Current situation of Nanocellulose in Japan

Hiroyuki Yano
Research Institute for Sustainable Humanosphere,
Kyoto University

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 nanocellulsoe 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

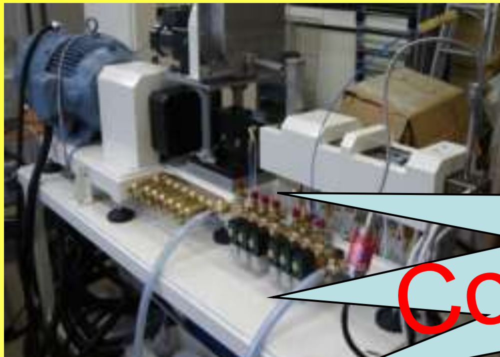
Public research organizations:
Advanced Industrial Sci. & Techol. (AIST, Dr. Endo & Dr. Lee group)
Kyoto Municipal Research Institute (Dr. Kitagawa group)
+3-5 group

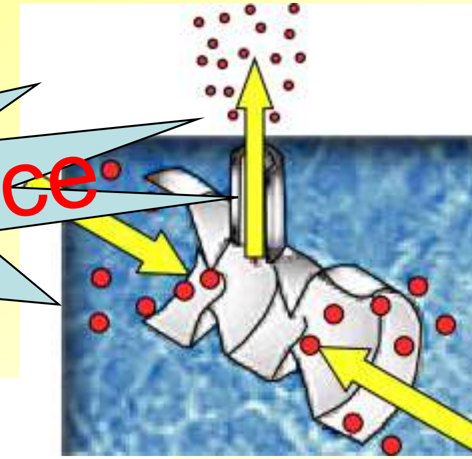
Company:
Oji Paper, Nippon Paper Industry, Sugino Machine, Masuko Sangyo, Mitsubishi Paper, Daicel Chemical, Asahi Kasei Fibers, Mitsubishi Chemical, DIC, Sumitomo Rubber, Kao, Toppan
+5-10 companies

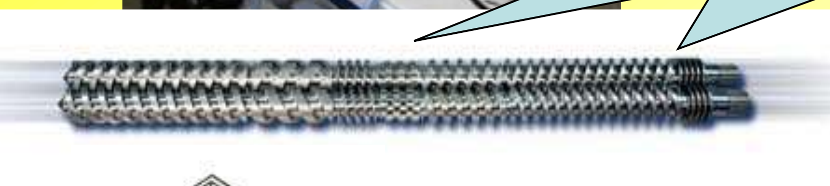
RISH, Kyoto Univ.

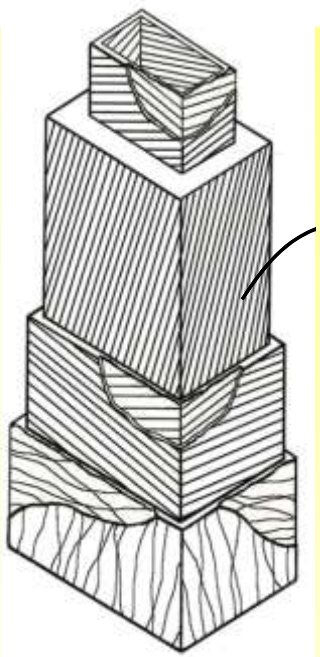
Extraction of nanofibers from wood/plant fibers

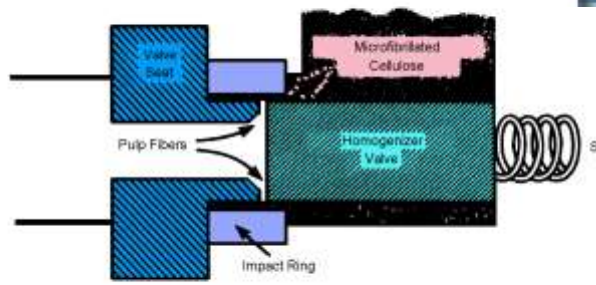
Cost and Performance











Facilities for fibrillation

High speed blender

High pressure homogenizer

Ultra high pressure homogenizer

Grinder

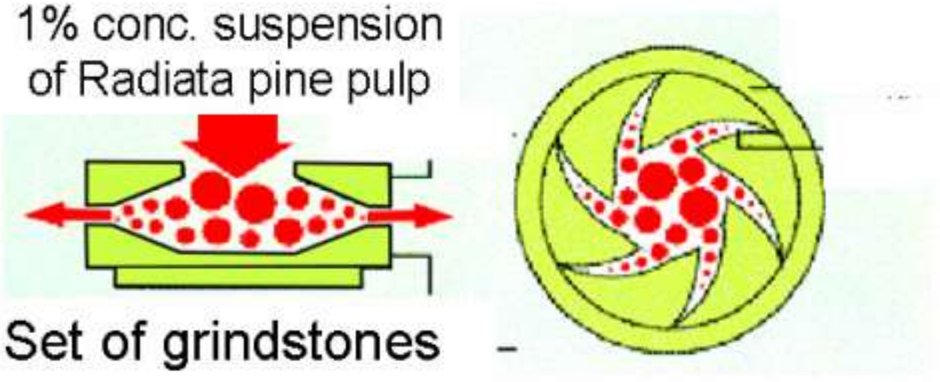
Batch-type beads mill

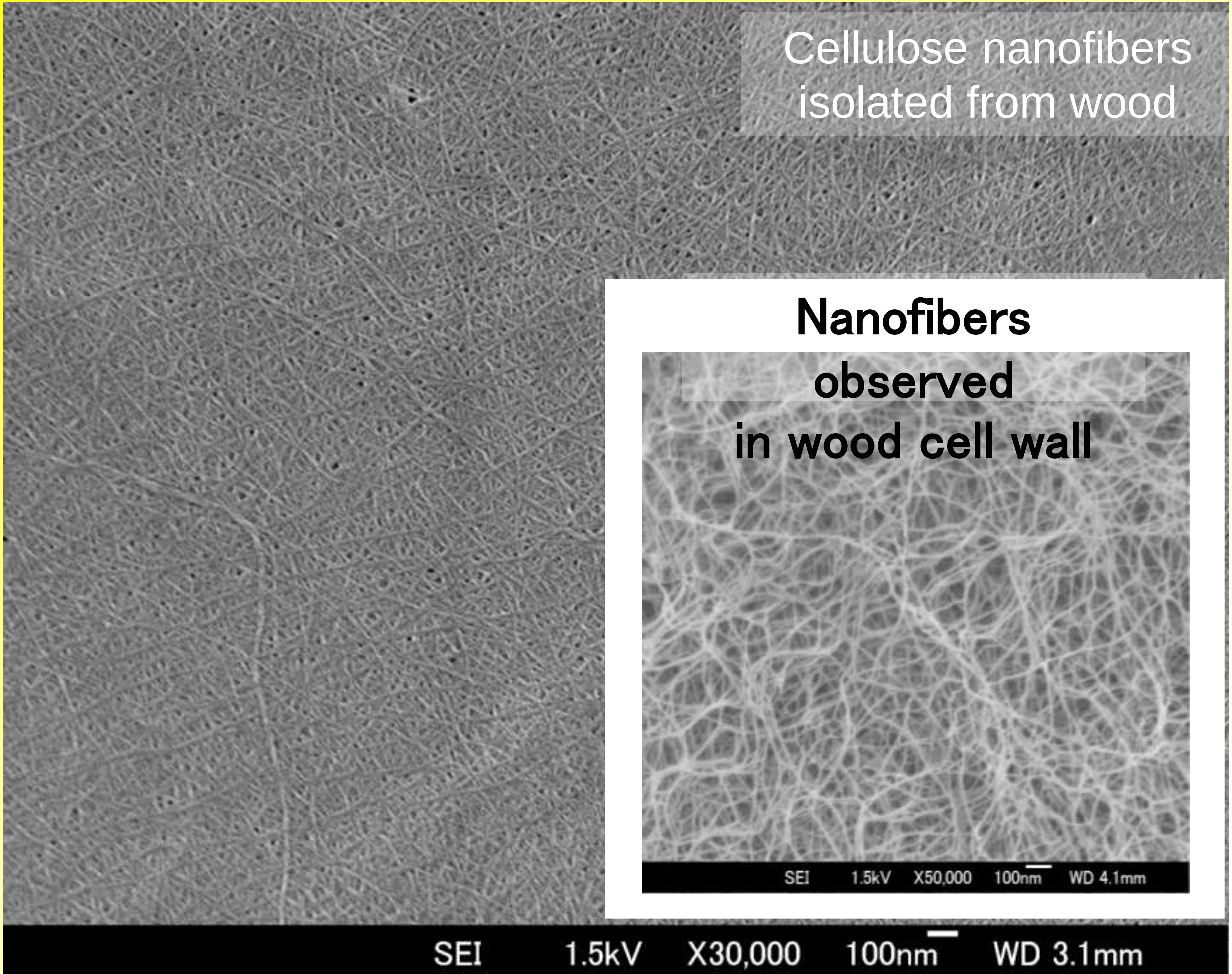
Continuous beads mill

Twin screw extruder

Grinder treatment

Never- dried pulp




Cellulose nanofibers
isolated from wood
Nanofibers
observed
in wood cell wall
SEI 1.5kV X50,000 100nm WD 4.1mm
SEI 1.5kV X30,000 100nm WD 3.1mm

