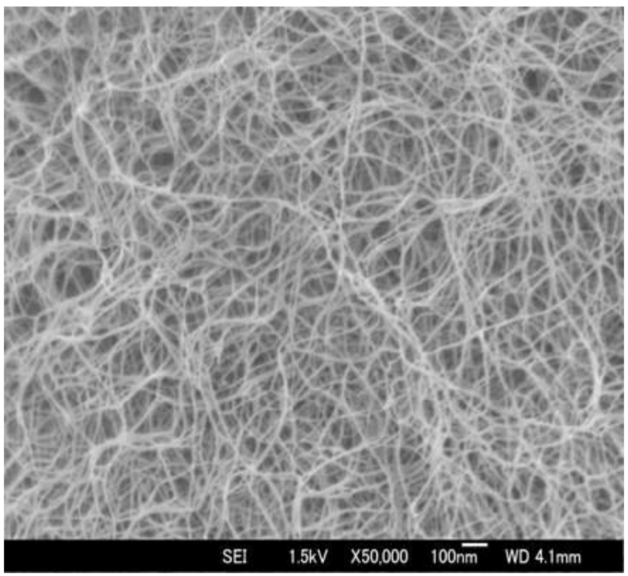
Potential of Cellulose Nanofiber-based Materials

Hiroyuki Yano
Research Institute for Sustainable Humanosphere
Kyoto University



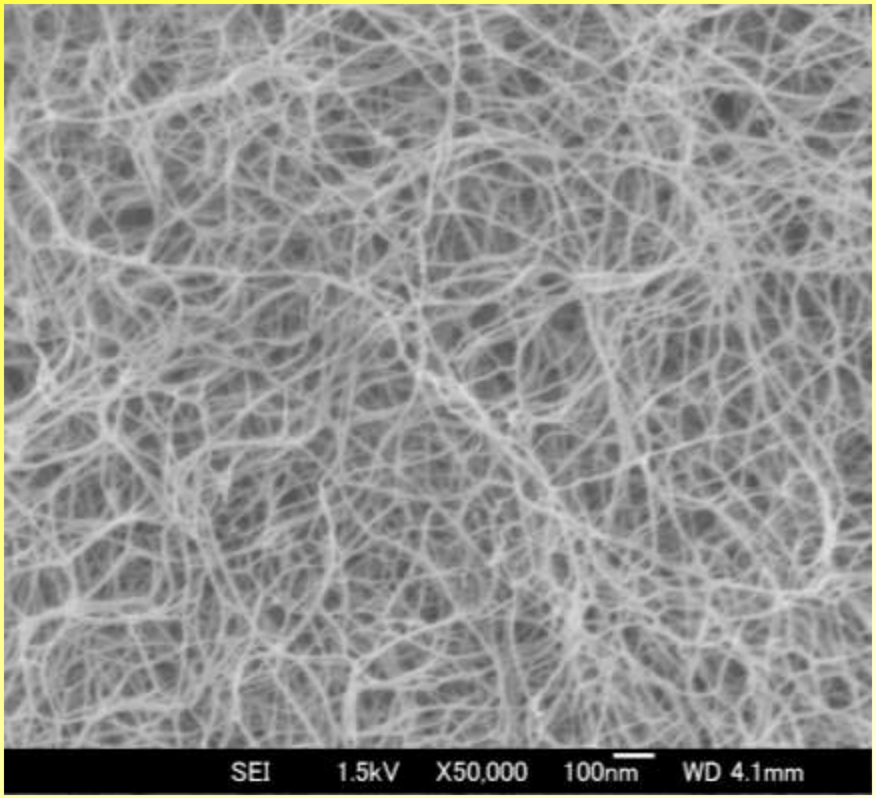
Green- nanomaterials for Sustainable Society

Plant Biomass: The most abundant organic resources made of water and CO_2 by solar energy

Plant Biomass: $1.8x10^{12}$ton   Crude oil: $0.15x10^{12}$ton

Wood Cellulose Nanofibers

The most abundant bio-nanofibers on earth



Cellulose nanofibers or a cellulose microfibril bundle in the wood cell wall (Awano, Kyoto univ.)

1 Trillion tons:1×10^{12} tons

Cellulose Nanofibers:CNF

- Semi-crystalline extended chains

  Young's modulus:138-141GPa （-200~+200℃）

  (T. Nishino et al. J. Polym Sci., Part B, 1995, Proc.2nd Intn'l Cellulose Conf,2007)

  Tensile strength:3GPa → aramid fibers

  (Based on D.H. Page, F., El-Hosseiny J. Pulp Paper Sci. 1983)

  Thermal expansion coefficient：0.1 ppm/K → quartz glass

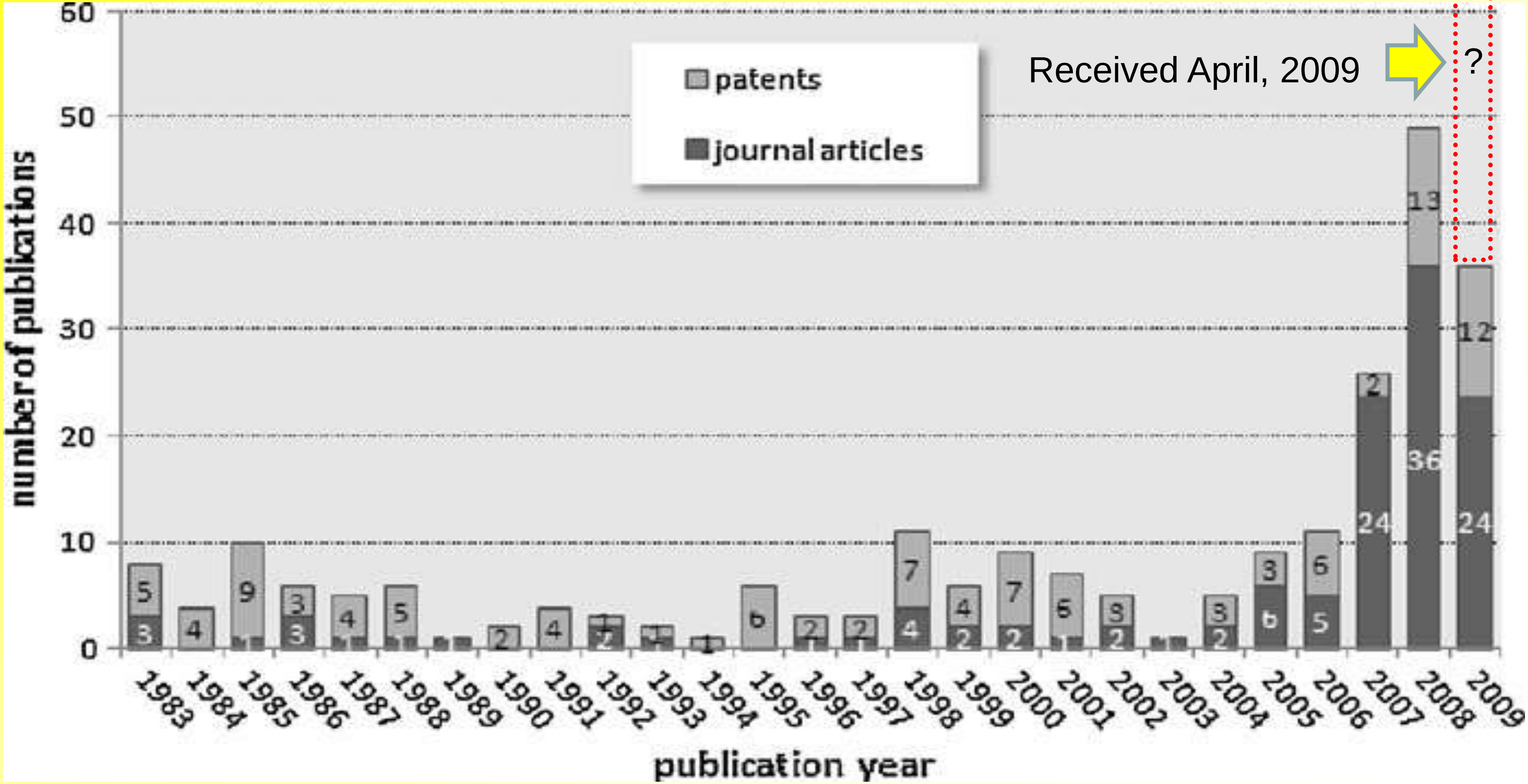
  (T. Nishino, Personal communication, 2004)

  High specific surface area

- High value-added: 0.1 € /kg wood or 0.5 € /kg pulp

  → 10-20 € /kg?

Patents and Journal articles on Nanocellulose

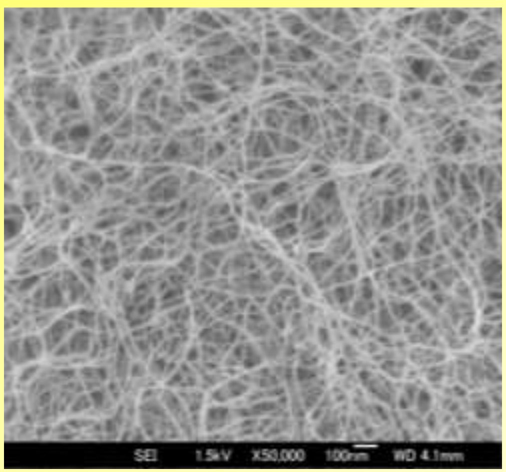


“microfibrillated cellulose”and its synonyms such as “nanofibrillar cellulose”,“cellulose nanofibers” and “cellulose nanofibrils”

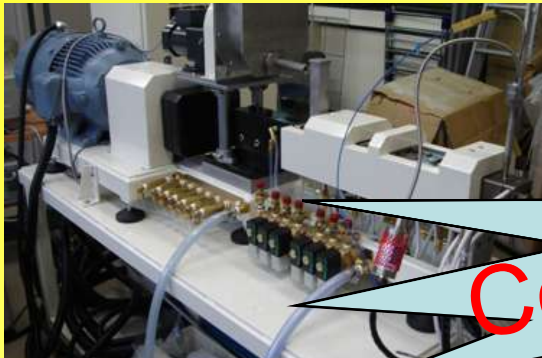
I. Siro´ and D. Plackett, Cellulose, 2010, Received April, 2009

