no thermal transition up to 200°C, low CTE value)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Av. Fiber diameter (nm)</td>
<td>30~100</td>
</tr>
<tr>
<td>Sheet weight (g/m²)</td>
<td>3~20</td>
</tr>
<tr>
<td>Thickness (µm)</td>
<td>7~80</td>
</tr>
<tr>
<td>Porosity (vol%)</td>
<td>~85</td>
</tr>
<tr>
<td>Surface area (m²/g)*</td>
<td>~55</td>
</tr>
<tr>
<td>CTE **</td>
<td>~10</td>
</tr>
</tbody>
</table>

* B.E.T. method
** Coefficient for a thermal expansion between 50~200°C
Large surface area and high porosity

Example of addition of a new functionality:
Control of a surface hydrophilicity

<table>
<thead>
<tr>
<th>Wet/Dry tenacity</th>
<th>Original CNF</th>
<th>Hydrophobic CNF</th>
</tr>
</thead>
<tbody>
<tr>
<td>{\text{kg/15mm}}</td>
<td>- */1.3</td>
<td>1.2/1.3</td>
</tr>
<tr>
<td>Wet/Dry tenacity ratio</td>
<td>%</td>
<td>90</td>
</tr>
</tbody>
</table>

* break at even very low tension

High resistance for general organic solvents

Low CTE value

CTE of CNF; 6.7 ppm
50~200°C

AsahiKASEI
ASAHI KASEI FIBERS
Examples of Application

Primal properties of CNF

- Adsorption of metal ion
- Affinity to protein
- Biocompatibility
- Hydrophilicity
- Hydrophobicity

Cellulose nanofiber sheet

- Functional Filter
- Basic material for a medical use
- Basic material for a low CTE film
- Separator for battery or capacitor...
  etc
nano-CELISH (Cellulose Nano Fiber)

Application 1: nano-CELISH Sheet

<table>
<thead>
<tr>
<th>Property</th>
<th>nano-CELISH Sheet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness</td>
<td>20 μm</td>
</tr>
<tr>
<td>CTE</td>
<td>7 ppm</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>18N/15mm</td>
</tr>
</tbody>
</table>
Application 2: Transparent Sheet

Using nano-CELISH

Using Filter Paper

- 優れた透明性: Transparent
- フレキシブル: Flexible
- 高寸法安定性: Low CTE

Each sample permeated with epoxy resin

<table>
<thead>
<tr>
<th>Transparent Sheet with nano-CELISH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness</td>
</tr>
<tr>
<td>Total Transparency</td>
</tr>
<tr>
<td>CTE</td>
</tr>
</tbody>
</table>
Nano-CELISH

Bacterial cellulose
CNF Reinforced Polypropylene

![Graph showing stress-strain relationship for different materials.](image)

Comparison of CTE (23-100°C)

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (g/cm³)</th>
<th>CTE (ppm/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polypropylene: PP</td>
<td>0.91</td>
<td>130</td>
</tr>
<tr>
<td>PP+CNF30% +additives</td>
<td>1.09</td>
<td>28</td>
</tr>
<tr>
<td>PP+Pulp40% +additives</td>
<td>1.07</td>
<td>38</td>
</tr>
<tr>
<td>Alluminum alloy</td>
<td>2.8</td>
<td>24</td>
</tr>
</tbody>
</table>

Suzuki, et al., 2010

Not enough!. Goal is 10% nanofibers with same performance
### CNF Reinforced Polyethylene

#### Comparison of CTE (23-100°C)

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (g/cm³)</th>
<th>CTE (ppm/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE</td>
<td>0.96</td>
<td>222.2</td>
</tr>
<tr>
<td>HDPE + CNF10% + additives</td>
<td>1.06</td>
<td>26.9</td>
</tr>
</tbody>
</table>

Suzuki, *et al.*, 2010
2. Cellulose Nanofiber Reinforced PLA/PP

![Stress-Strain Curves]

- PLA/MFC20%
- PP/MAPP/MFC5%
- PLA
- PLA/10%MFC Injection Molded Products
- PP

PLA/10%MFC Injection Molded Products
Background & Motivation
– CO₂ emission from wastes of packaging materials by incineration –

General waste in Japan
5.2 Mt / y

Industry waste in Japan
4.9 Mt / y

- Containers & packaging: 3.67 Mt, 70.6%
- Electricity / machinery: 0.18 Mt, 3.4%
- Others: 0.3 Mt, 5.8%

- Household commodity: 0.19 Mt, 3.9%
- Agriculture forestry fisheries: 0.19 Mt, 3.9%
- Transportation: 0.33 Mt, 6.8%
- Others: 0.21 Mt, 3%

Incineration disposal: 53% (5.4 Mt / y)

CO₂ emission: 6.7 Mt / year

New environmentally compatible packaging materials are needed.