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





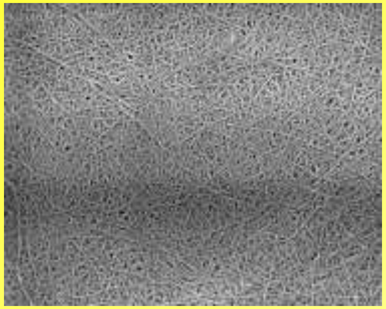



K.Abe, 2007

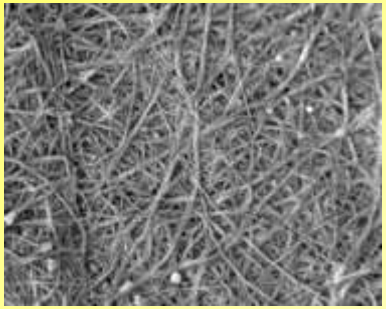
Comparison of Nanofibers

K.Abe, 2007

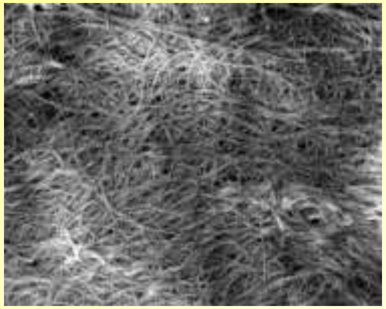
Wood



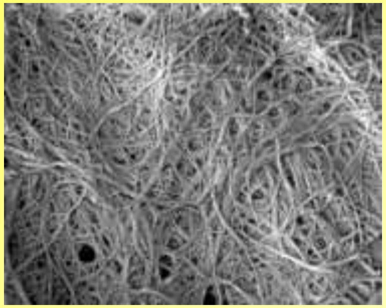
Sea weed



Rice straw

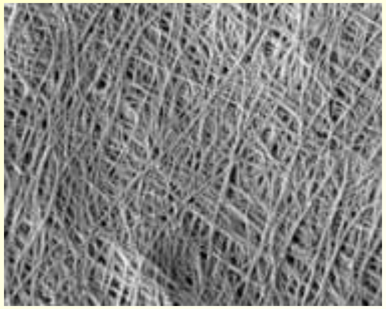


Potato tuber

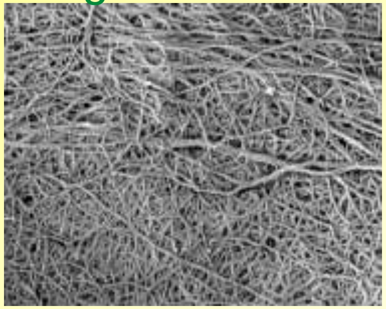


Water weed

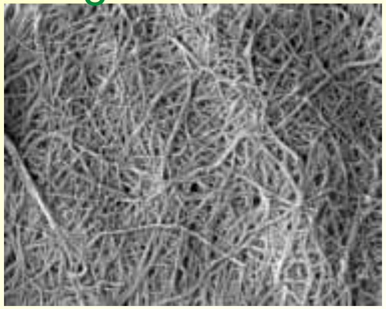
Cassava



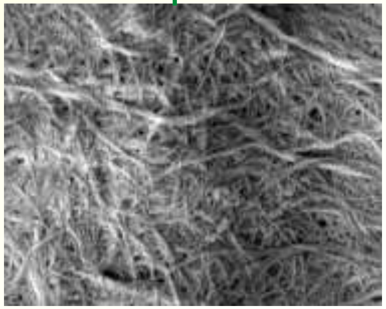
Sugarcane



Sugar beet



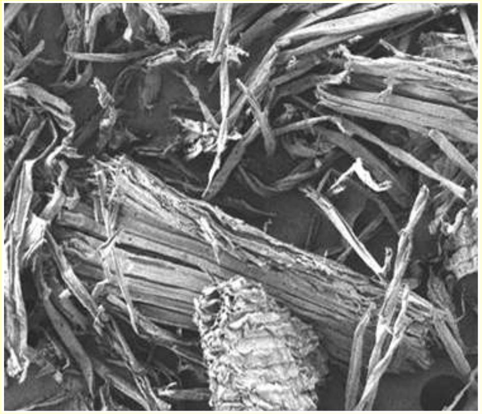
Sweet potato



Nanofibrillation using High-speed Blender

Blender, 37000rpm

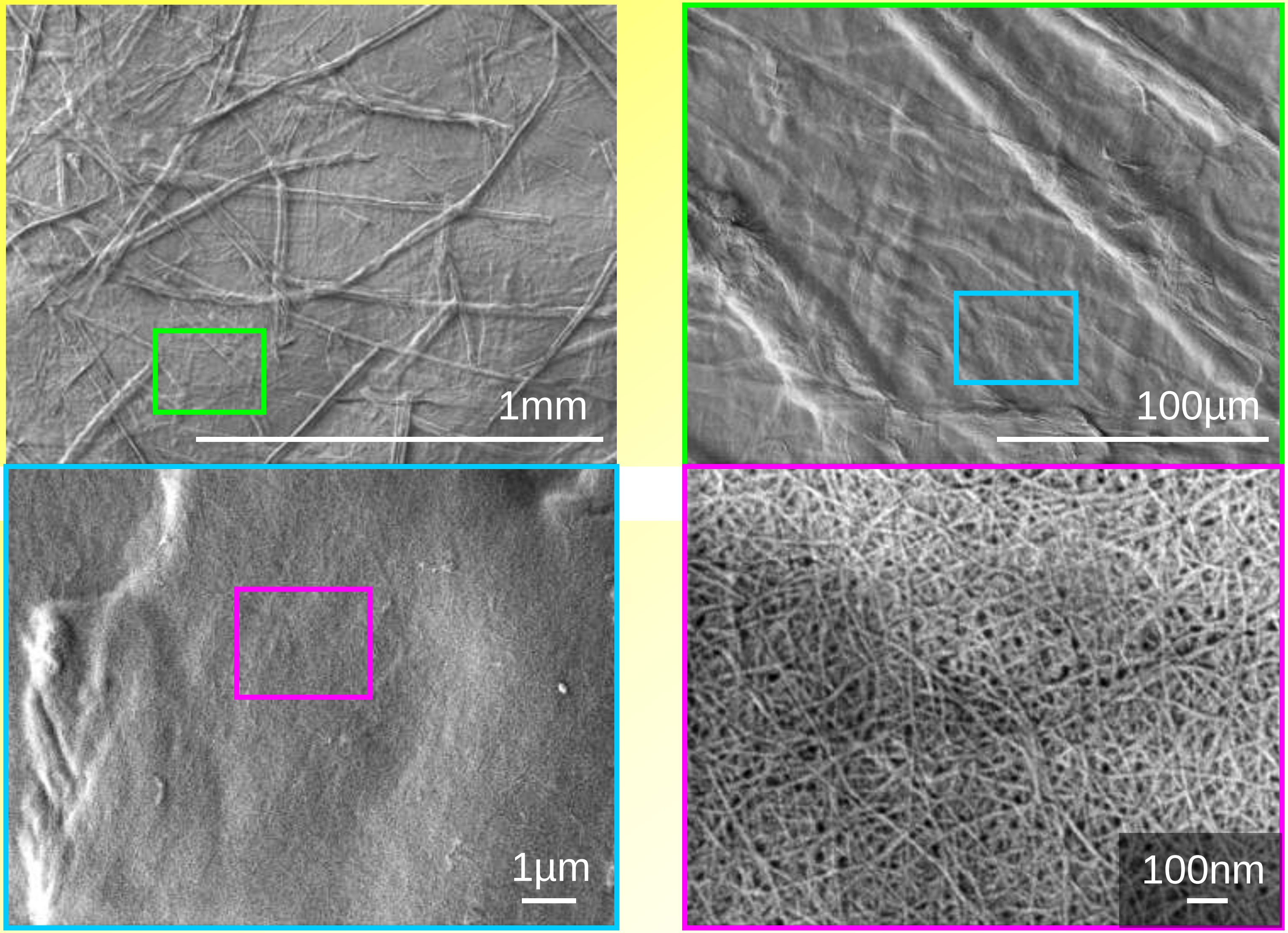
Never-dried pulp
($NaClO_2$ treated)



0.7wt% water slurry

Uetani and Yano, 2008

Agitation for 1 min by high speed blender



Uetani and Yano, 2008

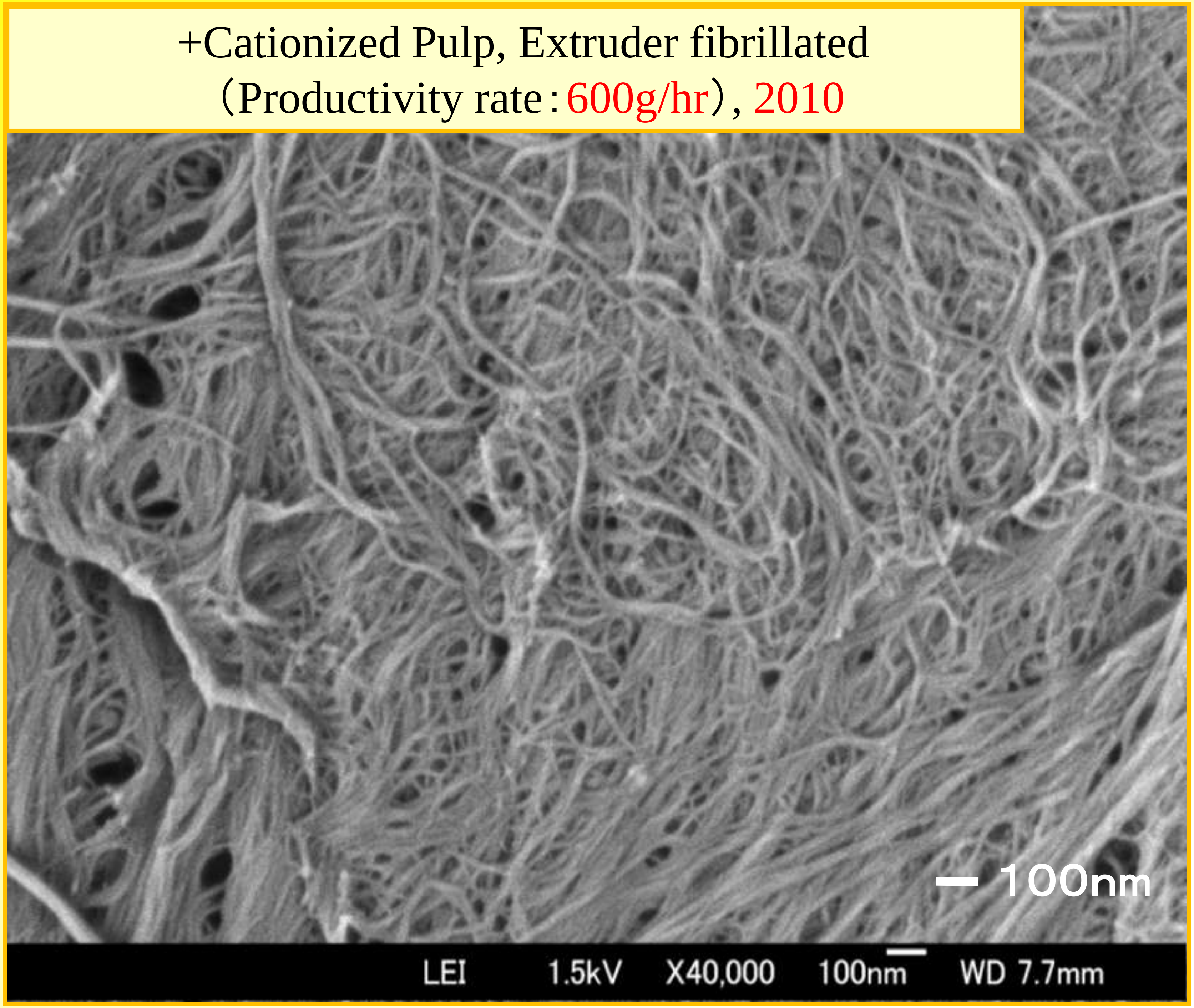
Kneading using twin screw extruder

Wood Pulp (KP)

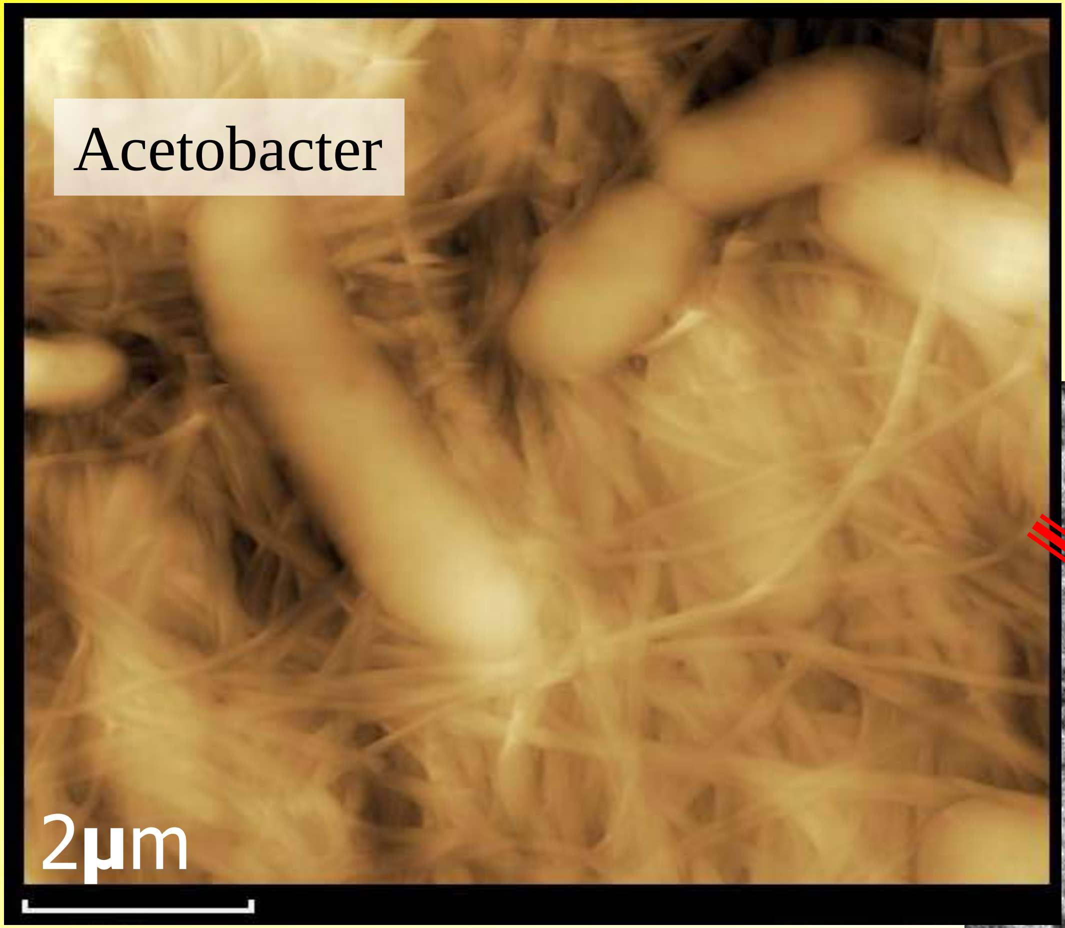
Disk Refiner

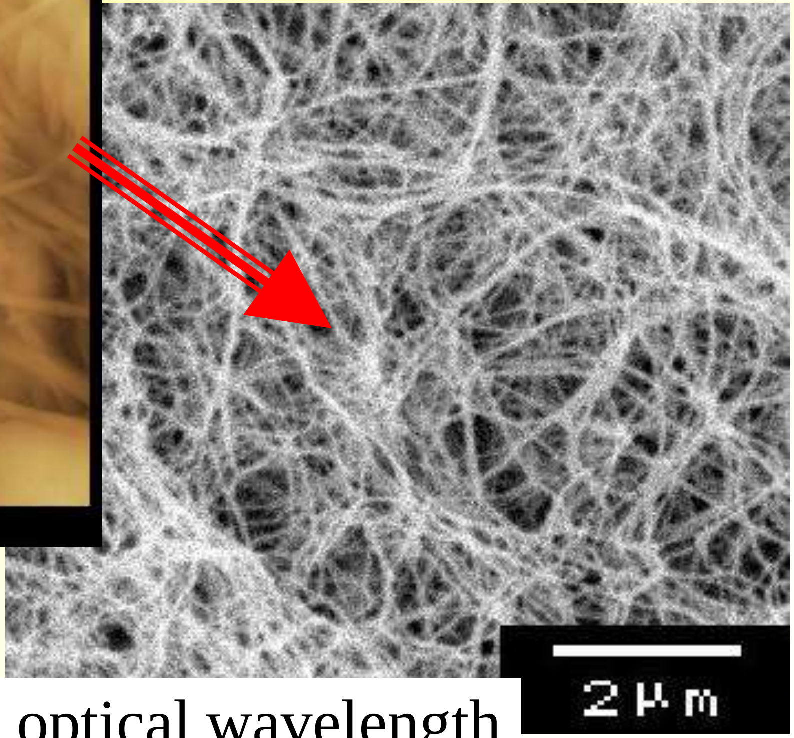
Kneading

+Cationized Pulp, Extruder fibrillated
（Productivity rate：600g/hr）, 2010



Bacterial Cellulose

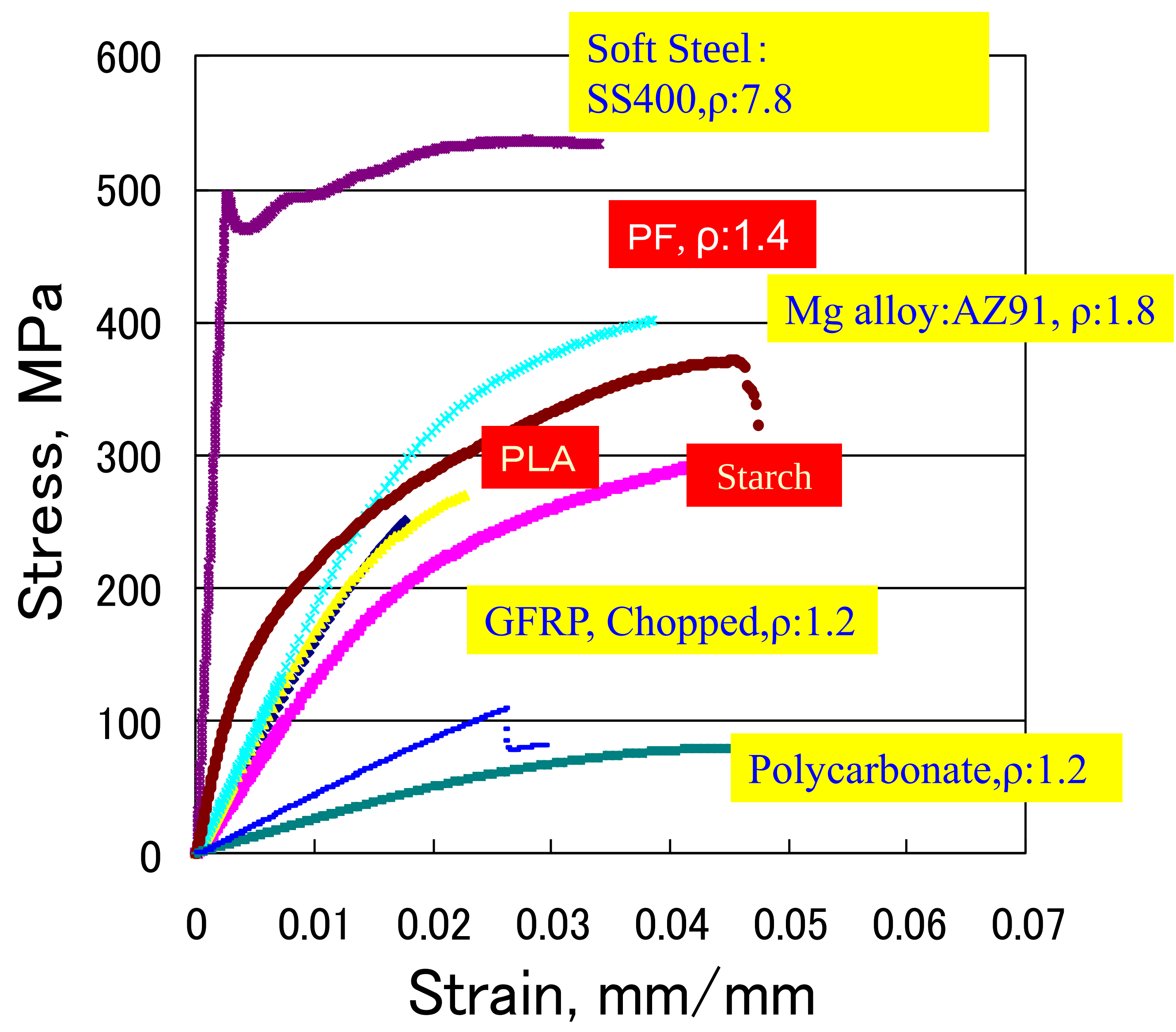




50 nm wide： one-tenth the size of the optical wavelength

Applications

1) Light weight and High strength Cellulose NF-based Composites



NEDO Green Sustainable Chemical Process Programs from 2009 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 high performance cellulose nanofibers reinforced plastics for automotive parts