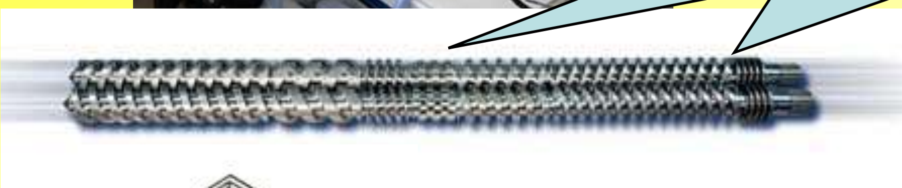
Topics

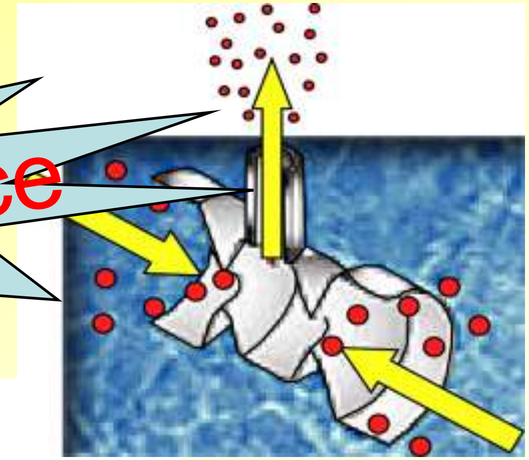
1. Extraction of cellulose nanofibers
2. Optically transparent materials
3. Structural materials



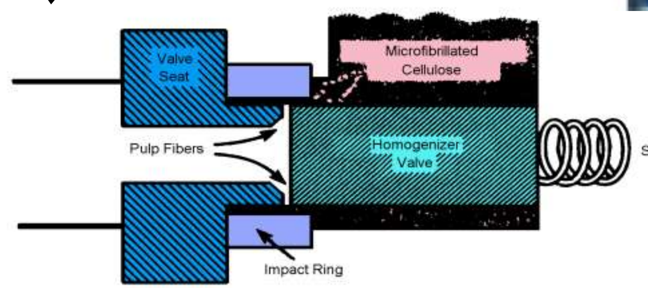
Extraction of nanofibers from wood/plant fibers

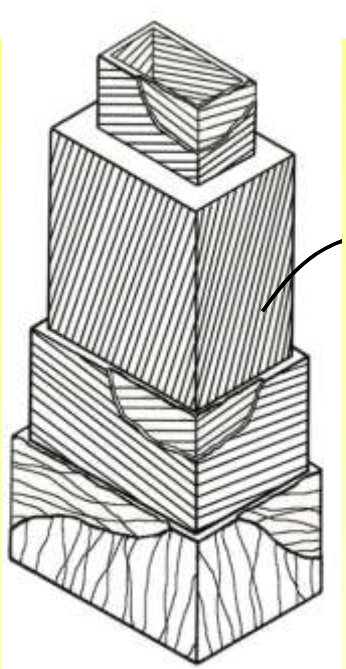






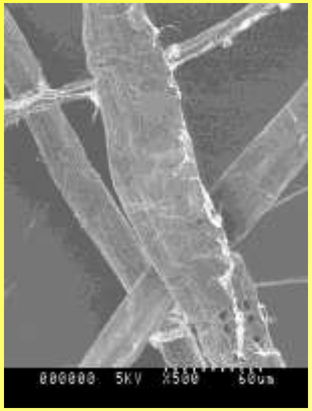
Cost and Performance





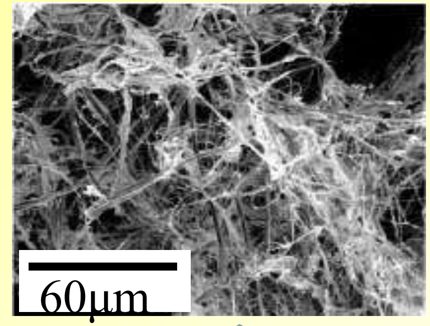
1. Fibrillation by a high-pressure homogenizer

Pulp fiber (NBKP)

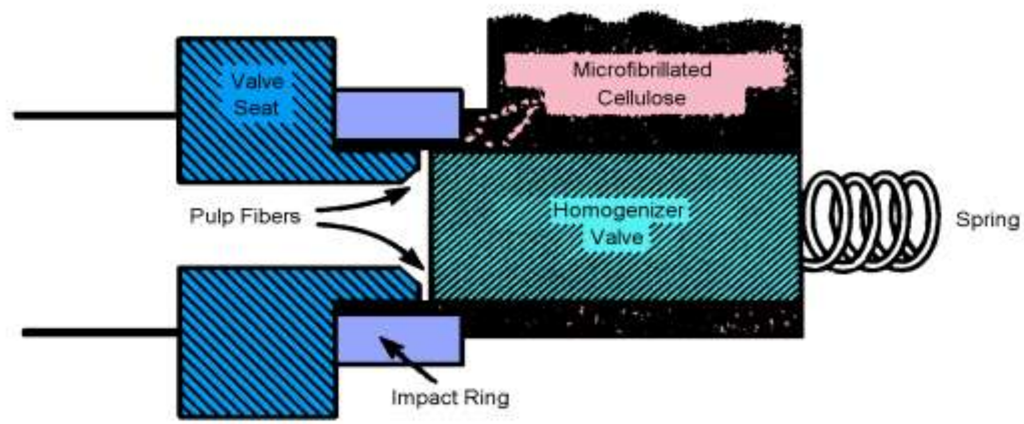


Disk Refiner

Microfibrillated cellulose (MFC)



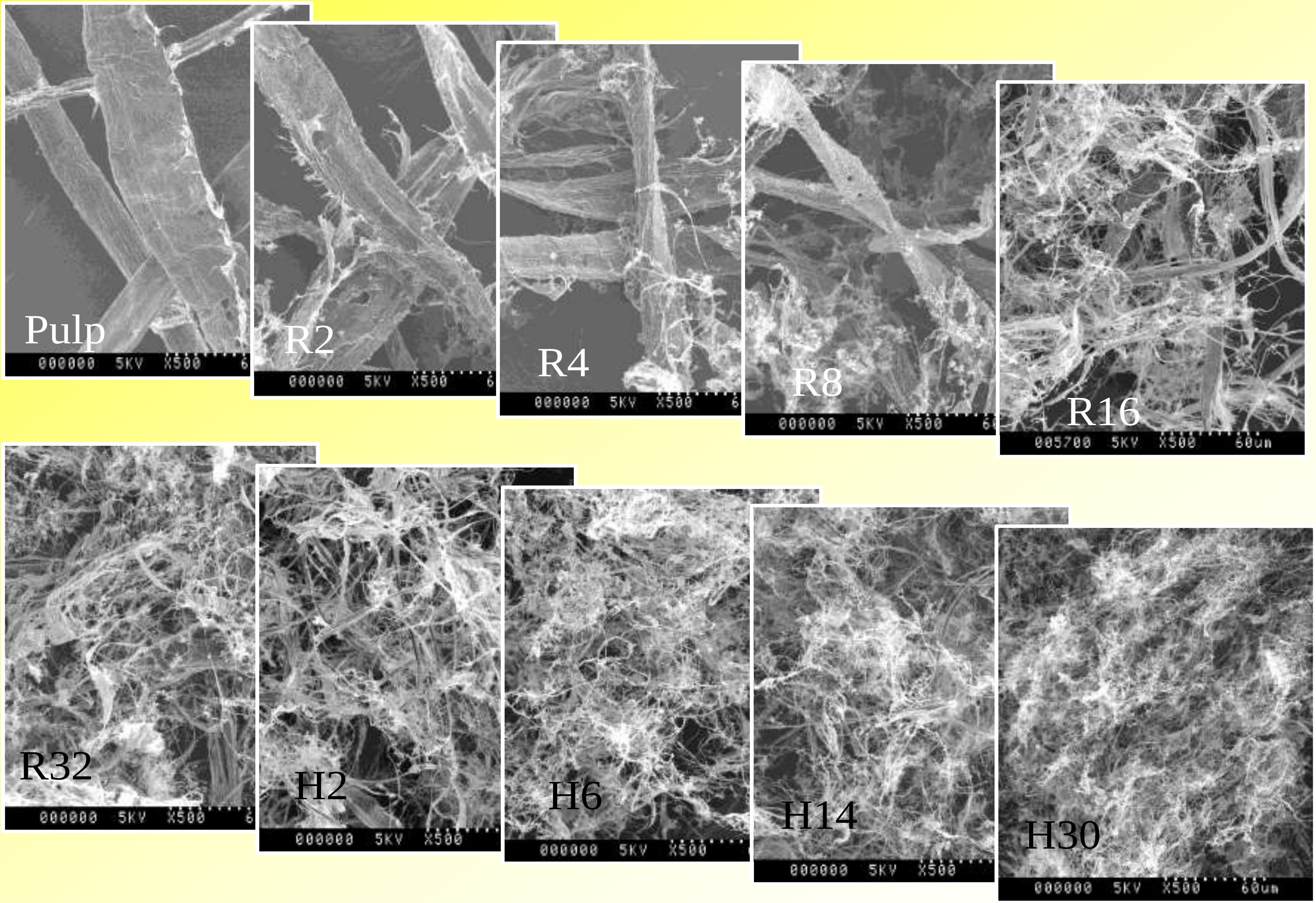
- **PRESSURE DROP**
- **SHEAR**
- **IMPACT**

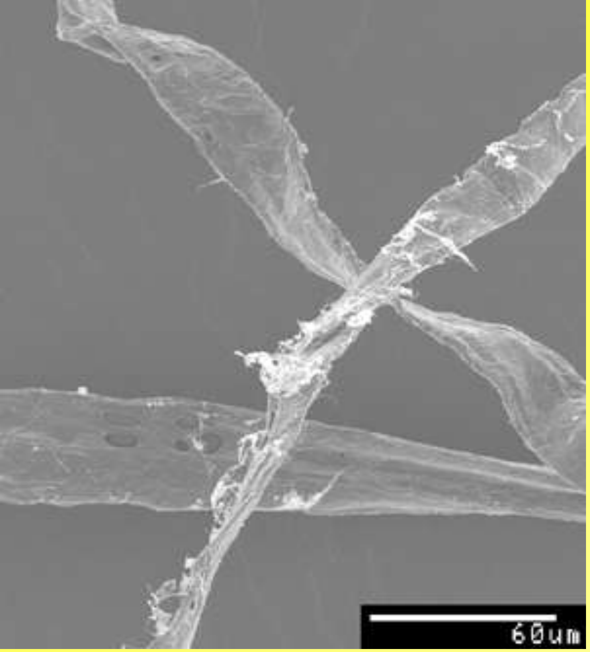


Hi-pressure homogenizer

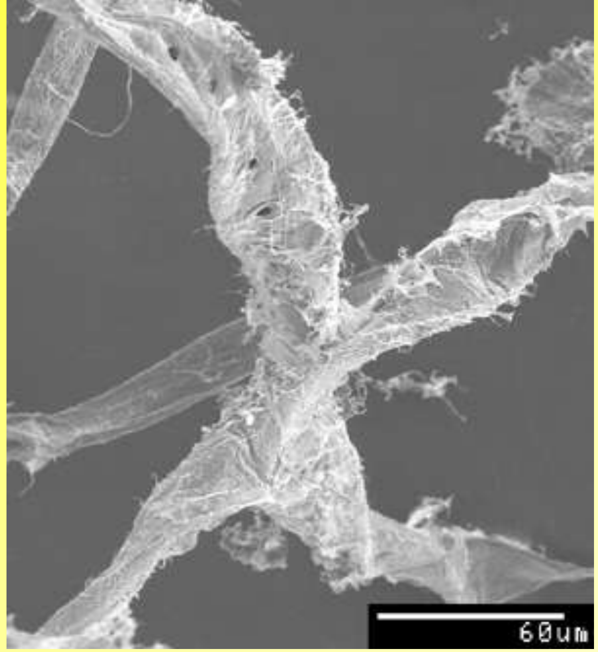
Turbak A F, Snyder F W, Sandberg K R., 1983