TEMPO-oxidized cellulose nanofibers having extremely high oxygen barrier properties

Nippon Paper has developed a lab production system of 0.5 kg-scale TEMPO-oxidized pulp in one batch process with TEMPO recycling system.
現在、弊社研究所の動きは、ナノセルロースによる強化樹脂の開発の優先順位は低い状態で、薬品添加、機能性食品、再生医療、機能性フィルムの開発に特化しております。
Based on the technology developed during the production of microfibrillated cellulose (MFC), we newly developed “Nanocelish”
セルロースナノファイバーについて

CNF: 繊維径4nm ~ 100nm, アスペクト比＞100
目標アスペクト比（L/D）=1000以上　 Ex) L: 100μm, D: 100nm

繊維径

原料パルプの繊維: 数10μμ
粉末パルプ
パルプ

ナノファイバー領域
セルリッシュ

CNF: 繊維径4nm ~ 100nm, アスペクト比>100

セルリッシュKY-100G: ～1 μの繊維の混合物

セルロースナノファイバー
セルロースナノファイバー『ナノセリッシュ』の魅力

### セルロース繊維本来の性質

- 材料特性の優位性
  - 力学特性（強度・弾性率）
  - 低比重（軽量）
  - 低線膨張係数

### ナノファイバー効果

- ナノサイズ効果
  - 光学特性（透明）
- 超大比表面積効果
  - 界面増 → 表面機能化

### セルロース繊維の性質

<table>
<thead>
<tr>
<th>性質</th>
<th>セルロース</th>
<th>ガラス</th>
</tr>
</thead>
<tbody>
<tr>
<td>強さ (GPa)</td>
<td>3.5</td>
<td>2</td>
</tr>
<tr>
<td>結晶弾性率 (*100GPa)</td>
<td>1.4</td>
<td>0.7</td>
</tr>
<tr>
<td>密度 (g/cm3)</td>
<td>1.45</td>
<td>0.7</td>
</tr>
<tr>
<td>熱膨張係数 (ppm/k)</td>
<td>2.26</td>
<td>0</td>
</tr>
</tbody>
</table>

- 環境にやさしい材料
  - CO₂削減

『ナノセリッシュ』で、
- 高強度/軽量/低熱膨張率
- 環境対応
を生かし、新規材料の創出が可能になります。
ダイセル化学グループのナノファイバーと技術を生かした新規素材は様々な新規製品の開発を加速させることができます。

まとめとご提案

●『ナノセリッシュ』は機械特性と光学特性に優れる高機能発現素材であり、新たな高機能材の創出に大きく寄与する可能性を秘めています。

●『ナノセリッシュ』は他に例を見ない高アスペクト比を示す繊維であり、複合材料のハイパフォーマンス化に有効です。

●ダイセル化学グループはセリッシュの製造・販売実績を持つだけでなく、セルロースの取り扱い技術はもとより豊富な樹脂群とそれらを加工する技術も保有しています。

ダイセル化学グループのナノファイバーと技術を生かした新規素材は様々な新規製品の開発を加速させることができます。
Twin Screw Extruder, 15mm diameter (Productivity rate: 56g/hr)

High pressure homogenizer, 14 passes

High shear speed, Extruder, 15mm (Productivity rate: 600g/hr)

+ Cationized pulp, Extruder, 15mm (Productivity rate: 600gr/hr)
Agitation for 1 min by high speed blender

Wood Pulp

Uetani and Yano, 2008
Nanofibrillation of Pulp by High Speed Agitation

Uetani and Yano, 2008
5. Nanofibrillation of pulp by kneading

1% pulp slurry

Disk Refiner

Solid content: 30%

Kneading machine: 60rpm, 20min

Yano, 2003
After kneading

× 200  Surface fibrillation by refiner  × 2000

Yano, 2003