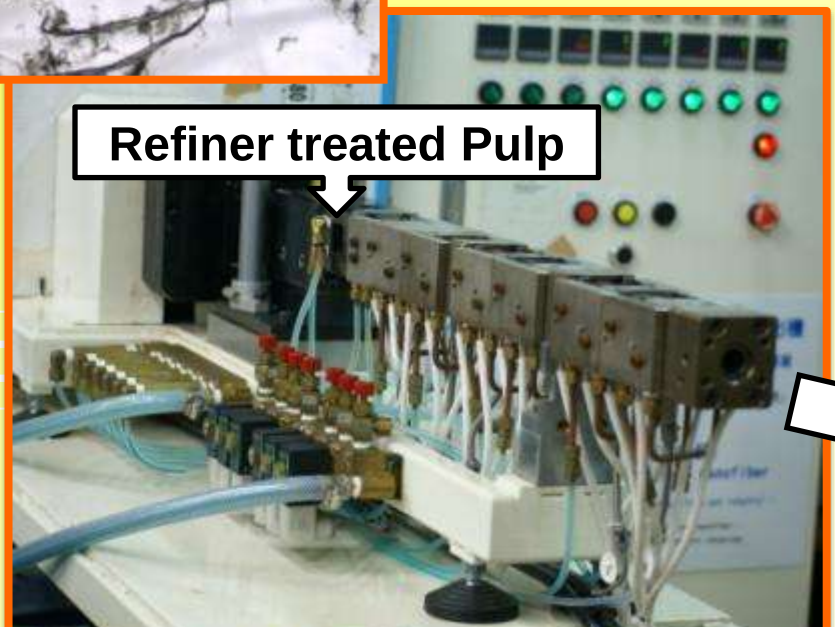
Organizations: Kyoto University, Kyoto Municipal Institute, Oji Paper, Mitsubishi Chemical , DIC
Advisers: Toyota Autobody, Nissan, Suzuki, Denso, Japan Steel Works

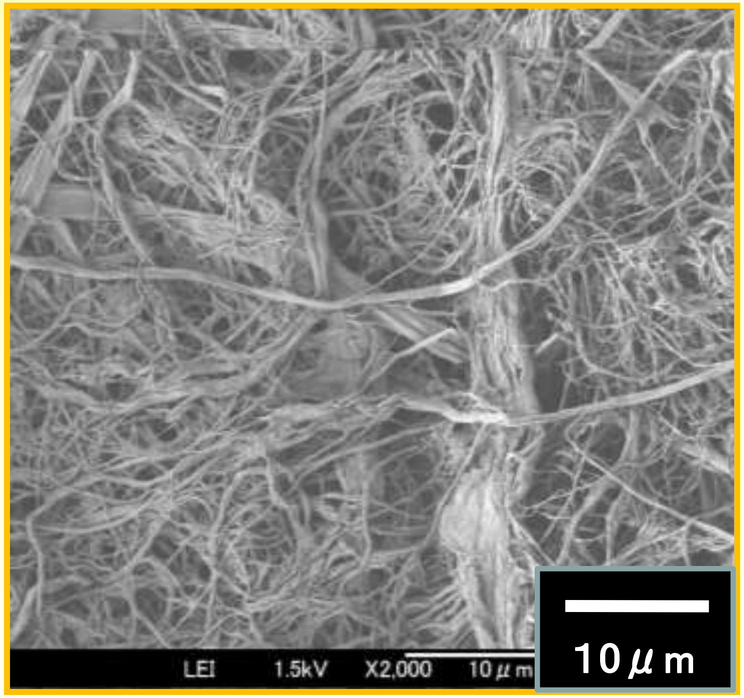
The project consists of three parts as follows:

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





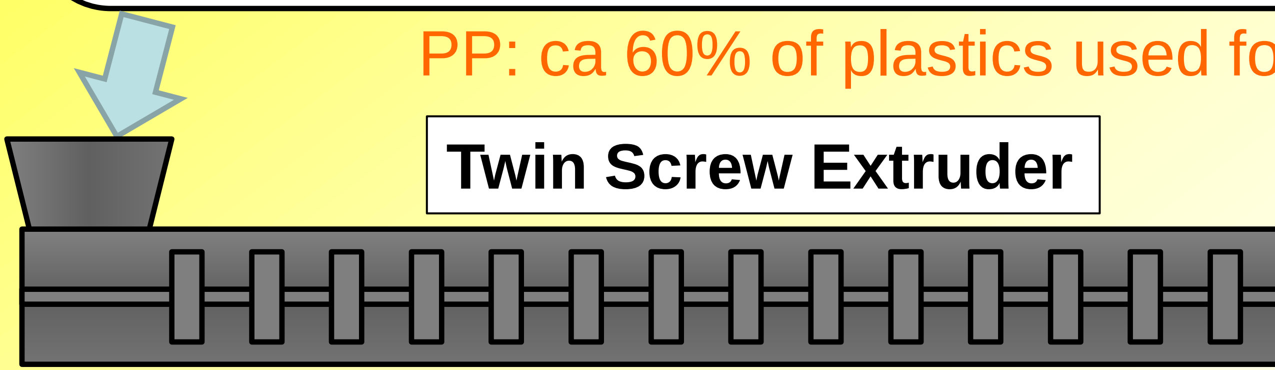
Preparation of Cellulose NF/PP composites: Injection molding

Refiner treated Pulp:NBKP

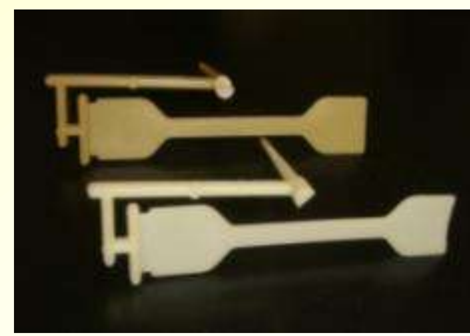
Polypropylene:PP

additives

PP: ca 60% of plastics used for automotive parts



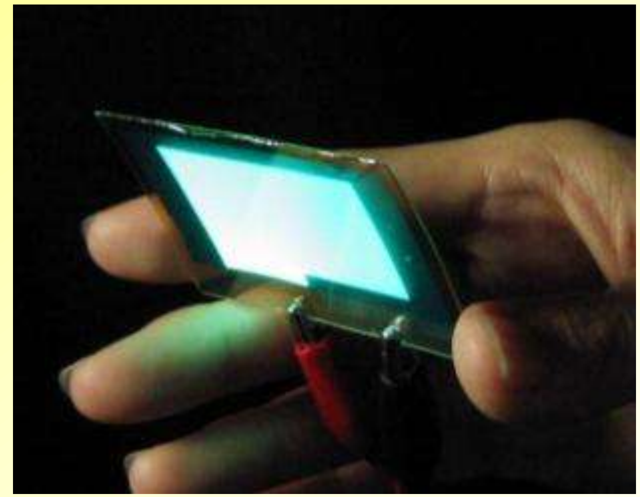
Nanofibrillation & Compounding



Allowing nanofibriilation and well-mixed compounds,

Injection Molding

2. Optically Transparent Cellulose Nanofiber Reinforced Composite



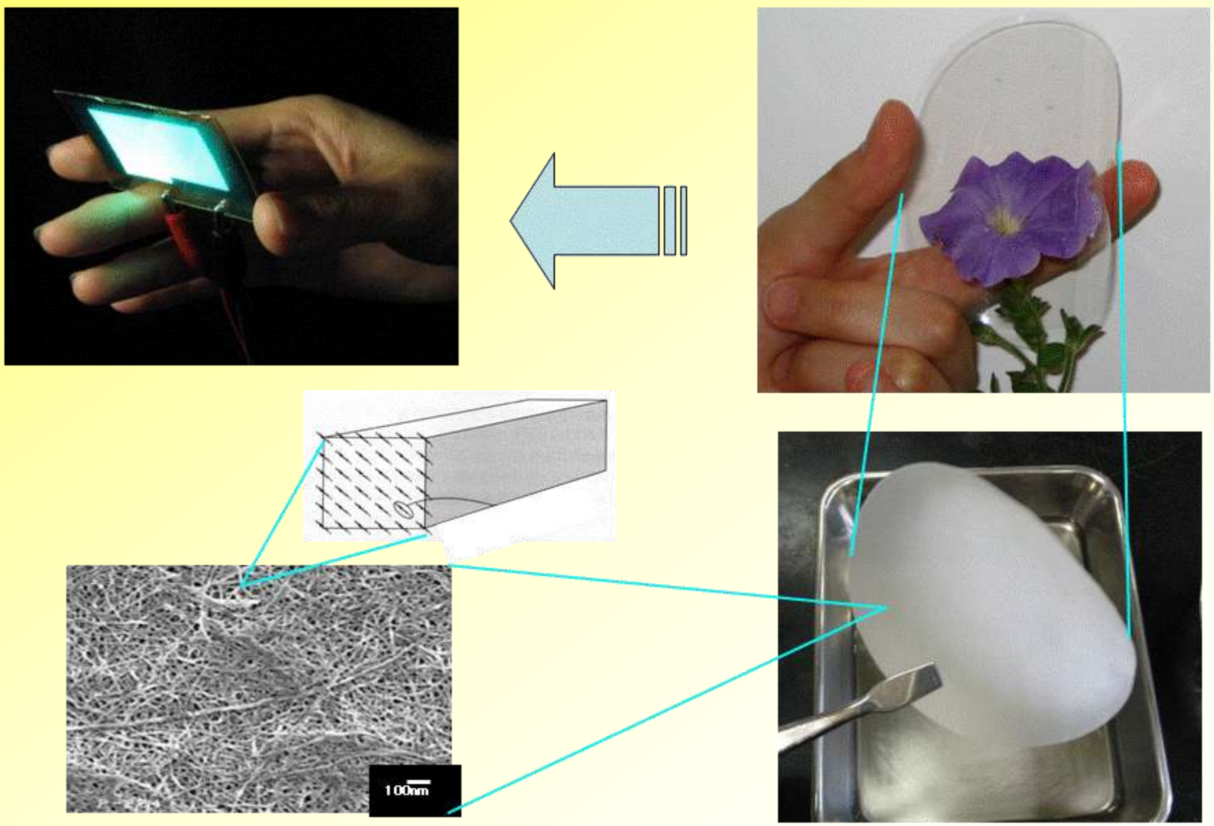
Optically transparent composite reinforced with cellulose nanofiber (left).
Organic EL (OLED) emitted on the transparent composite (right).

As strong as steel, as thermally stable as glass, and as bendable as plastics

Oji Paper Co.,Ltd.

MITSUBISHI CHEMICAL

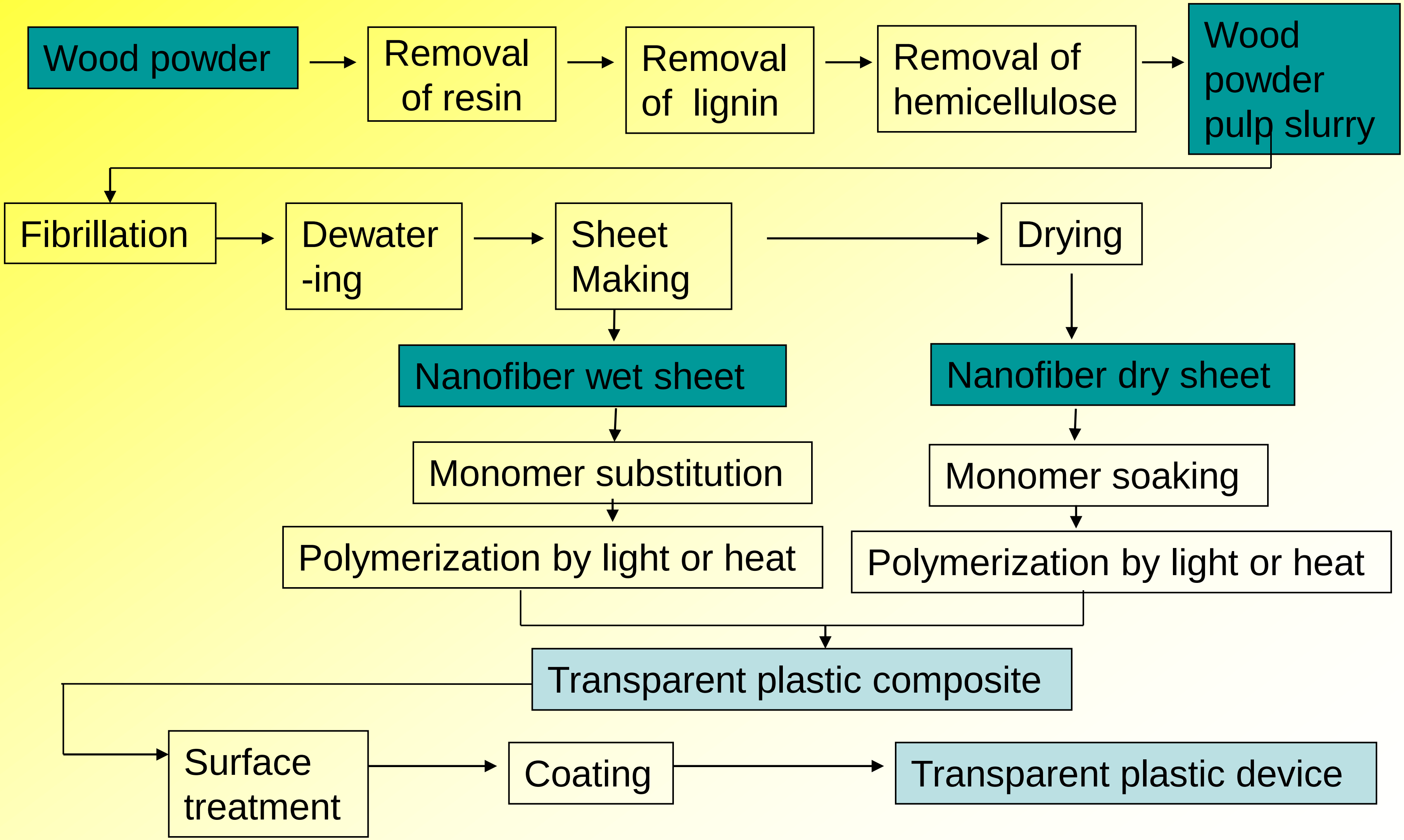
2010-2012 Collaborative Research for the Commercialization of Nano Fiber Cellulose Composite Sheet for Plastic Substrate



Oji Paper Co.,Ltd.