Nanofibrillation of NBKP

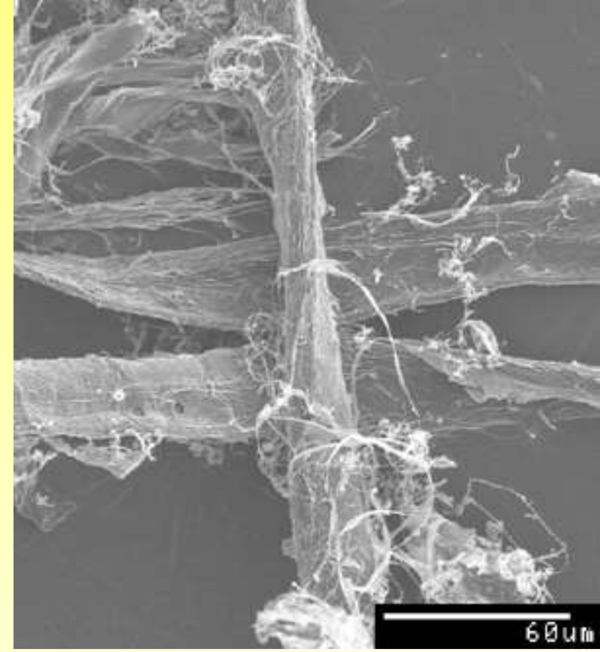




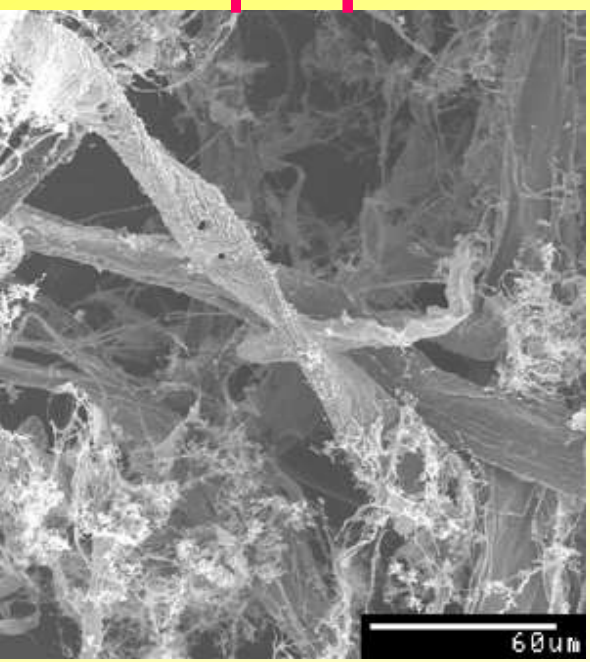
pulp



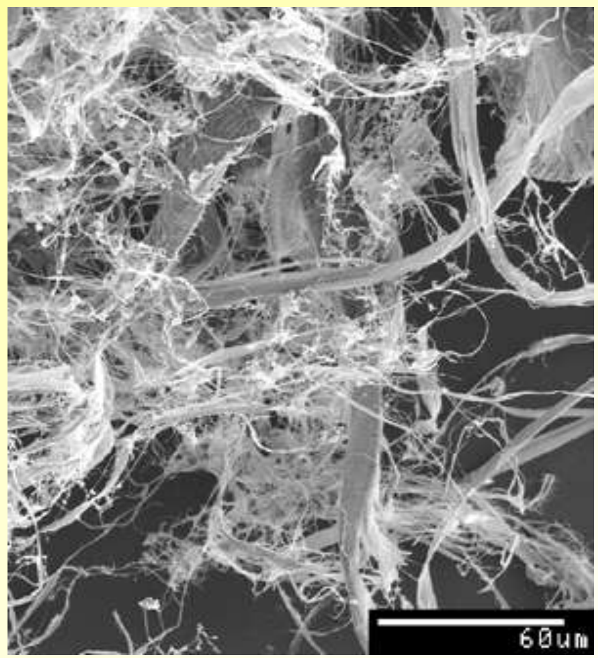
R2



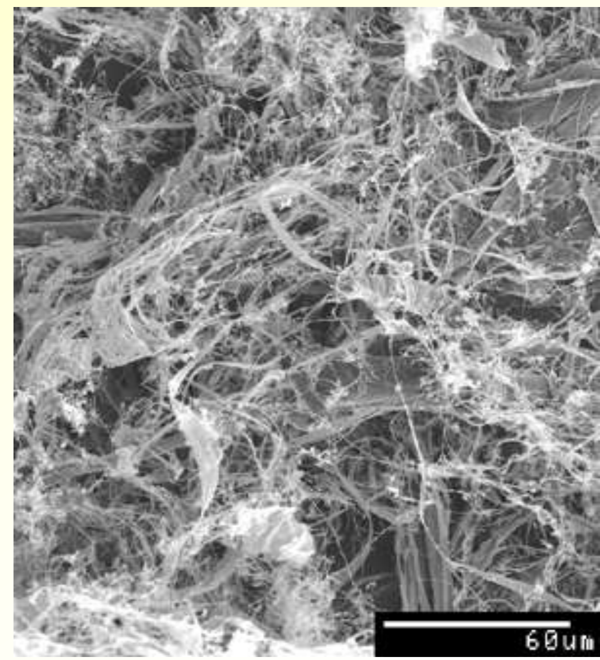
R4



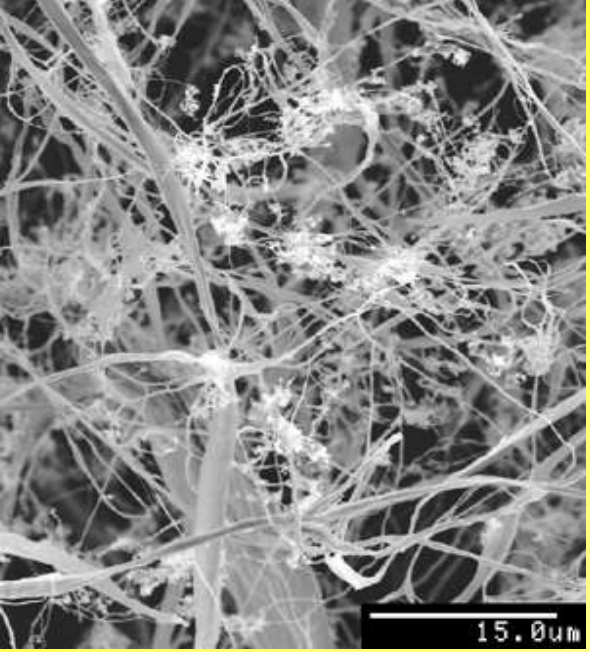
R8



R16

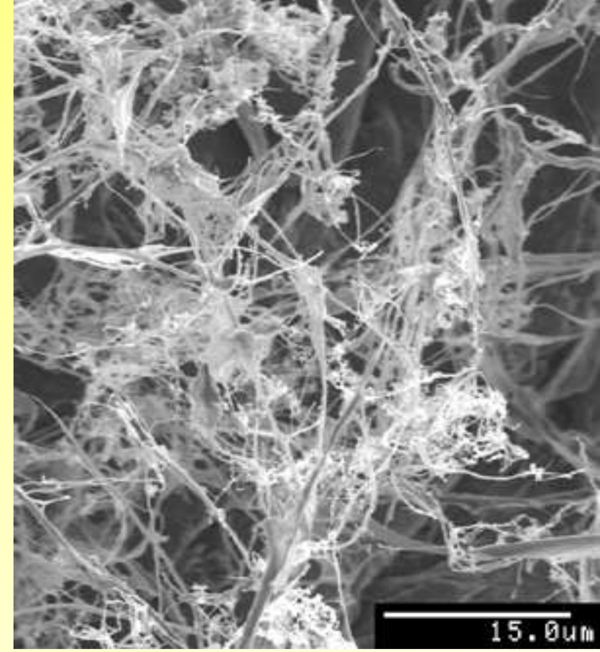


R30

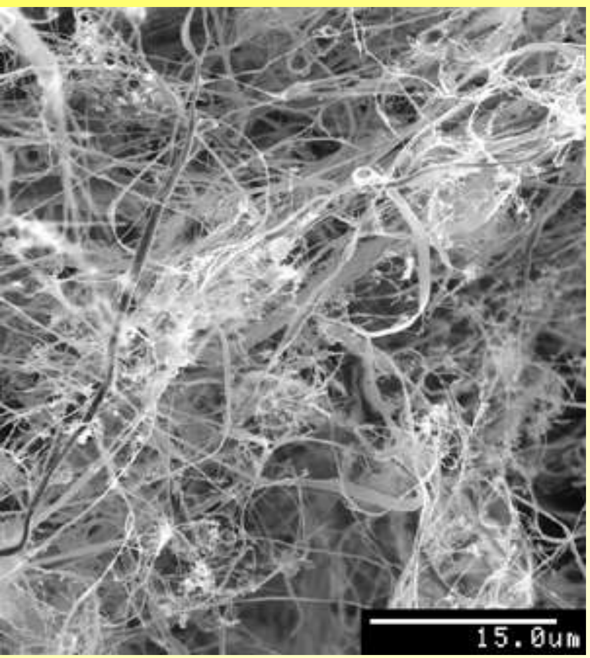


R30

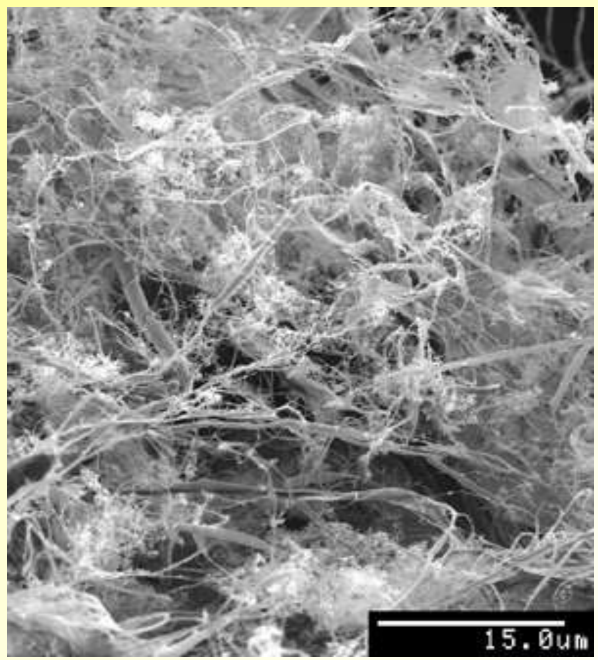
R30+H2



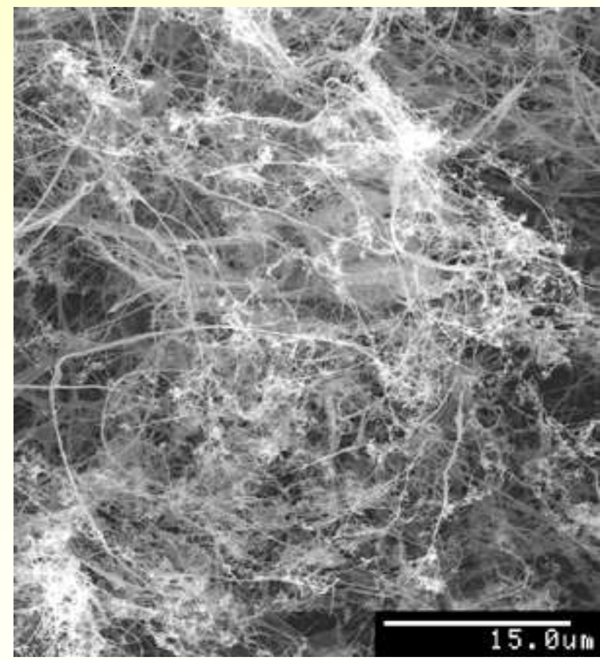
R30+H6



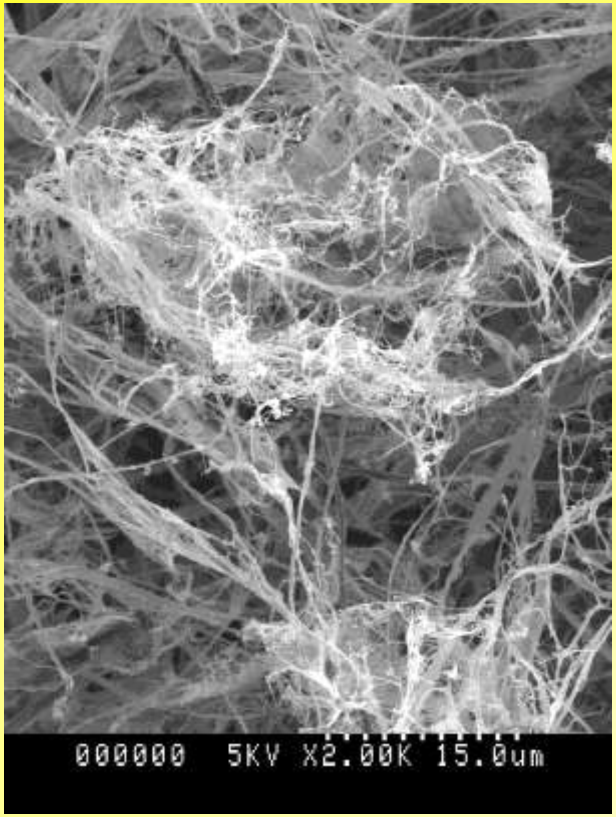
R30+H14

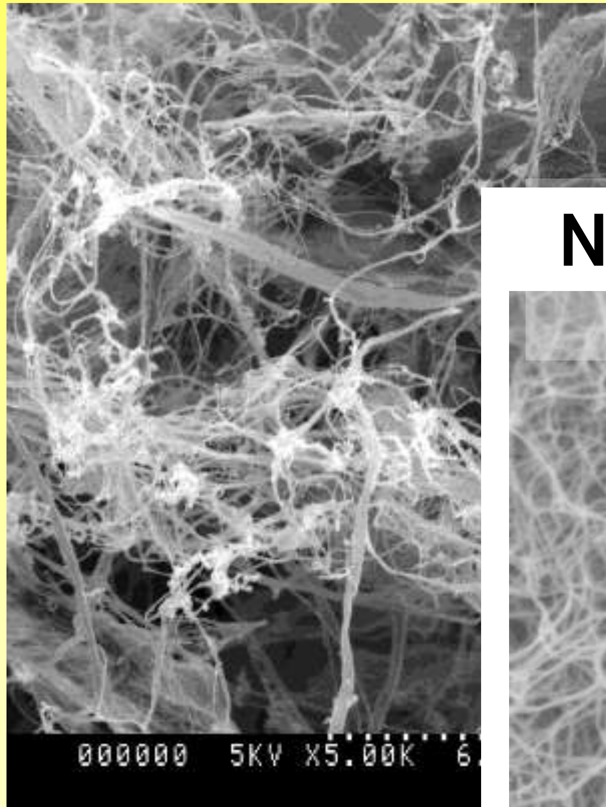


R30+H22



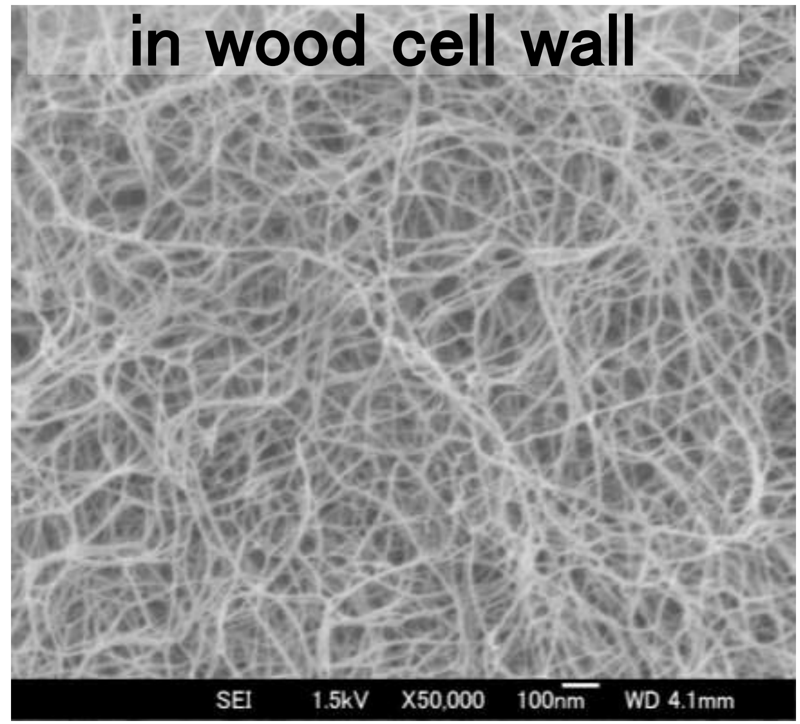
R30+H30



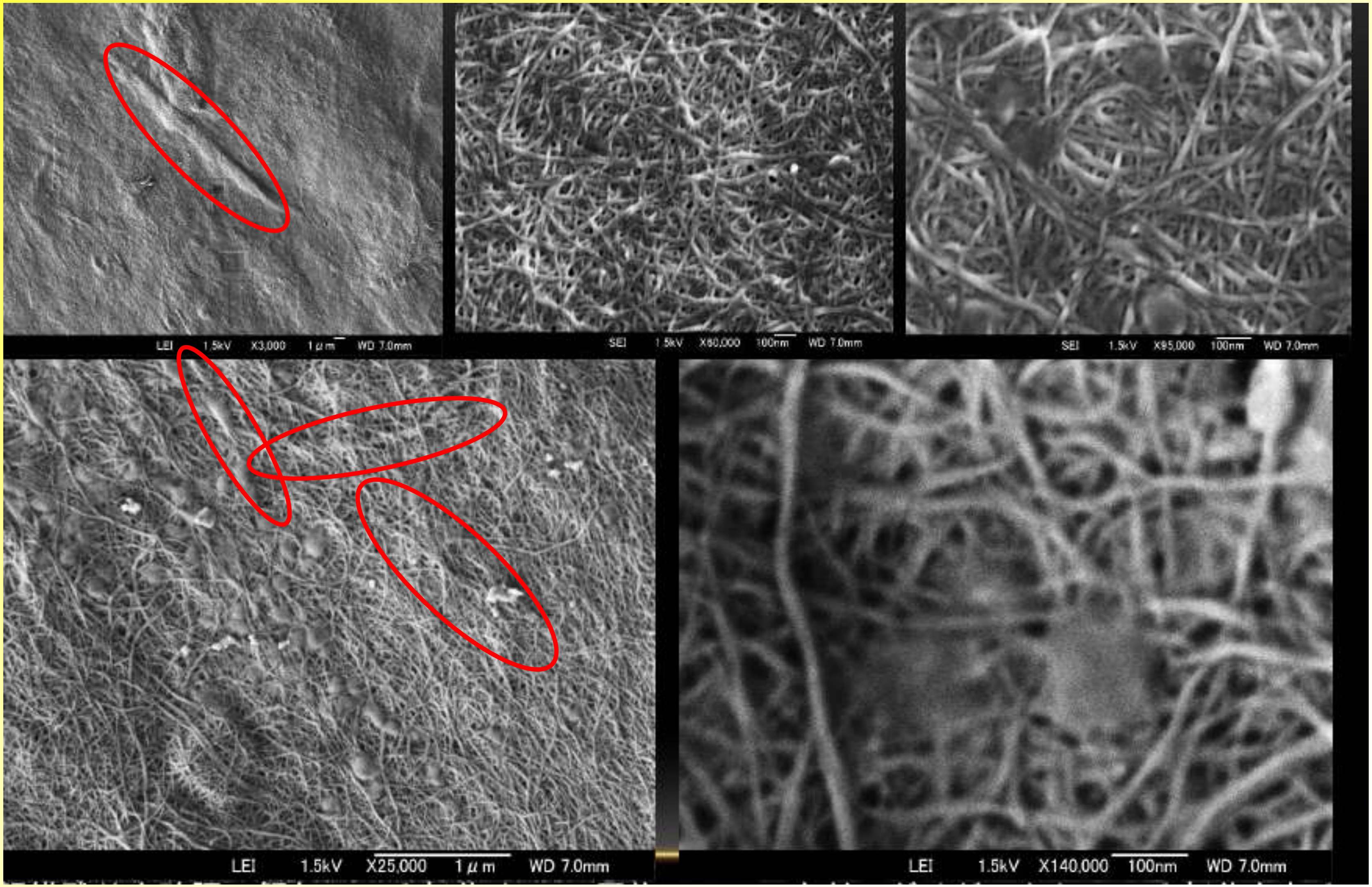


R30+H14

Nanofibers observed in wood cell wall

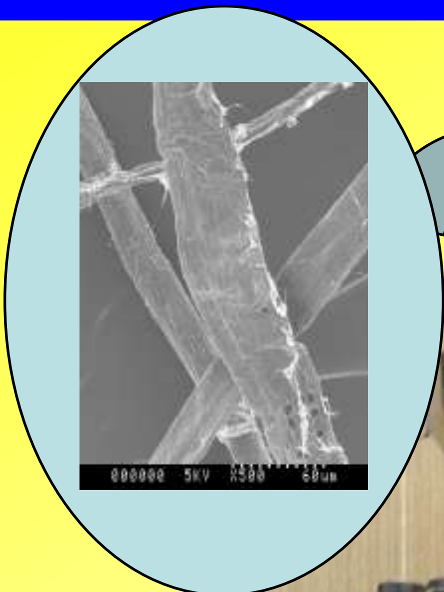


2. Fibrillation of never-dried pulp ($NaClO_2$ treated) by a high-pressure homogenizer, 10 passes

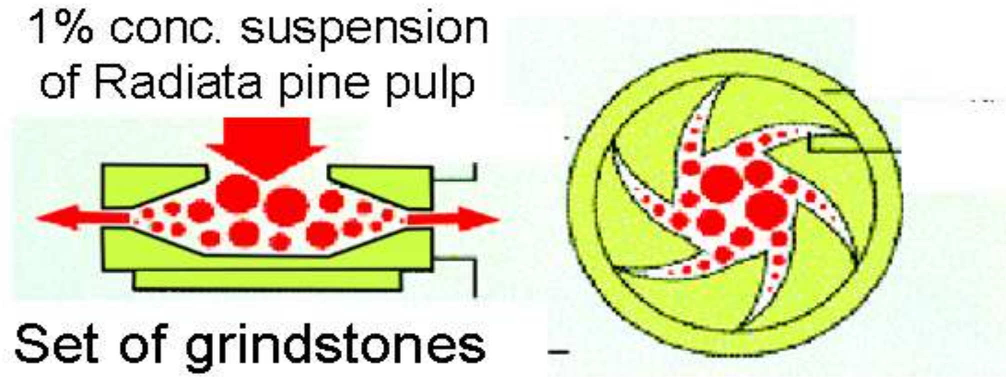


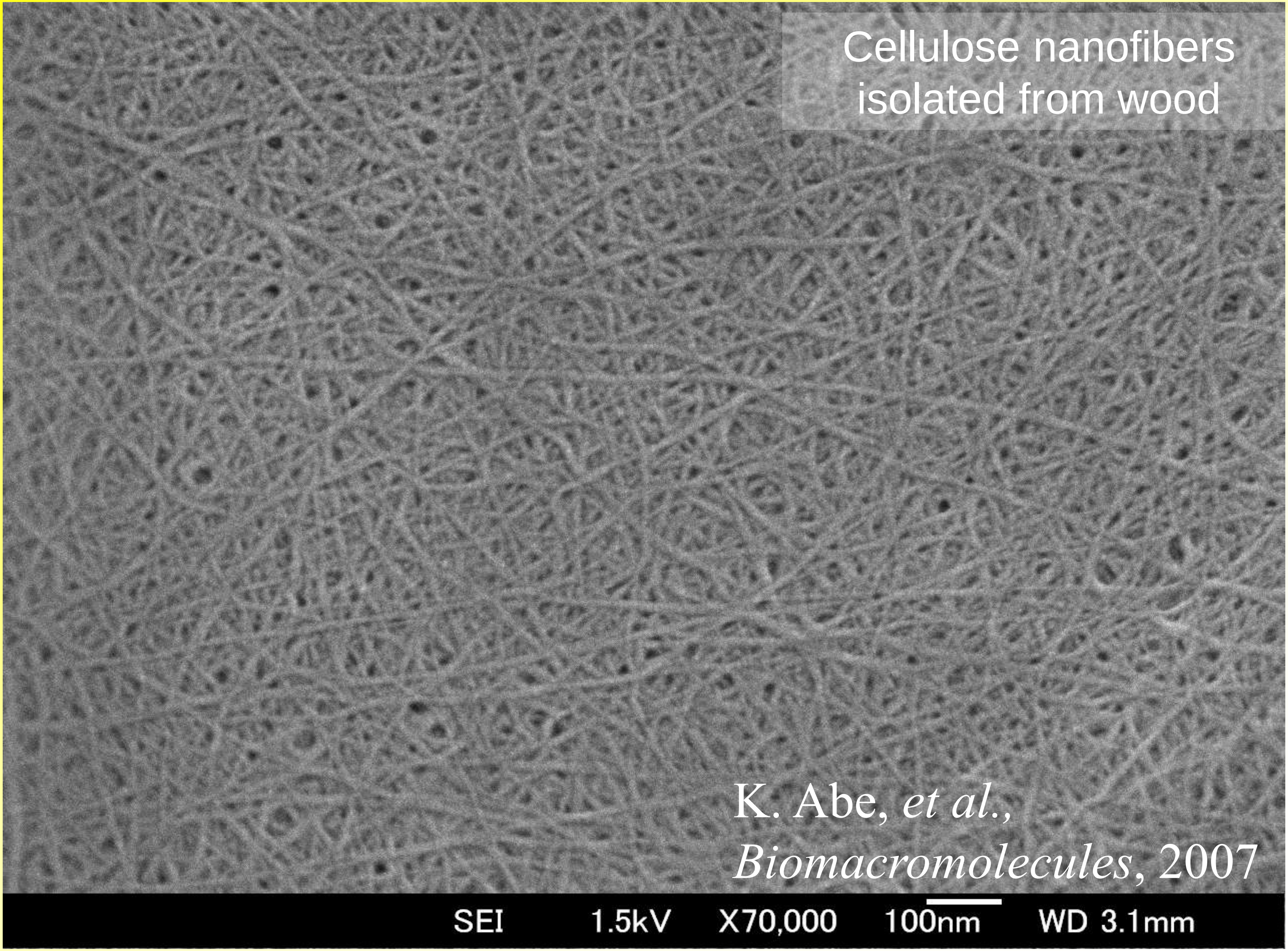
Uetani, et al., 2010

3. Fibrillation by a Grinder



Never- dried pulp





Cellulose nanofibers
isolated from wood
K. Abe, *et al.*,
Biomacromolecules, 2007
SEI
1.5kV
X70,000
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