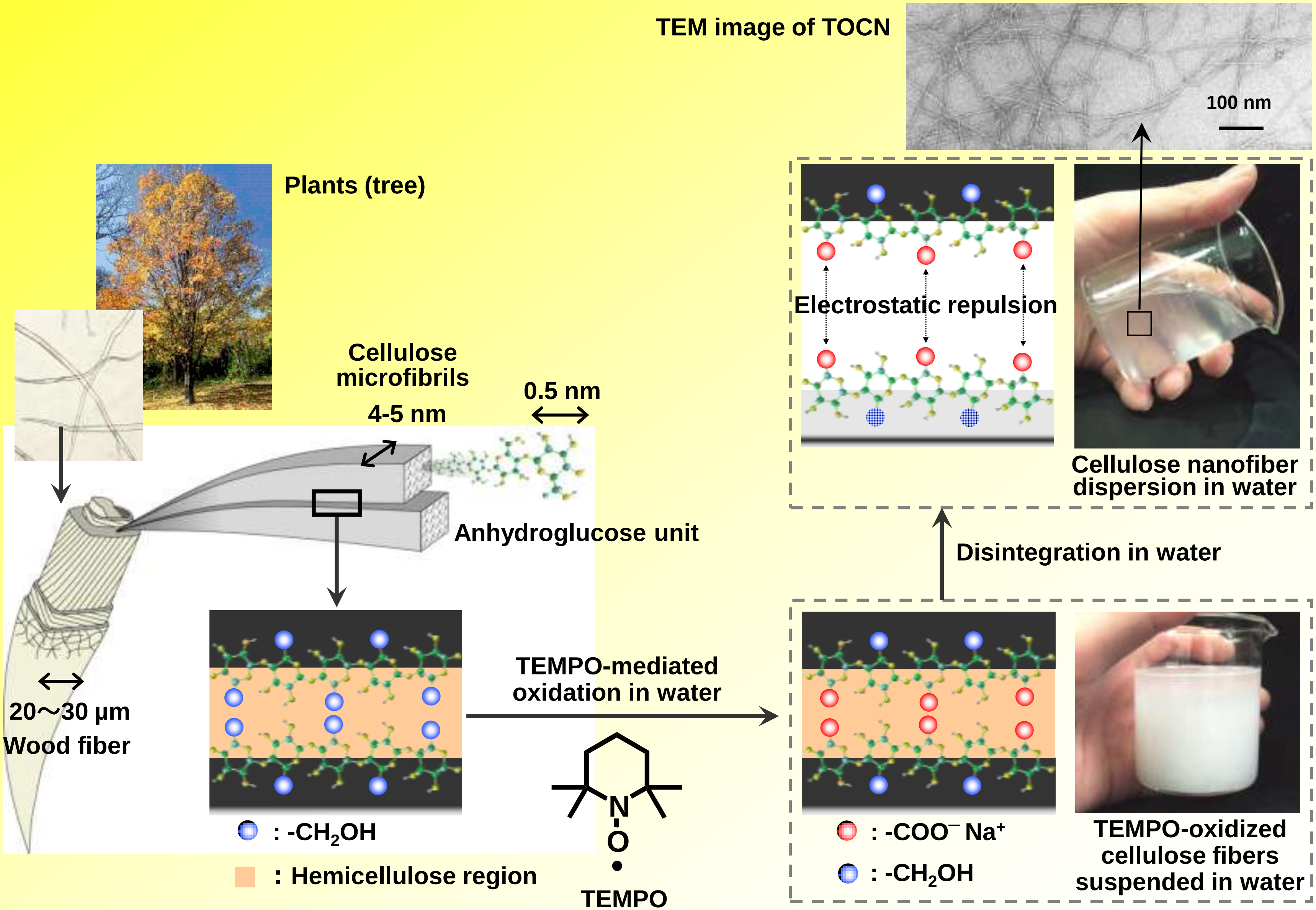
MITSUBISHI CHEMICAL

Development for mill scale Manufacturing



Prof. A. Isogai, Univ. of Tokyo

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



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**

UT

The University of Tokyo

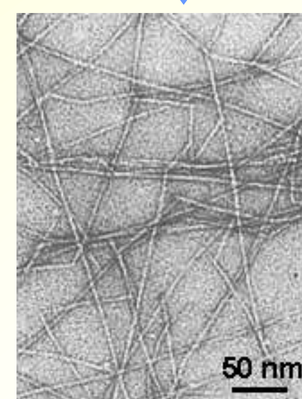
Total concept of wood biomass refinery, utilizing TEMPO-oxidized cellulose nanofibers

Forest biomass resources

Pulping / bleaching

Wood cellulose

TEMPO-oxidation
Disintegration
in water



TEMPO-oxidized cellulose nanofibers

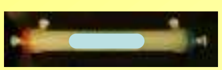
TEMPO-oxidized cellulose nanofibers are

New bio-based nanomaterials

with high strengths, high transparency, low CTE, high gas-barrier properties,

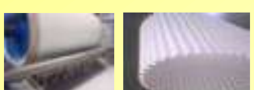
possibly supporting sustainable society, secure / safe society, information technology etc.

Modification
Compositing
Processing



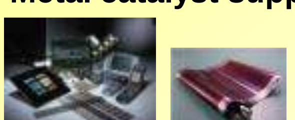
Bio filters

Medical & healthcare

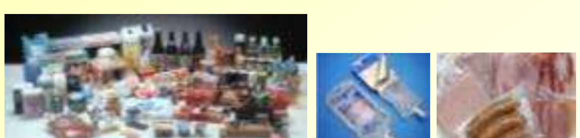


Metal catalyst support

Bio-fibers for industrial use



Electronics devices



High-performance packaging materials

Carbon neutral

National Institute of Advanced Industrial Science and Technology
AIST

Research activities in

Biomass Technology Research Center (BTRC),

National Institute of Advanced Industrial Science and Technology (AIST)

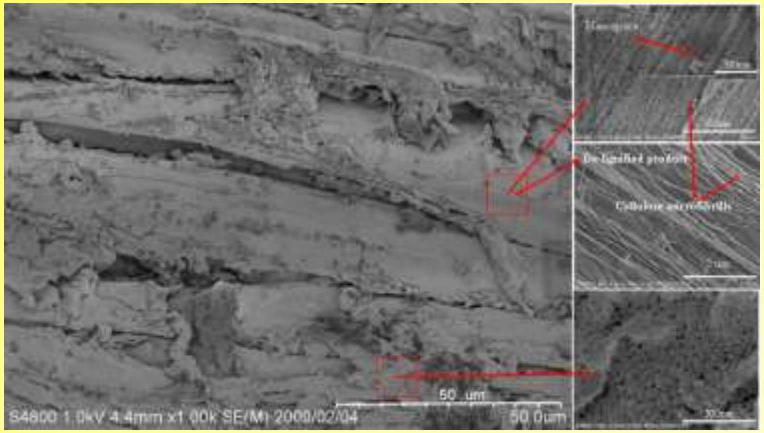
Dr Endo & Dr Lee

Nanofibrillation and Nanocomposites

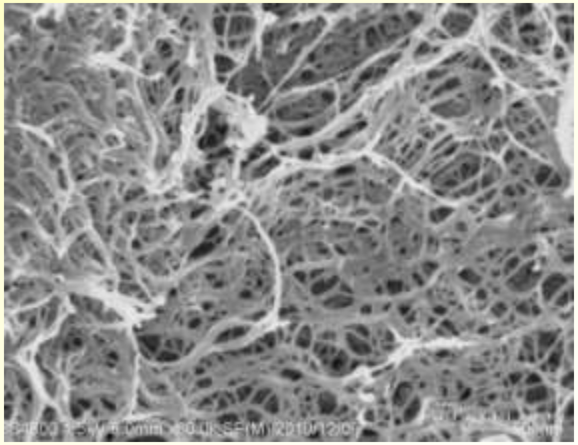
Hot-water and ozone treatment to loosen cell wall $\xrightarrow{\text{Mechanical grinding}}$ Cellulose nanofiber and ligno-cellulose nanofiber $\xrightarrow{\text{Application}}$ ○Pretreatment for improving enzymatic saccharification ○Nano-composite material

Disk mill, extruder, high-pressure homogenizer etc.

1. Hot-water treatment and mechanical grinding



Loosened cell wall structure is effective to improve fibrillation efficiency

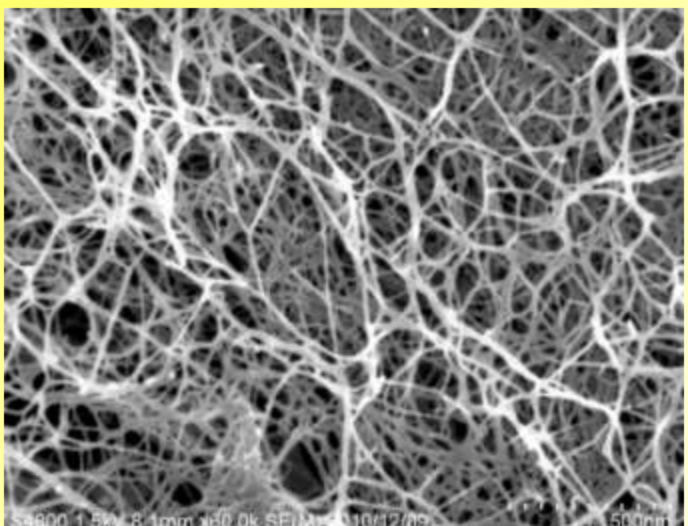


- Material: wood powder, non-bleached pulp, etc.
- Temperature 130-200℃, Pressure 1Mpa-5Mpa
- Mainly hemicellulose extraction
- Producing porous structure

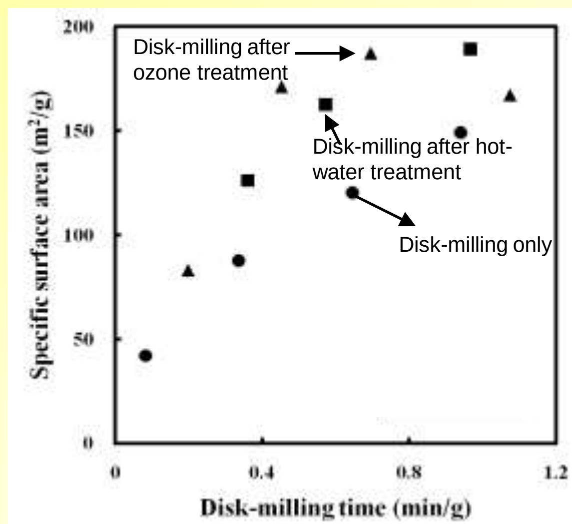
- Wide range of fiber diameter can be obtained.
- Increase of surface area to enhance enzymatic degradation
- Application for improving mechanical properties of conventional wood-plastic composite

2. Ozone treatment to loosen cell wall before and after mechanical grinding

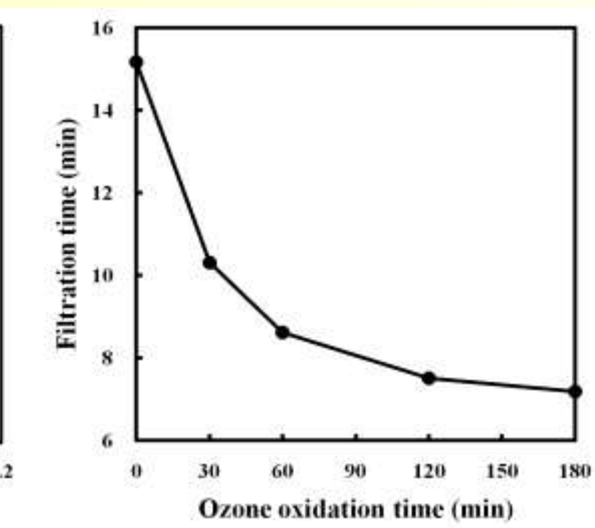
- Lignin degradation is effective to improve mechanical fibrillation efficiency
- Can be combined with hot-water treatment
- Surface oxidation and surface charge change
- Reduction of filtration time for preparing nanopaper
- Control of molecular weight (degree of polymerization)
- Treating ozone amount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

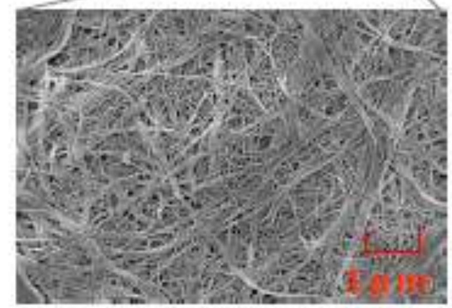


Reduction of filtration time for preparing nanofiber sheets

Other Companies

— Development article —

*C*ellulose *N*anofiber non woven *F*abrics（*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 the 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℃, low CTE value)