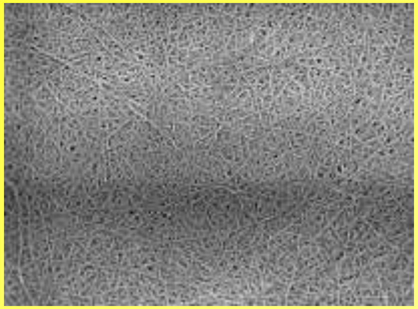



K.Abe, 2007

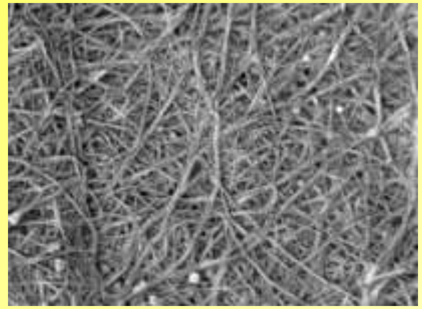
Comparison of Nanofibers

K.Abe, 2007

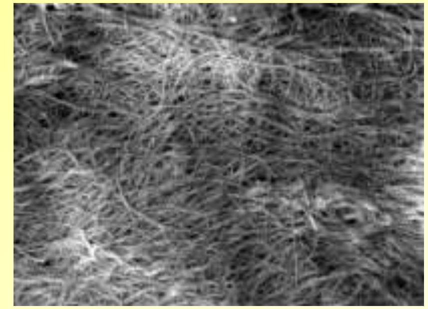
Wood



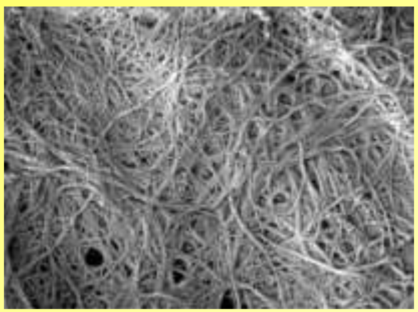
Sea weed



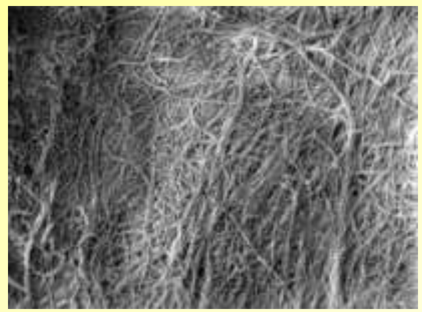
Rice straw



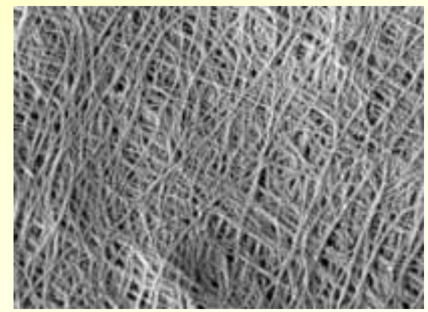
Potato tuber



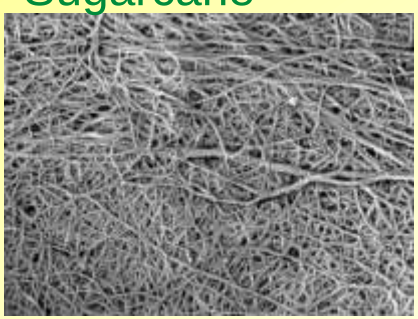
Water weed



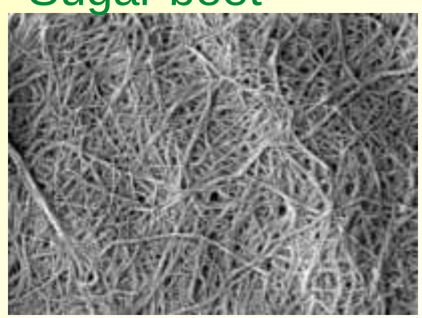
Cassava



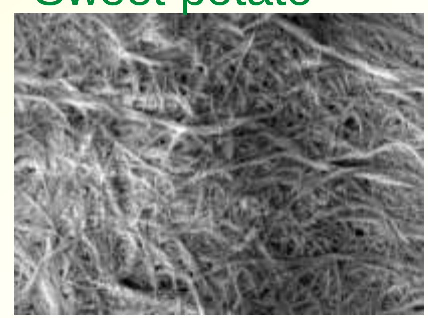
Sugarcane



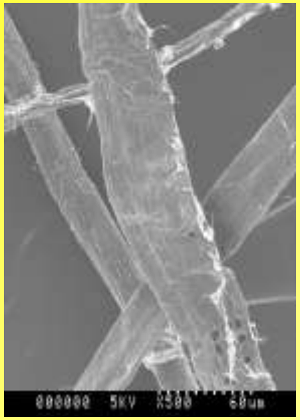
Sugar beet



Sweet potato



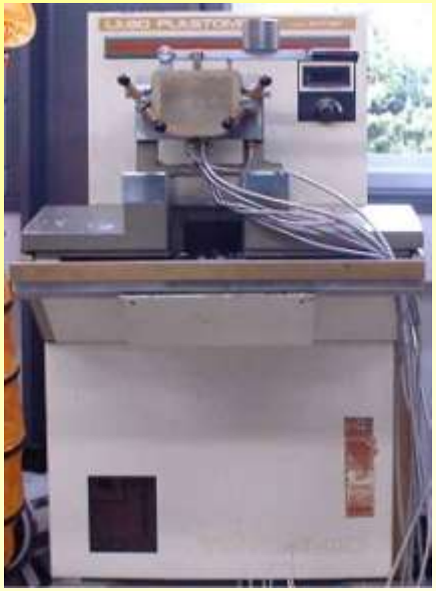
5. Nanofibrillation of pulp by kneading



1% pulp slurry

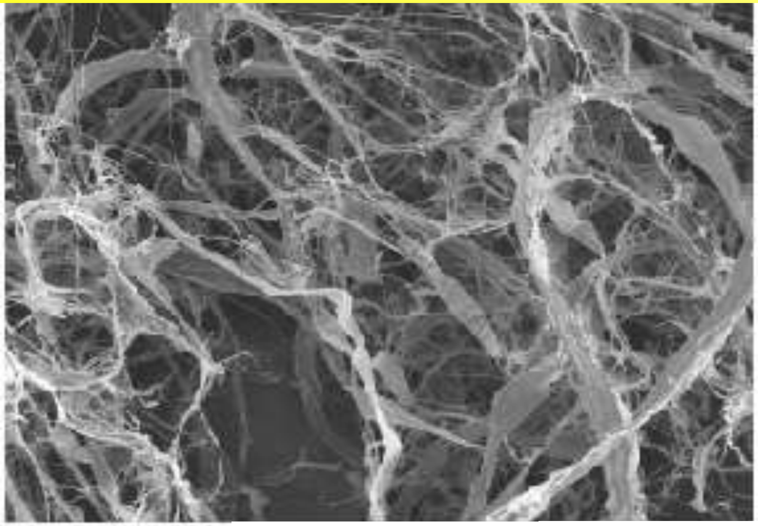
Disk Refiner

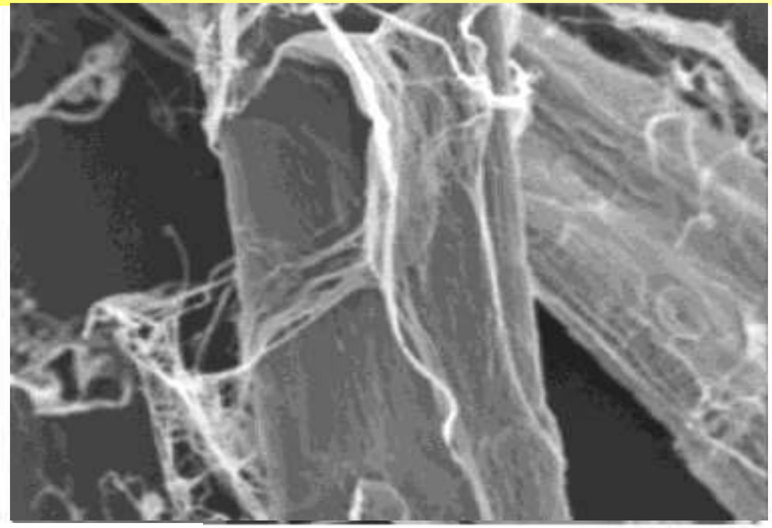
Solid content: 30%



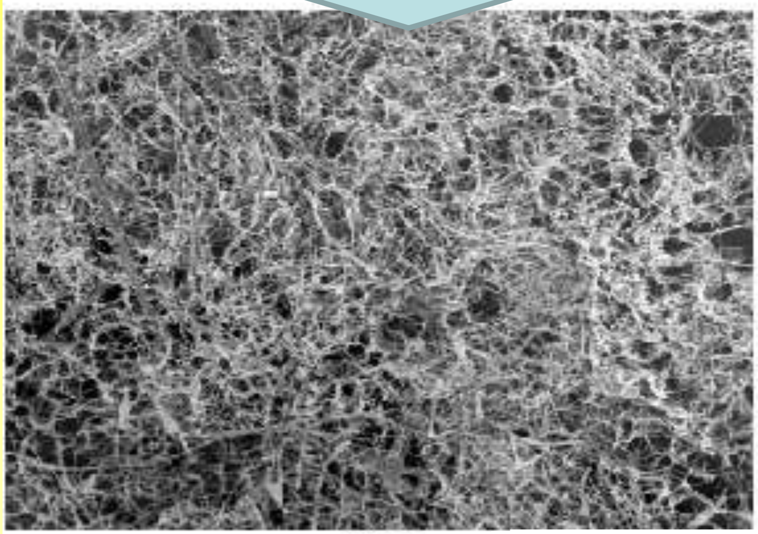
Kneading machine :
60rpm, 20min

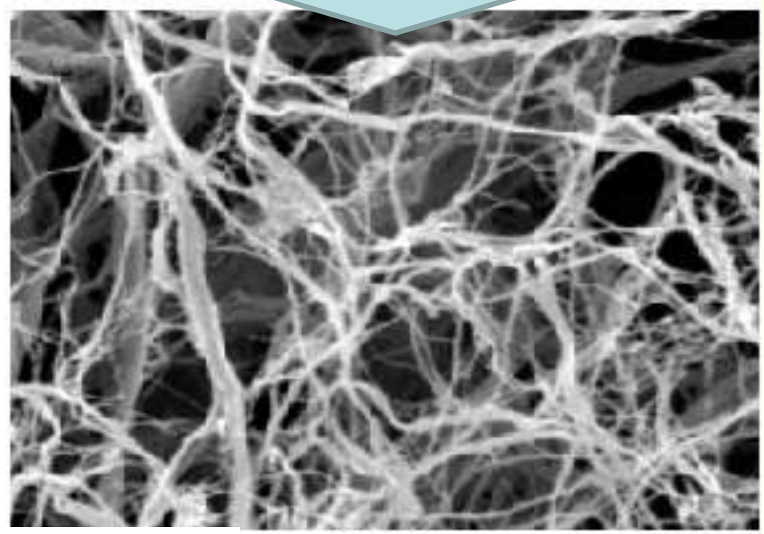
Yano, 2003





×200　リファイナー8回処理　×2000





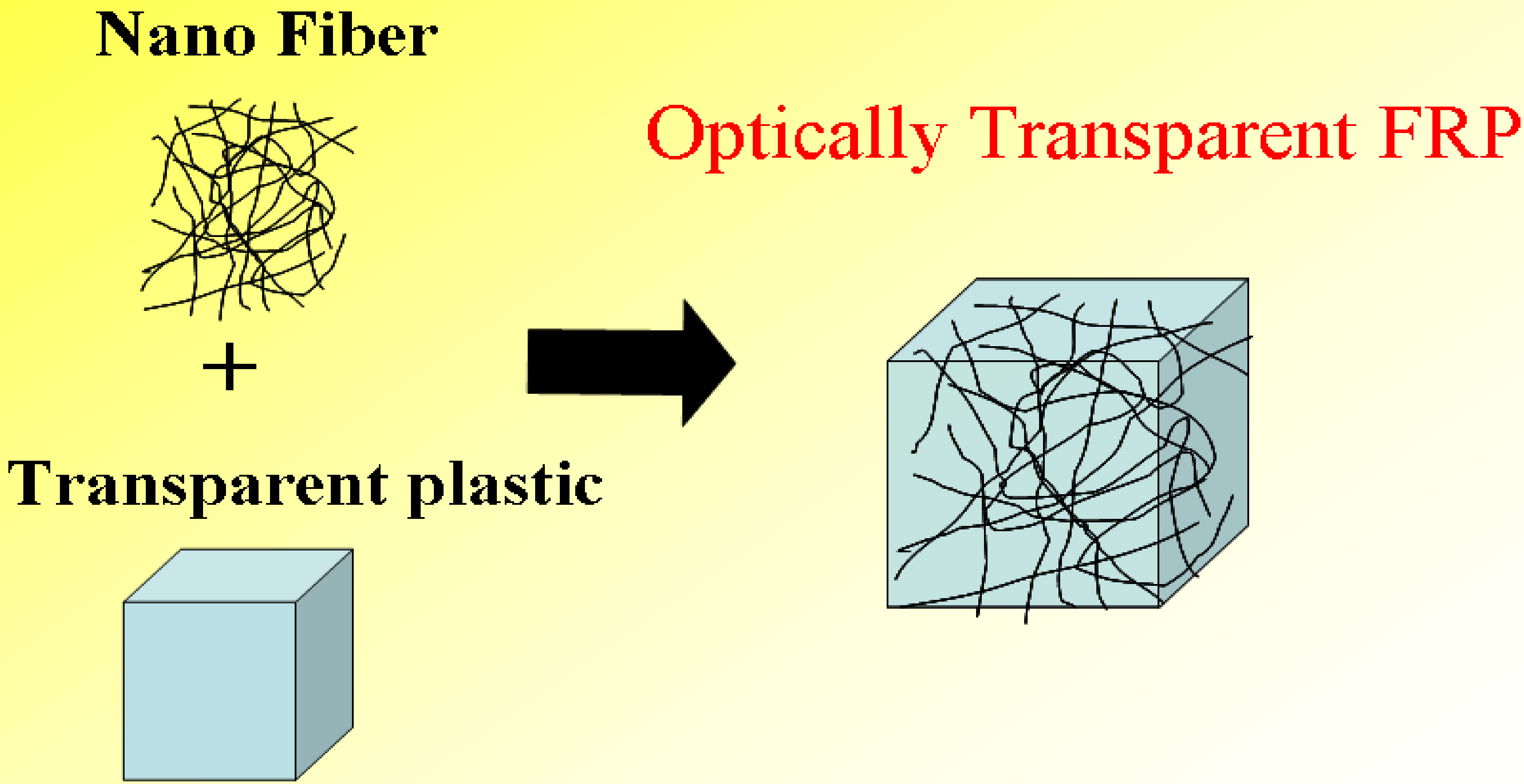
×200　After kneading　×2000

Yano, 2003

Topics

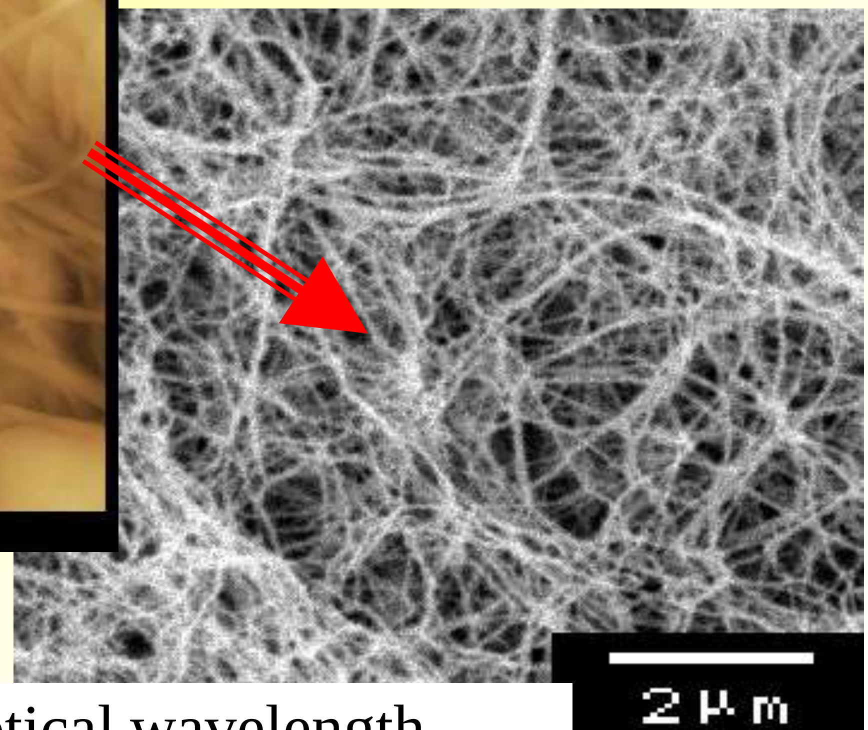
1. Extraction of cellulose nanofibers
2. <u>Optically transparent materials</u>
3. Structural materials