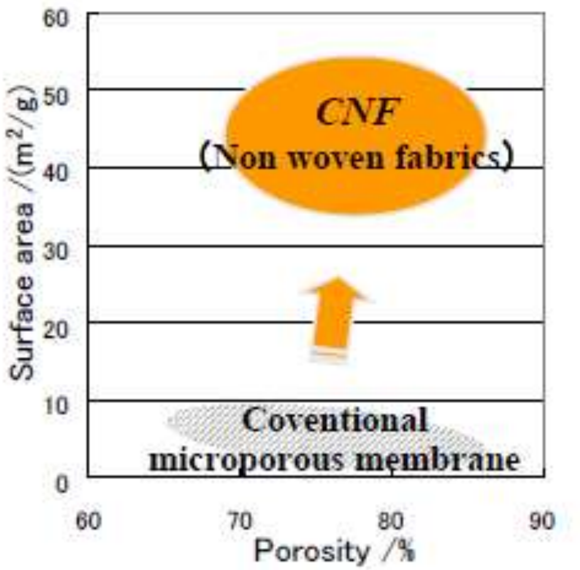
＜Structural Factors and Property＞

Av. Fiber diameter (nm)	30~100
Seet weight (g/m²)	3~20
Thickness (μm)	7~80
Porosity (vol%)	~85
Surface area (m²/g)*	~55
CTE **	~10

* B.E.T. method

** Coefficient for a thermal expansion between 50~200℃

Lagre surface area and high porosity



High resistance for general organic solvents

	MeOH	Acetone	DMSO
CNF	 Non swollen	 Non swollen	 Non swollen
Cellulose acatate	 swollen	 soluble	 soluble
Cellulose nitrate	 soluble	 soluble	 soluble

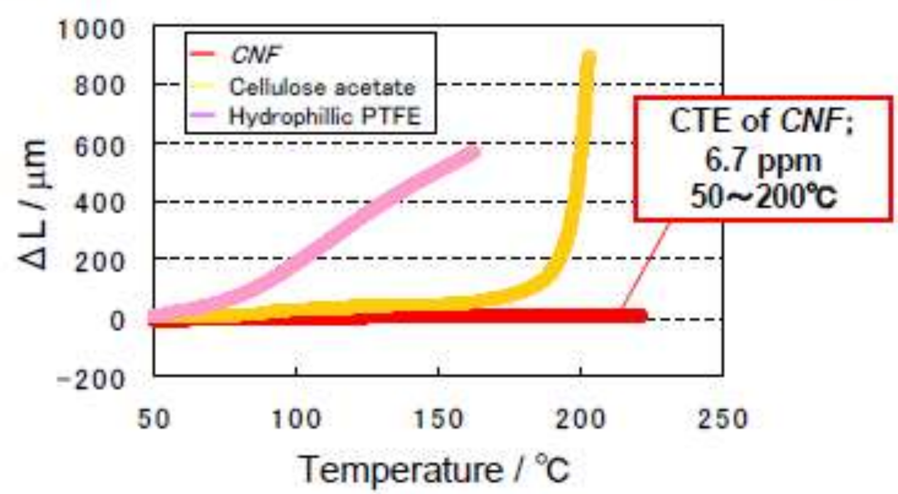
Example of addition of a new functionality; Control of a surface hydrophilicity

Original *CNF* → Hydophobic *CNF* (Surface modified *CNF*)

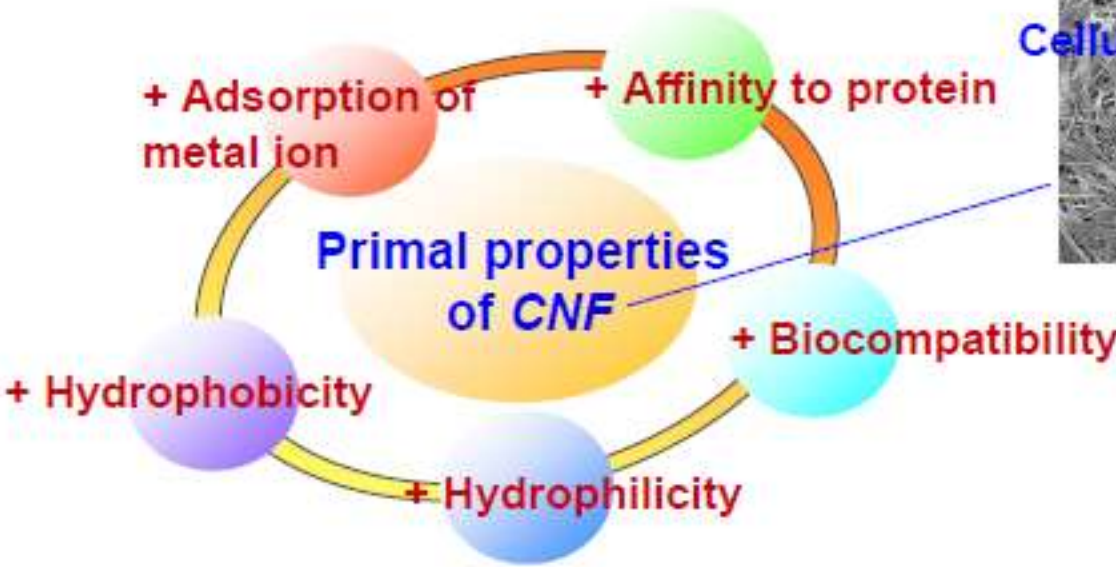
		Original CNF	Hydrophobic CNF
Wet/Dry tenacity	kg/15mm	$-^{*}$ /1.3	1.2/1.3
Wet/Dry tenacity ratio	%	–	90

* break at even very low tension

Low CTE value



Examples of Application



* Functional Filter
* Basic material for a medical use
* Basic material for a low CTE film
* Separator for battery or capacitor

… etc

DAICEL CHEMICAL INDUSTRIES, LTD.

ナノセリッシュ

nano-CELISH（Cellulose Nano Fiber）

開発品

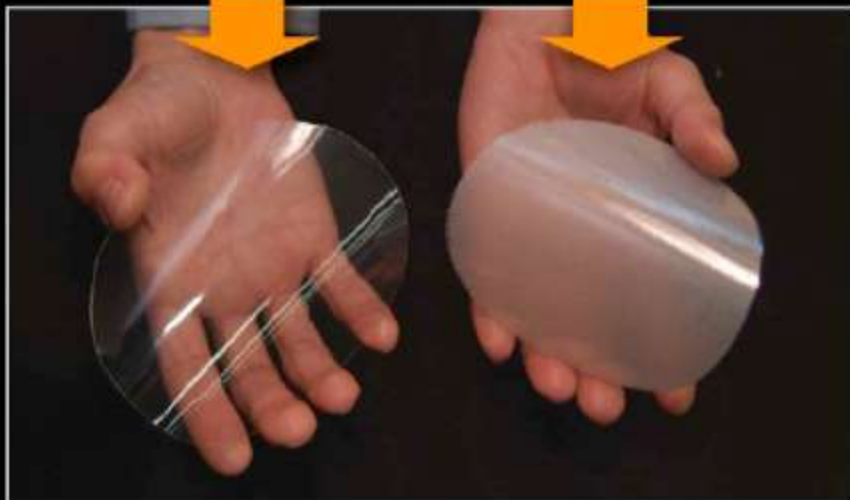
Application 1：ナノセリッシュシート nano-CELISH Sheet

nano-CELISH Sheet （Trial Product）

	nano-CELISH Sheet
Thickness	20 μm
CTE	7ppm
Tensile Strength	18N/15mm

Application 2：透明・低線膨張シート Transparent Sheet

Using nano-CELISH | Using Filter Paper

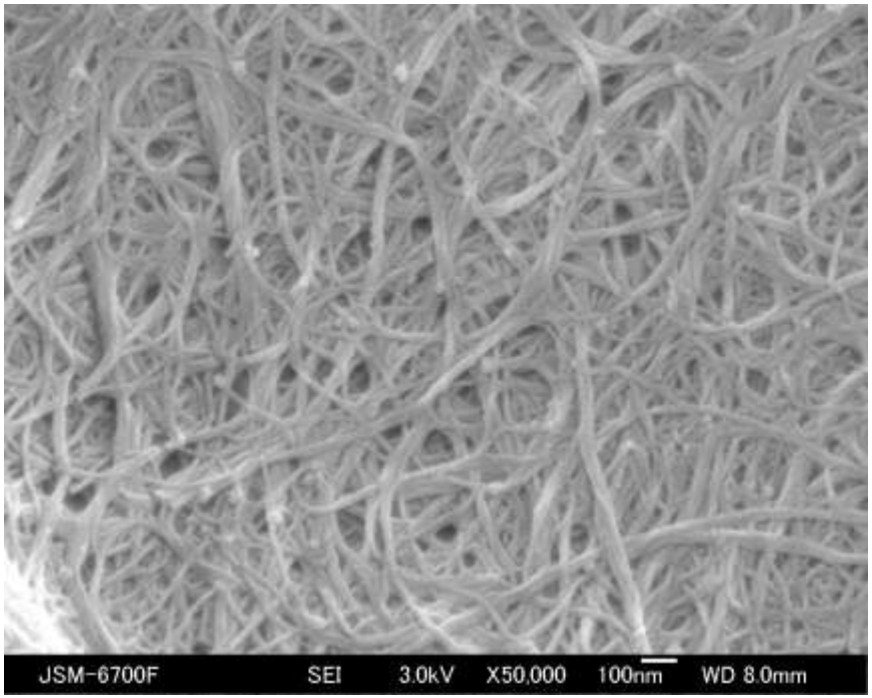


Each sample permeated with epoxy resin

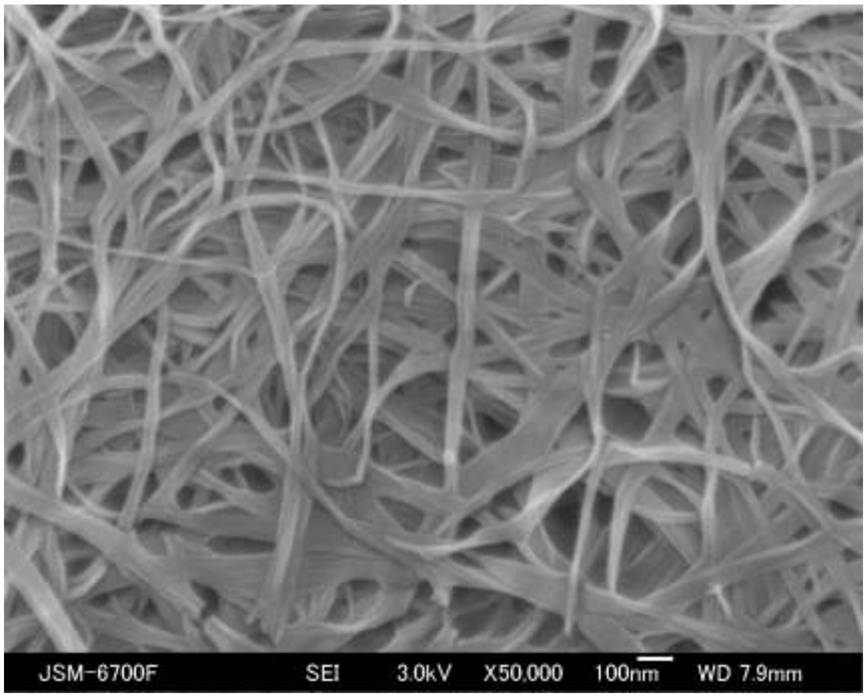
- 優れた透明性 Transparent
- フレキシブル Flexible
- 高寸法安定性 Low CTE

	Transparent Sheet with nano-CELISH
Thickness	100μm
Total Transparency	90%
CTE	20ppm

補足資料(写真)