Mechanical Reinforcement of Transparent Plastic



A component less than one-tenth the size of the optical wavelength can eliminate scattering

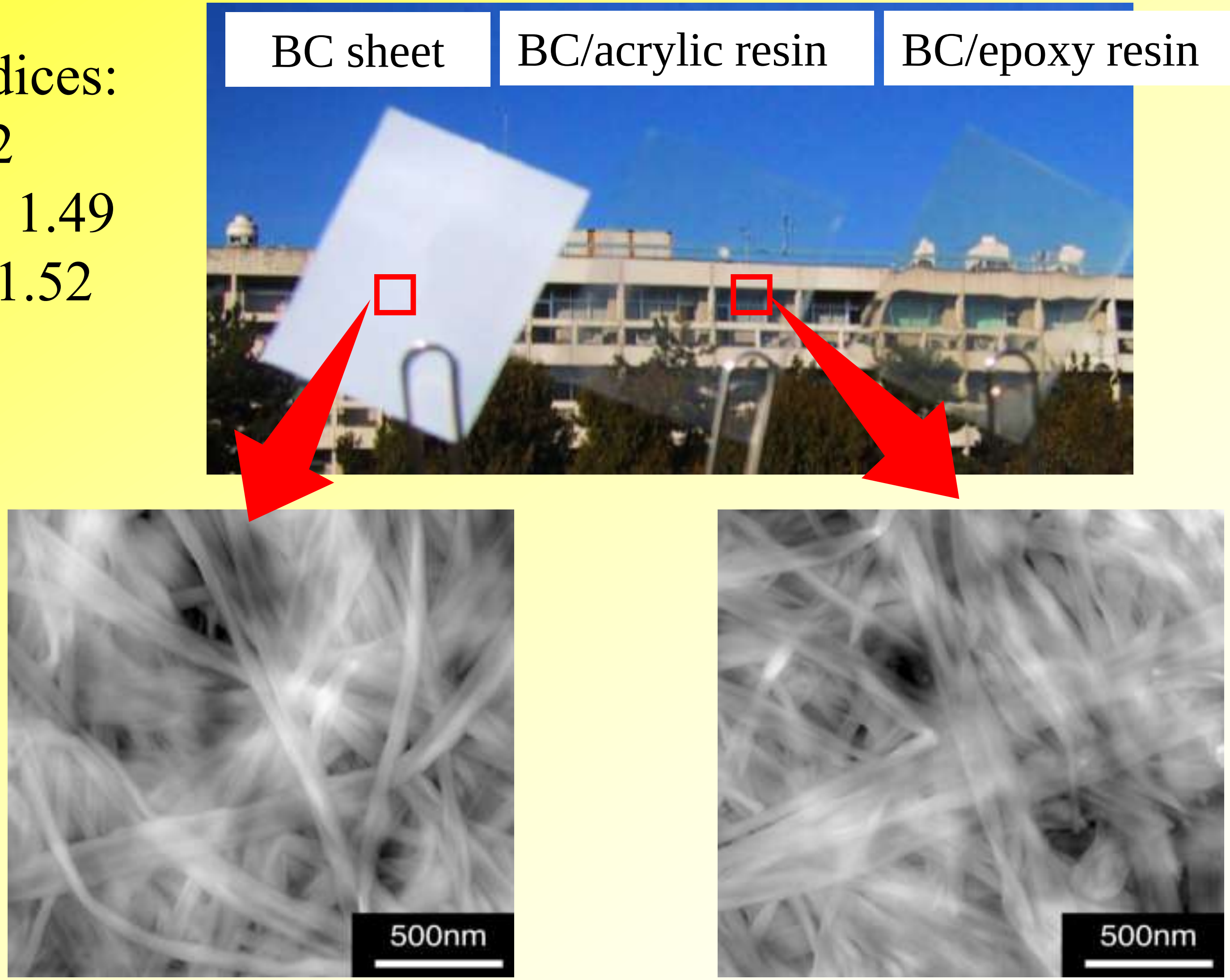
Bacterial Cellulose



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

Optically transparent at the fiber content of 60 to 70 %

Refractive indices:
BC: 1.54-1.62
Acrylic resin: 1.49
Epoxy resin: 1.52
(at 587.6 nm)



H.Yano, *et al.*, *Advanced Materials*, 2005

Cellulose Nanofibers

- Semi-crystalline extended chains

Young’s modulus:138-141GPa （-200~+200℃）

(T. Nishino et al. J. Polym Sci., Part B, 1995, Proc.2nd Intn'l Cellulose Conf,2007)

Tensile strength:3GPa → aramid fibers

(Based on D.H. Page, F., El-Hosseiny J. Pulp Paper Sci. 1983)

Thermal expansion coefficient：0.1 ppm/K

(T. Nishino, Personal communication, 2004)

→ quartz glass

Comparison with Commercial Transparent Materials

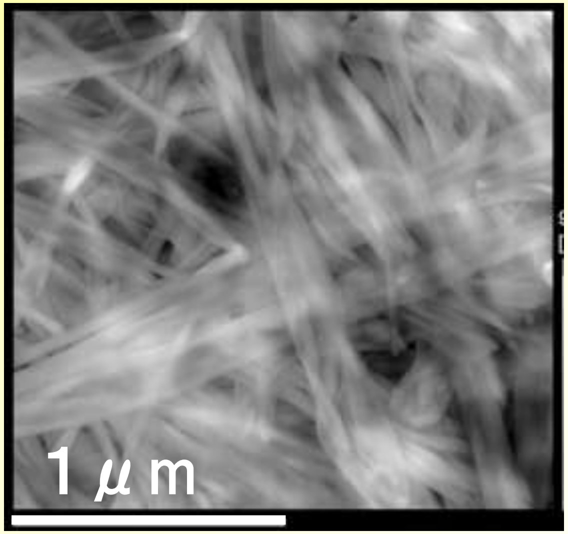
	CTE ppm/k	Tensile Strength MPa	Bending Strength MPa	Density g/cm^3
Glass	3-10	-	10-15	2.2
Polycarbonate	60-70	60-70	82-92	1.2
Polystyrene	60-80	46	70	1.05
PET	27	120-170	180-250	1.6
BC/resin sheet	3-7	325*	460**	1.2-1.4

* : BC + epoxy resin

** : BC + Phenolic resin

CTE : Coefficient of thermal expansion

Optically transparent composites reinforced with bacterial cellulose



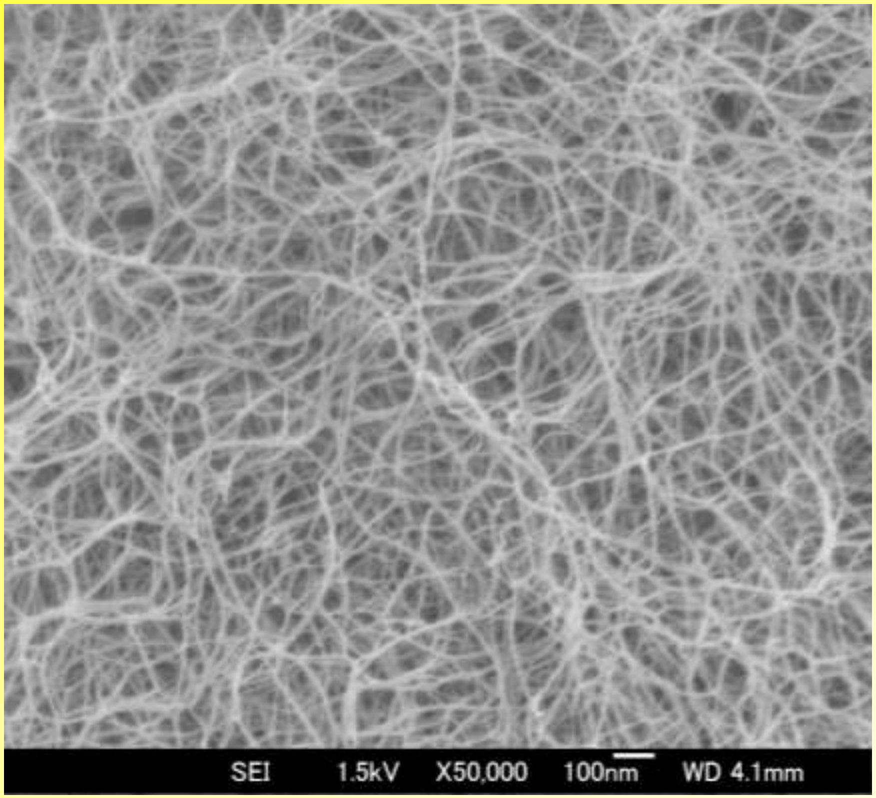
As strong as steel, as thermally stable as glass, and as bendable as plastics

H. Yano, *et al.*, *Advanced Materials,* 2005

Application:
Substrate for OLED (Organic Light-Emitting Diode)