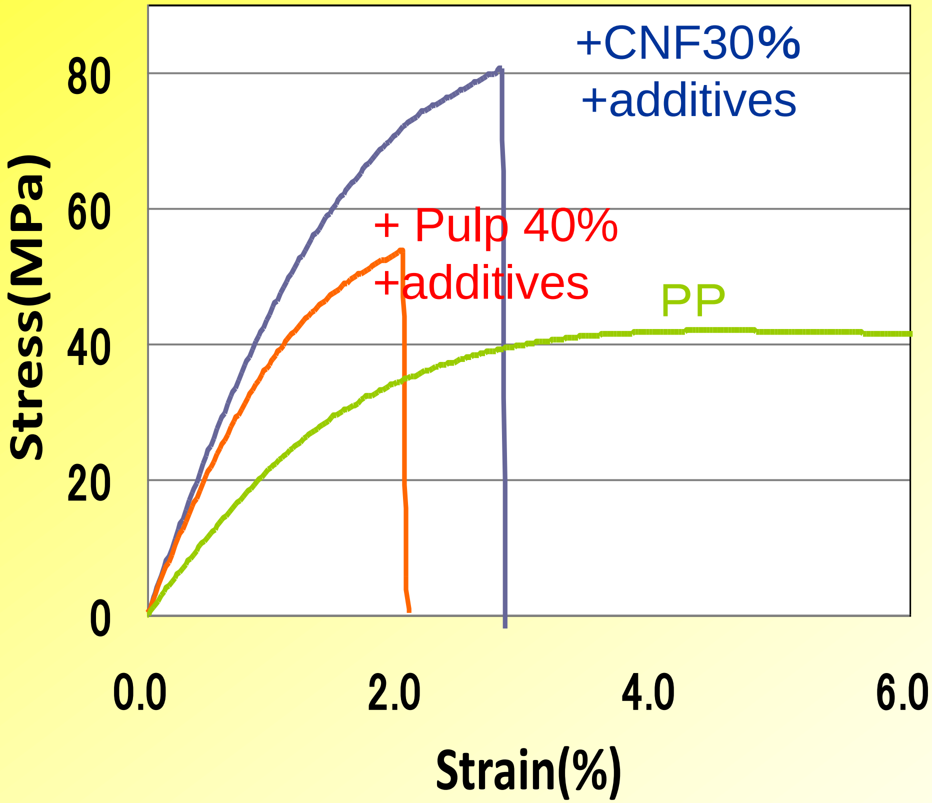


Nano-CELISH



Bacterial cellulose

CNF Reinforced Polypropylene



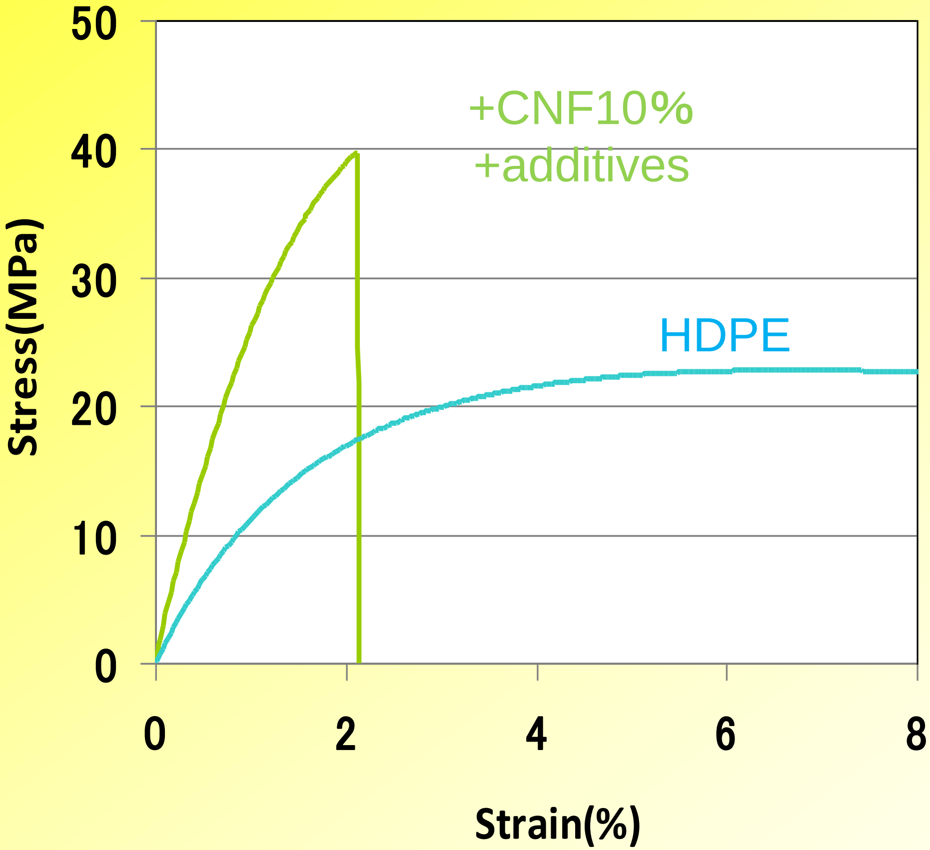
Comparison of CTE (23-100℃)

	Density (g/cm^3)	CTE (ppm/K)
Polypropylene: PP	**0.91**	**130**
PP+CNF30% +additives	**1.09**	**28**
PP+Pulp40% +additives	**1.07**	**38**
Alluminum alloy	**2.8**	**24**

Not enough!. Goal is 10% nanofibers with same performance

Suzuki, *et al.*, 2010

CNF Reinforced Polyethylene

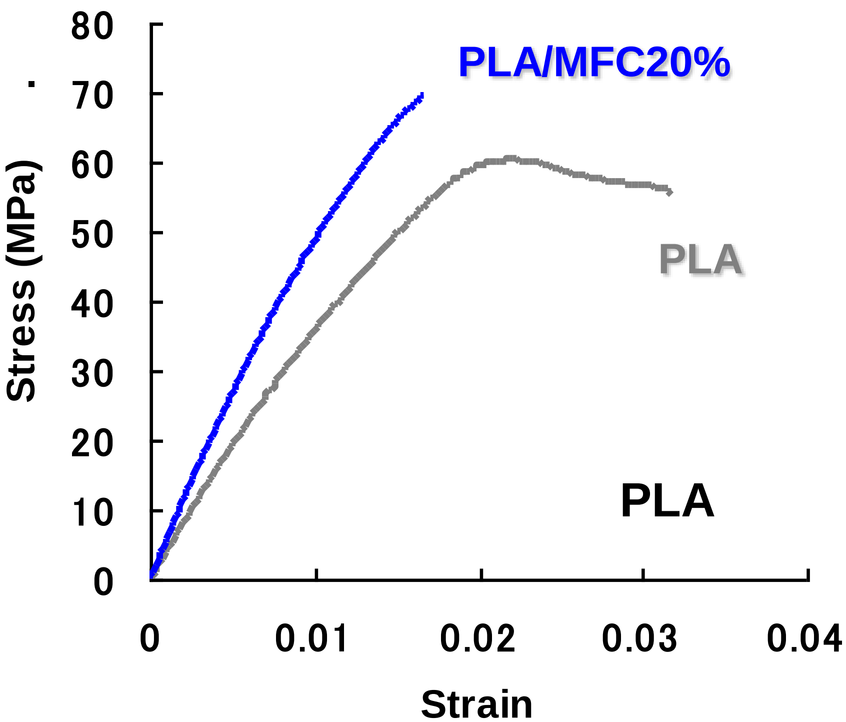


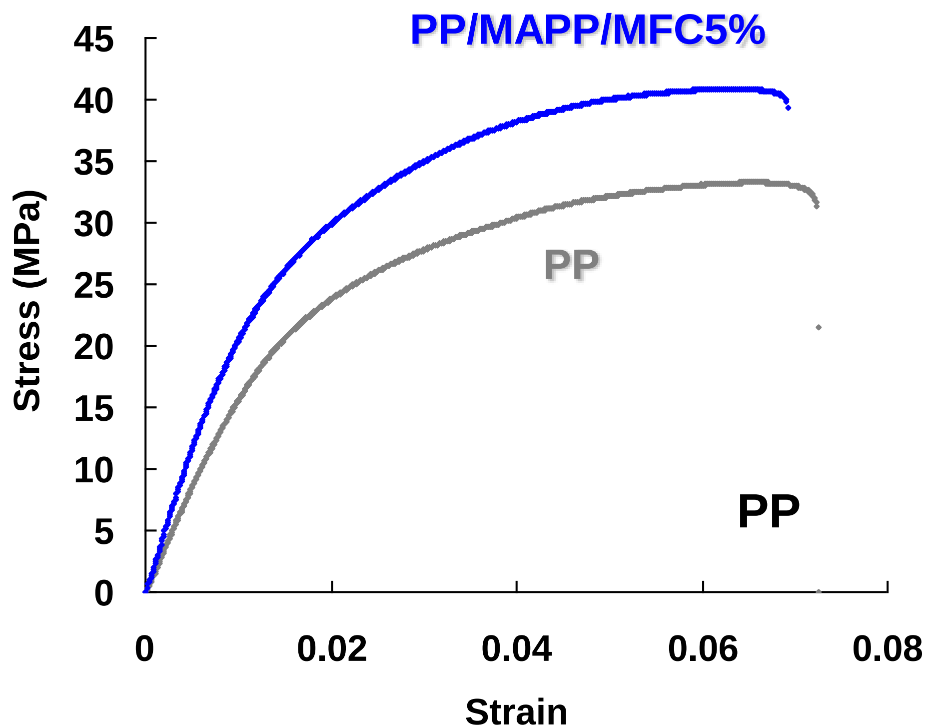
Comparison of CTE (23-100℃)

	Density (g/cm3)	**CTE** (ppm/K)
HDPE	0.96	222.2
HDPE +additives +MFC20%	1.06	26.9

Suzuki, *et al.*, 2010

2. Cellulose Nanofiber Reinforced PLA/PP

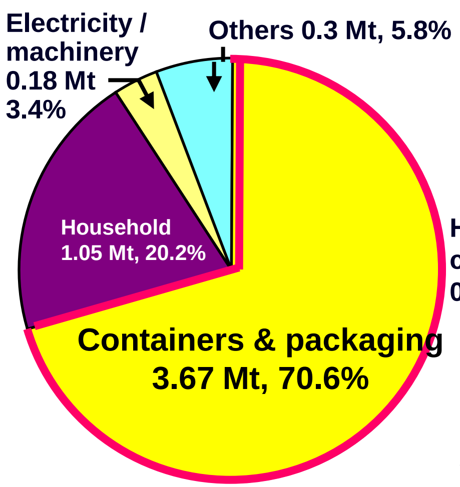




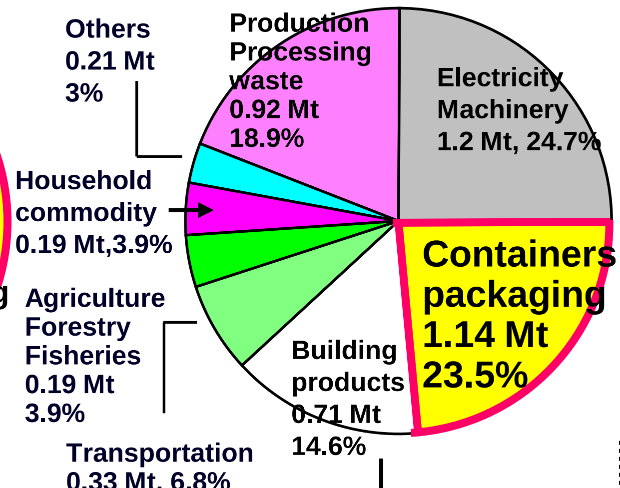
PLA/10%MFC Injection Molded Products

Background & Motivation
– CO_2 emission from wastes of packaging materials by incineration –

General waste in Japan
5.2 Mt / y



Industrial waste in Japan
4.9 Mt / y

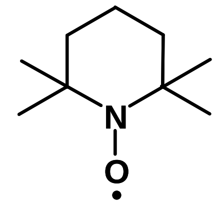


Incineration disposal: 53% (5.4 Mt / y)

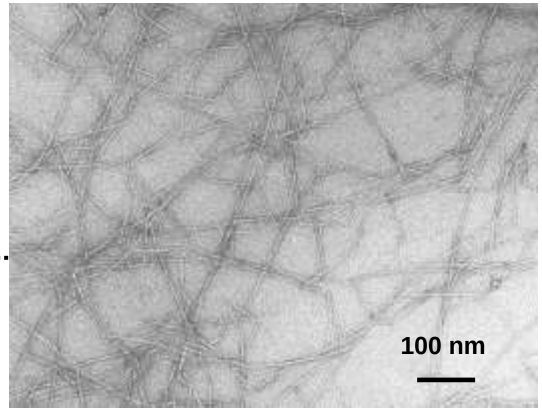
CO_2 emission: 6.7 Mt / year

New environmentally compatible packaging materials are needed.

TEMPO



Wood cellulose



TEMPO-oxidized cellulose nanofibers having extremely high oxygen barrier properties

Matching

Nippon Paper has developed a lab production system of 0.5 kg-scale TEMPO-oxidized pulp in one batch process with TEMPO recycling system.

CONFIDENTIAL
Daicel Chemical Industries, LTD.

『ナノセリッシュ』のご紹介

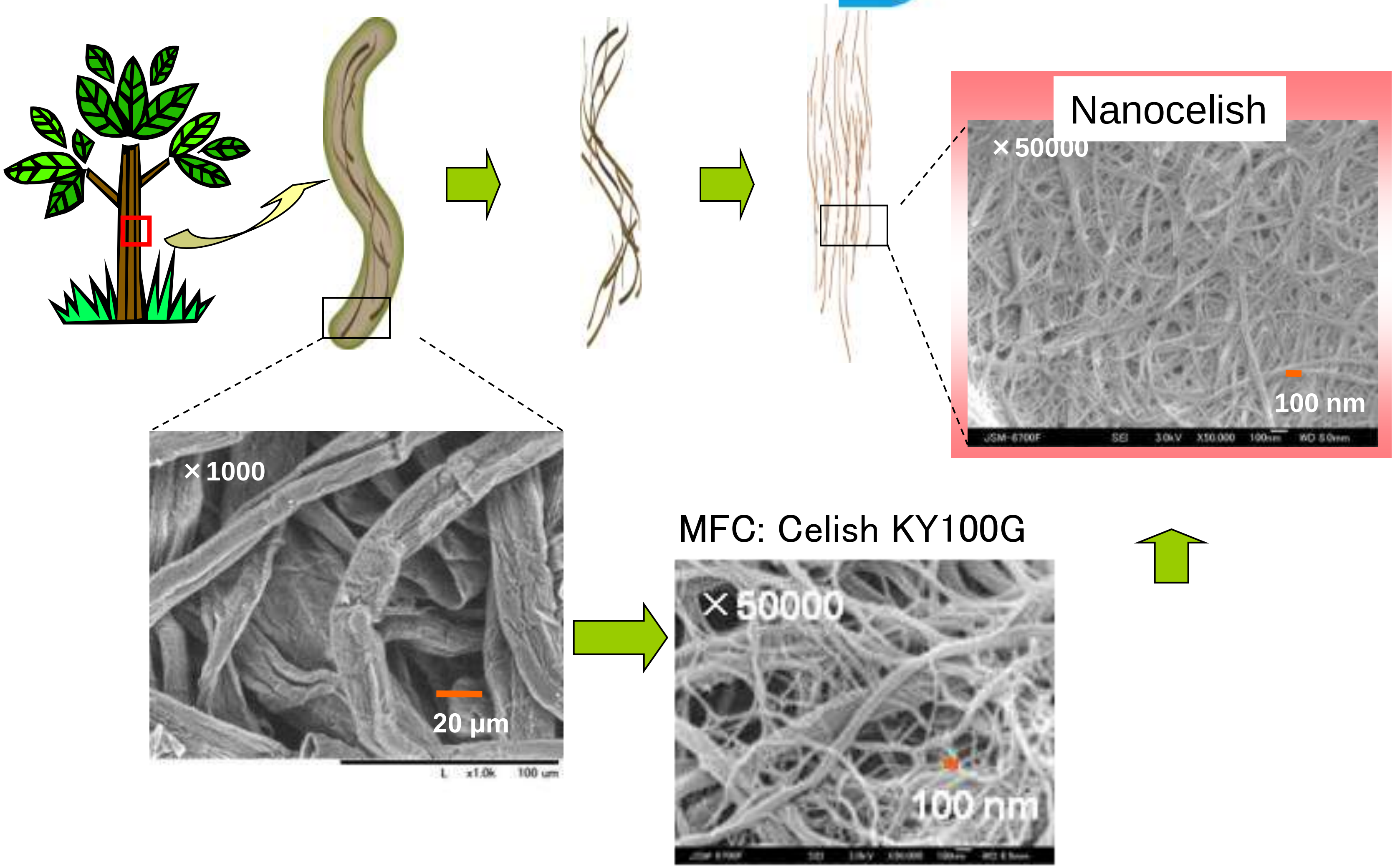
DAICEL CHEMICAL INDUSTRIES, LTD.

現在、弊社研究所の動き[illegible]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。

Innovation for Tomorrow
ダイセル化学工業株式会社

Cellulose nanofibers: Nanocelish

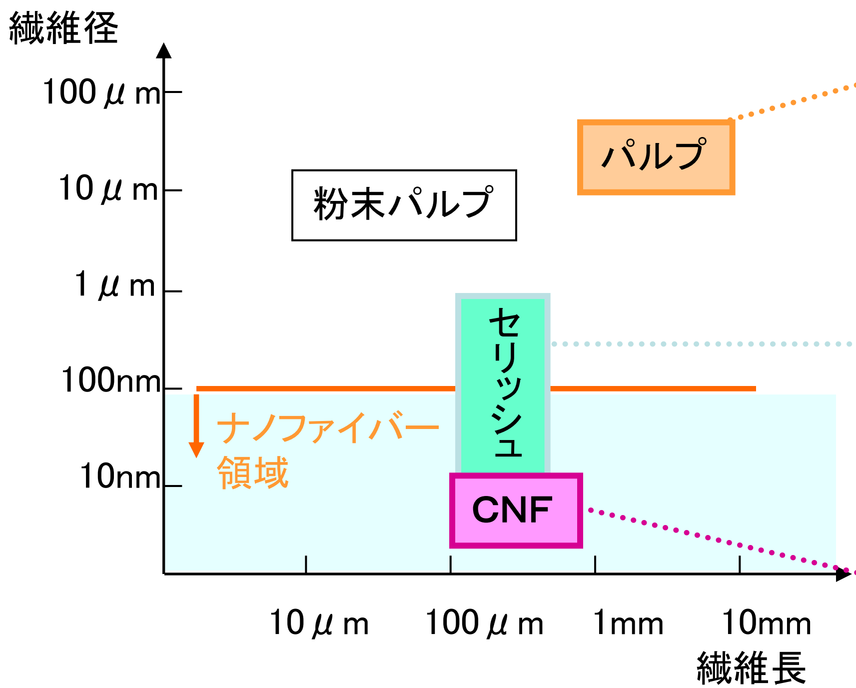
DAICEL CHEMICAL INDUSTRIES, LTD.

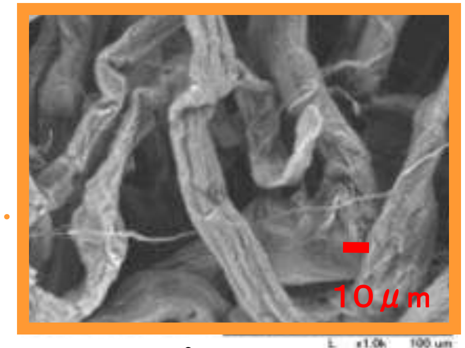


Based on the technology developed during the production of microfibrillated cellulose (MFC), we newly developed "Nanocelish"

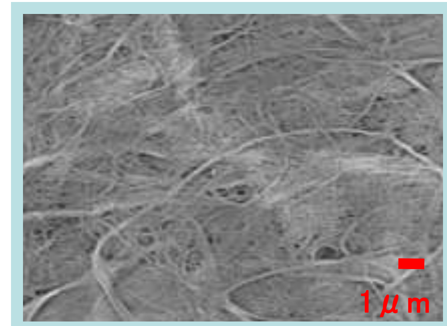
CNF：繊維径**4nm ~ 100nm**，アスペクト比＞**100**

目標アスペクト比（L/D）=1000以上　　Ex) L：100μm、D：100nm

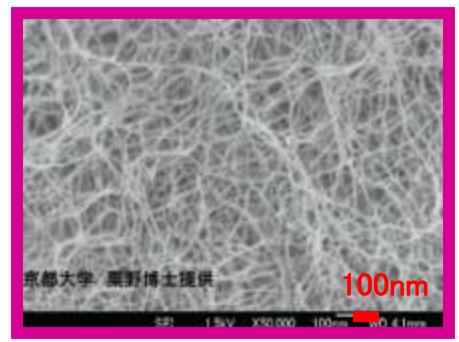




原料パルプの繊維：数10μ



セリッシュKY−100G：～1μの繊維の混合物

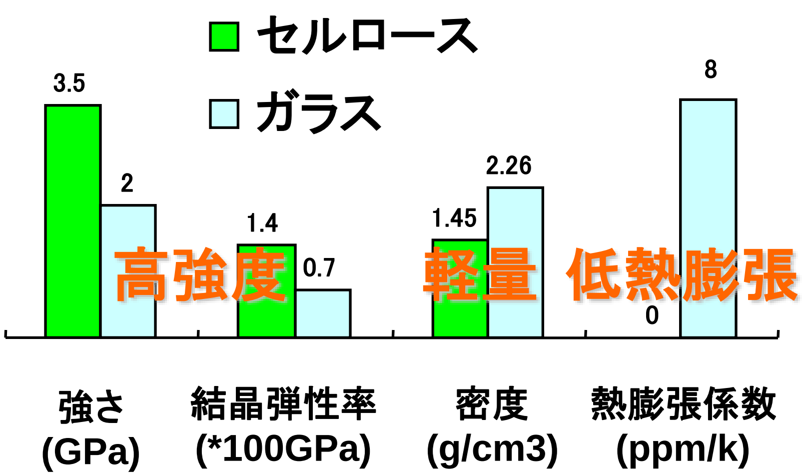


セルロースナノファイバー

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



- 環境にやさしい材料
  - -CO_2削減

＋

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

『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。

まとめとご提案

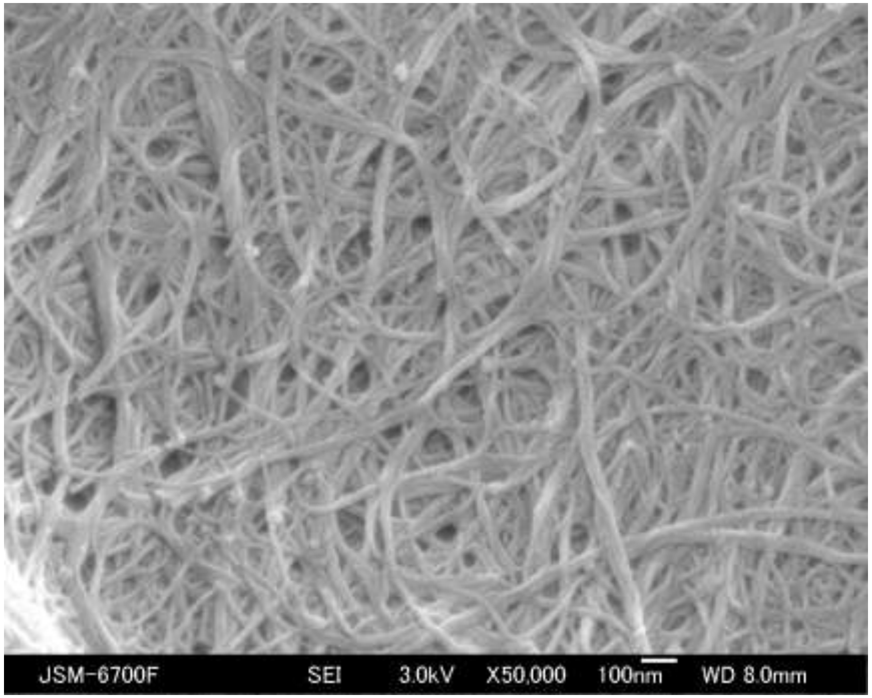
- 『ナノセリッシュ』は機械特性と光学特性に優れる高機能発現素材であり、新たな高機能材の創出に大きく寄与する可能性を秘めています。

- 『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。

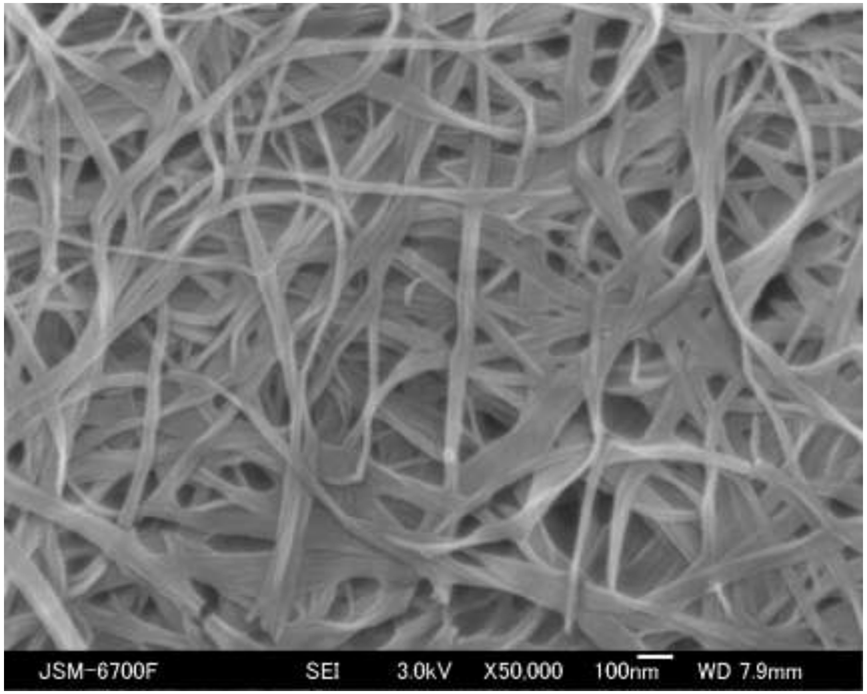
- ダイセル化学グループはセリッシュの製造・販売実績を持つだけでなく、セルロースの取り扱い技術はもとより豊富な樹脂群とそれらを加工する技術も保有しています。

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。

補足資料(写真)

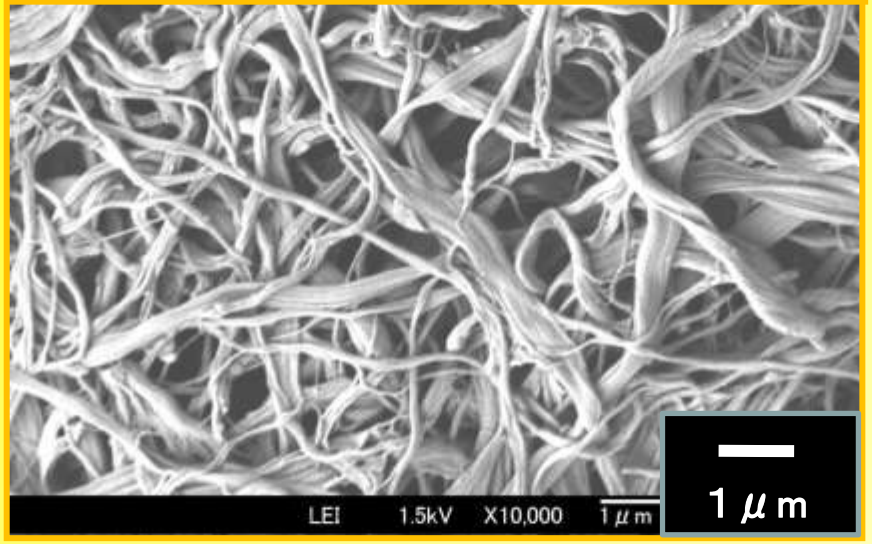


ナノセリッシュ

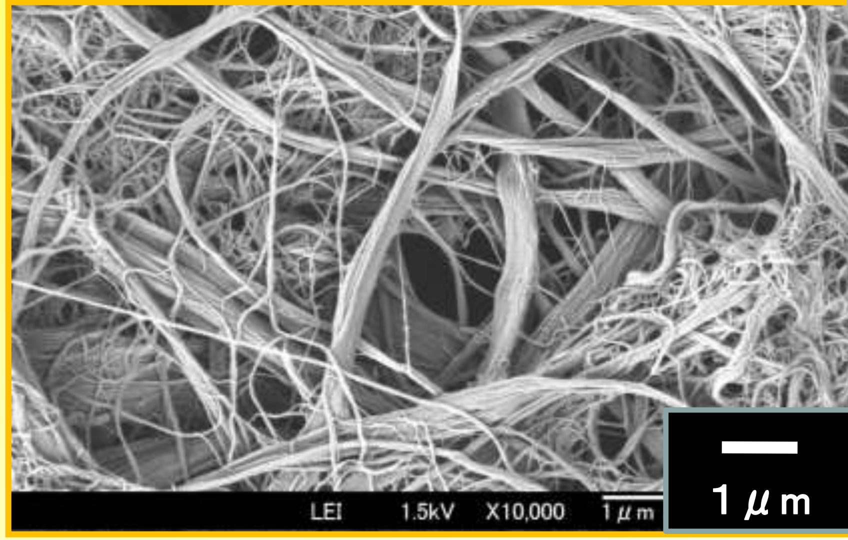


ナタデココ

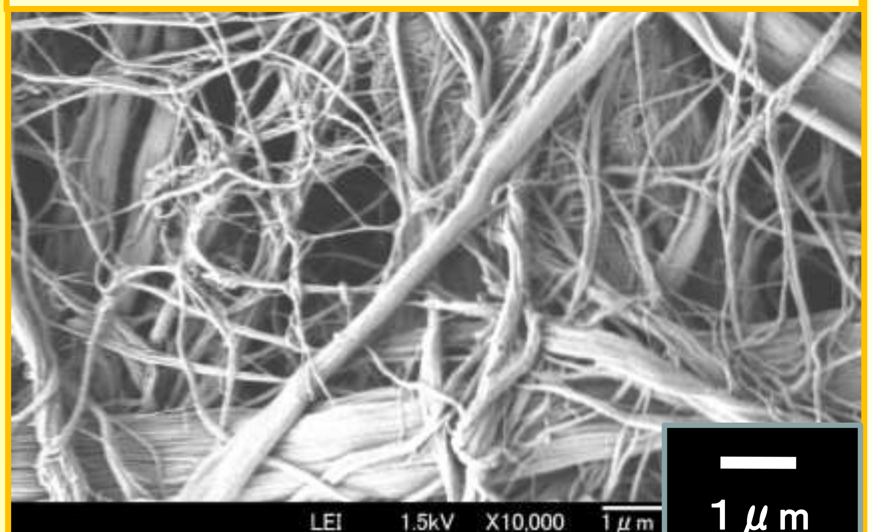
Twin Screw Extruder, 15mm diameter
（Productivity rate：56g/hr）



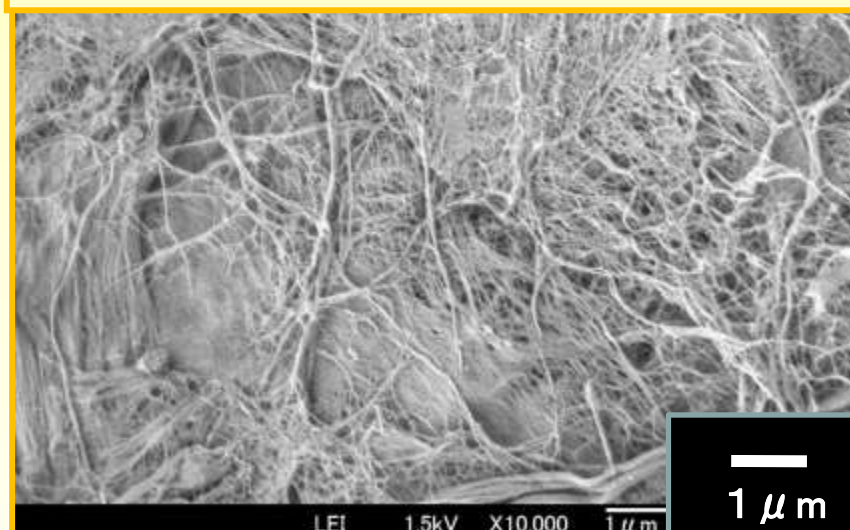
High pressure homogenizer, 14 passes



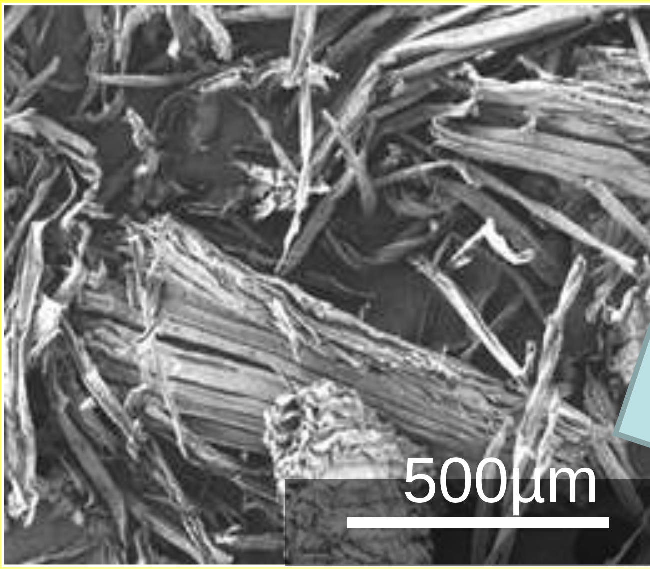
High shear speed, Extruder,15mm
（Productivity rate：600g/hr)



+ Cationized pulp, Extruder, 15mm
（Productivity rate：600gr/hr)

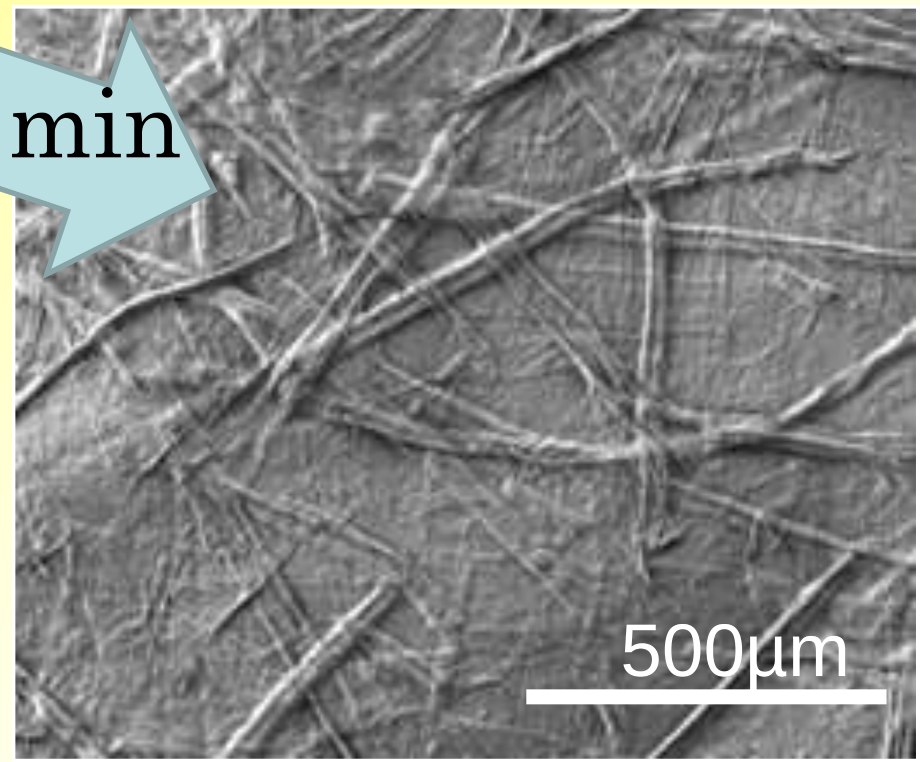


Agitation for 1 min by high speed blender



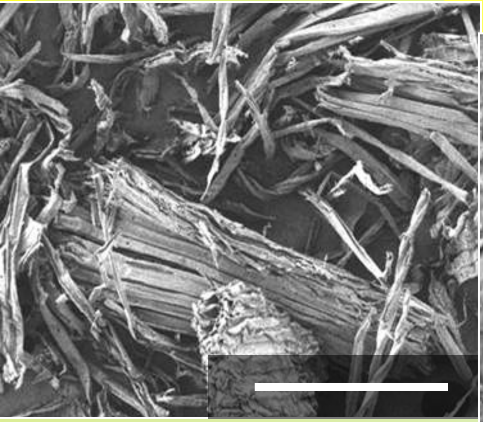
Wood Pulp

1 min

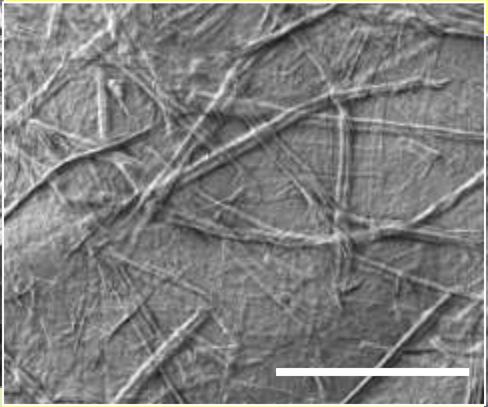


Uetani and Yano, 2008

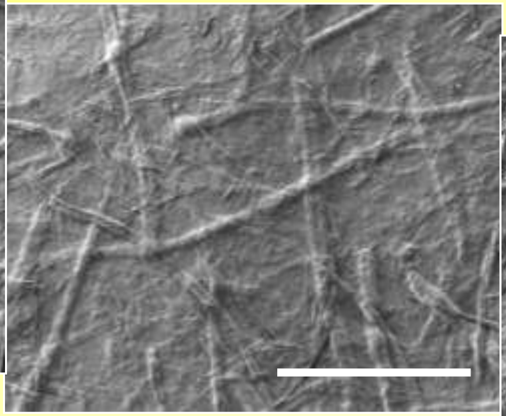
Nanofibrillation of Pulp by High Speed Agitation



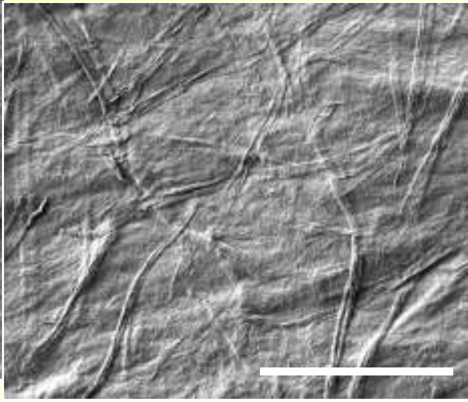
Pulp



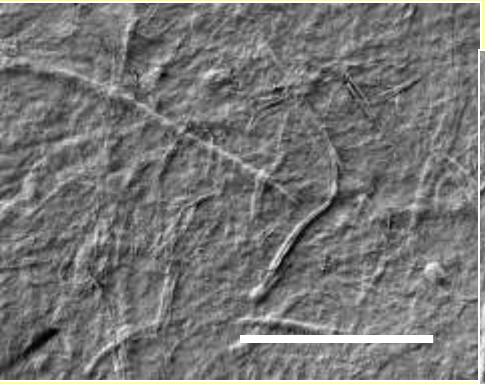
1 min



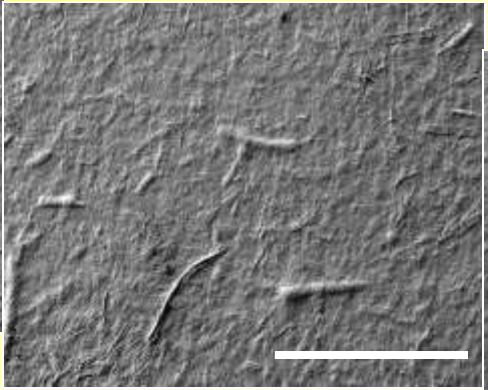
3 min



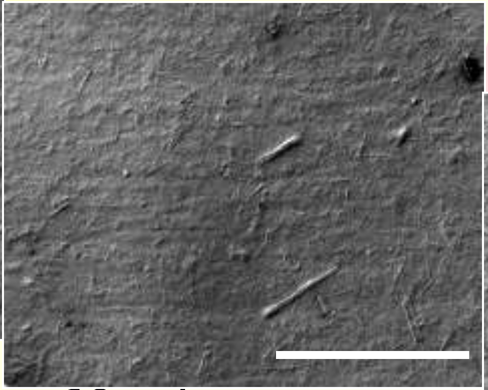
5 min



10 min

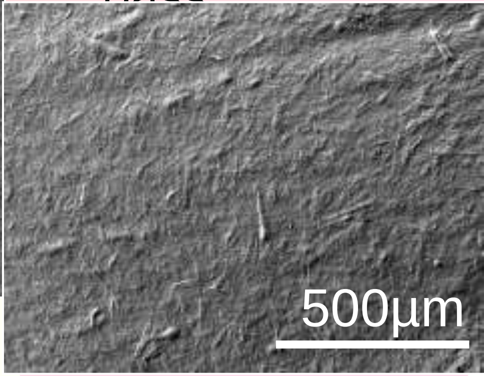


30 min



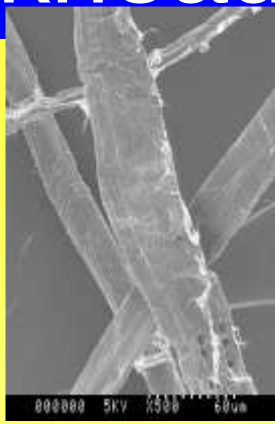
60 min

Grinder,1 pass



Uetani and Yano,

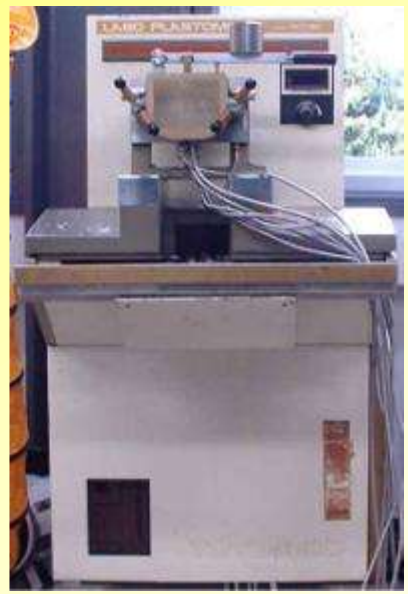
5. Nanofibrillation of pulp by kneading



1% pulp slurry

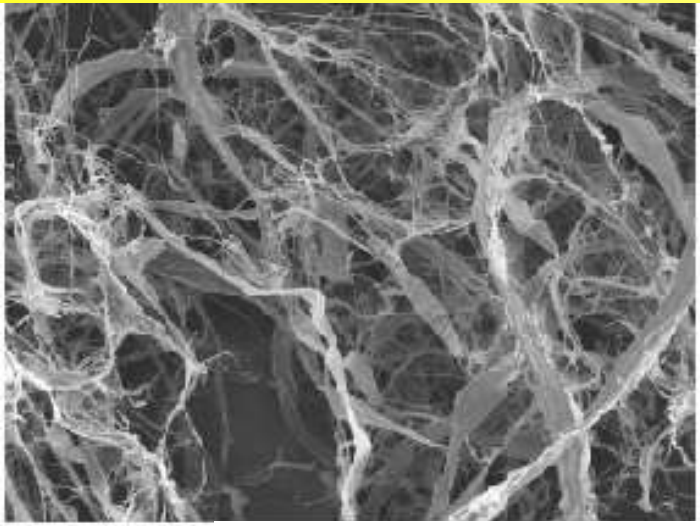
Disk Refiner

Solid content: 30%



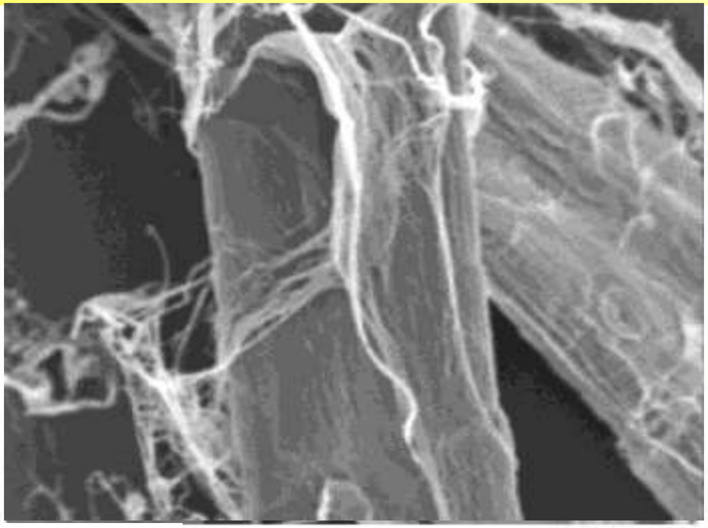
Kneading machine : 60rpm, 20min

Yano,



×200

Surface fibrillation by refiner



×2000

After kneading

Yano, 2003