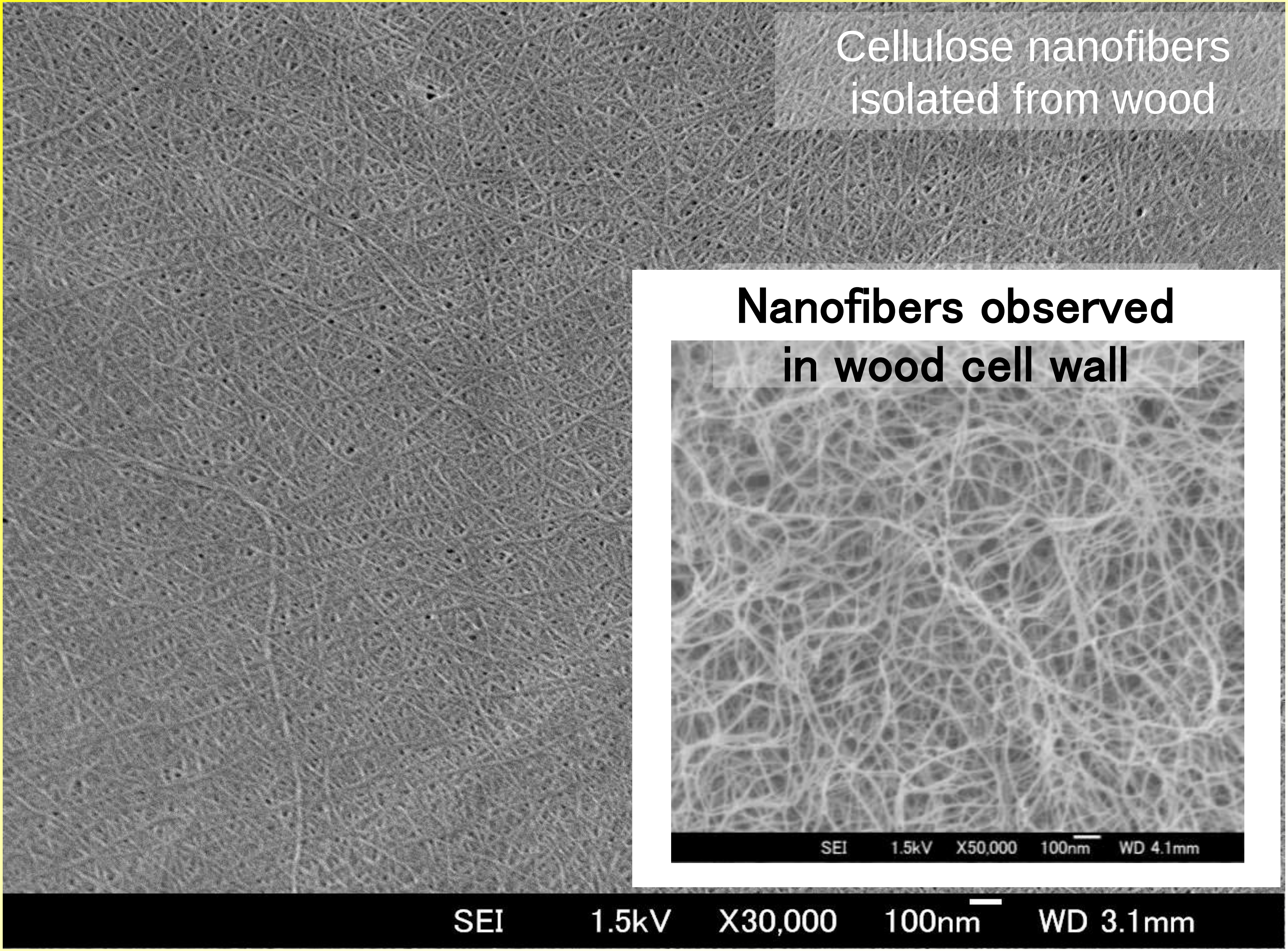
Wood Cellulose Nanofibers

The most abundant biomass resource on earth



Cellulose nanofibers or a cellulose microfibril bundle in the wood cell wall (Awano, Kyoto univ.)

1 Trillion tons:1×10^{12} tons

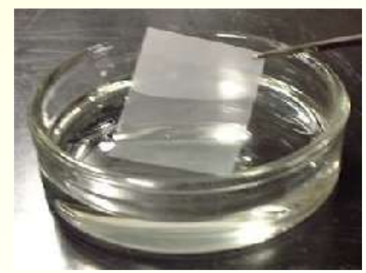

Cellulose nanofibers
isolated from wood
Nanofibers observed
in wood cell wall
SEI 1.5kV X50,000 100nm WD 4.1mm
SEI 1.5kV X30,000 100nm WD 3.1mm

Preparation of Cellulose Nanofiber Composites

1% Never-dried Pulp Slurry

Grinder treatment

Vacuuming filtration



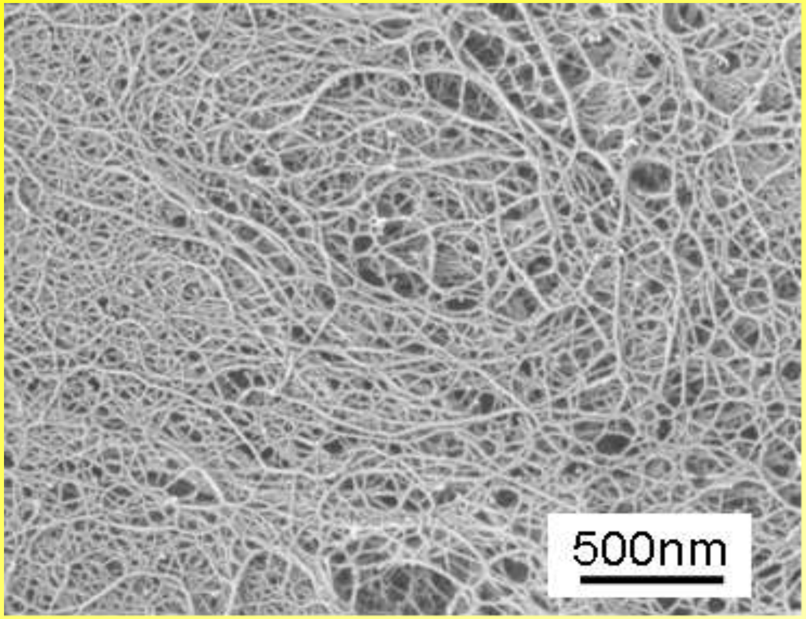
Acrylic Resin impregnation

UV cure

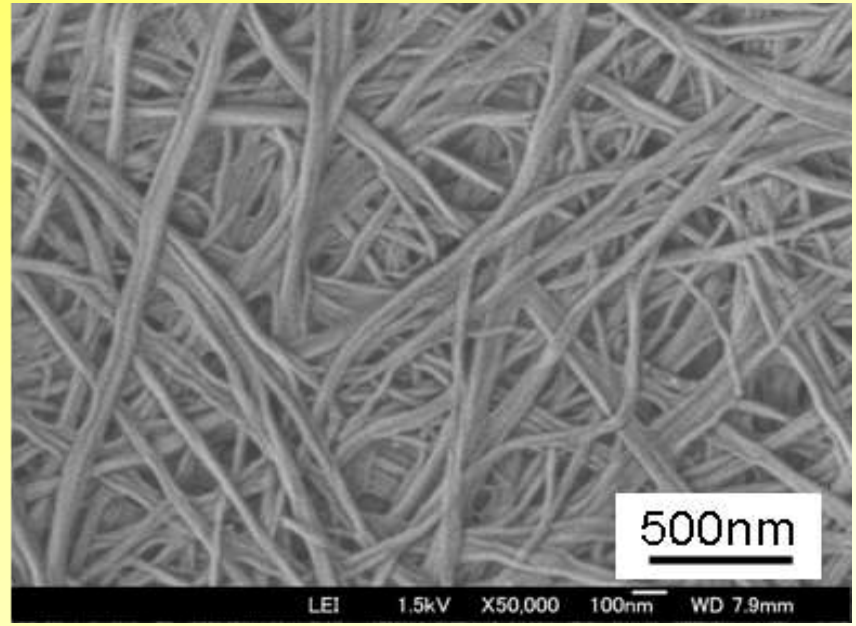
Nanocomposites

Fiber content::5-90 wt%

Optically transparent composites reinforced with wood cellulose nanofibers



Wood Nanofiber



Bacterial Cellulose

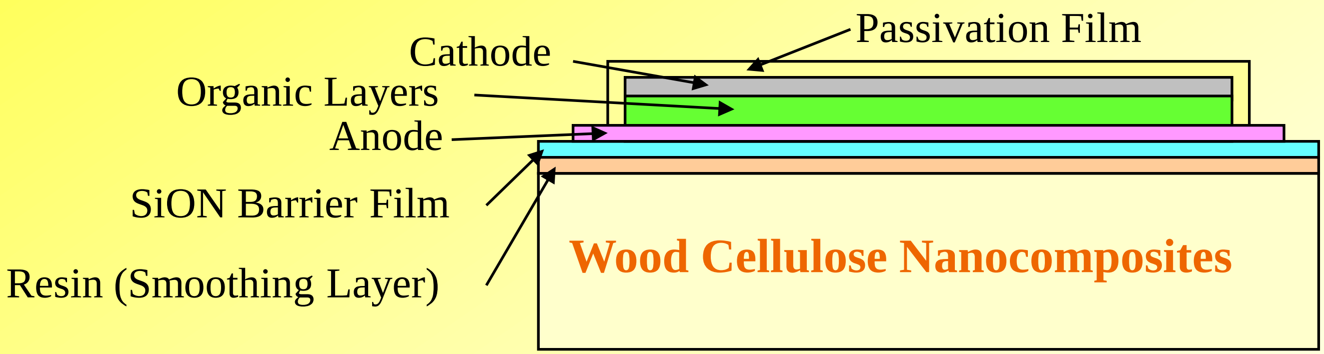
	Density (g/cm^3)	Light Transmittance[1] (%)	CTE[2] $(10^{-6}\ ^{o}C^{-1})$	E (GPa)	Tensile Strength (MPa)
Wood Nanofiber Composites	1.4	82.3	9.8	16.3	283
Bacterial Cellulose Composites	1.4	83.7	6.0	21.0	325

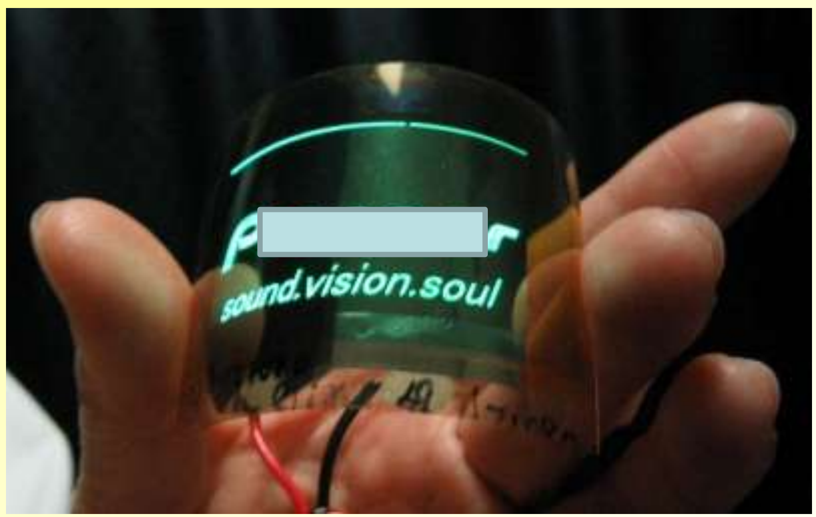
S. Iwamoto, *et al.*, *Biomacromolecules* (2007)

[1]600nm、[2]20～150℃

Luminescence of an OLED deposited on the wood nanofiber-composite

Device structure



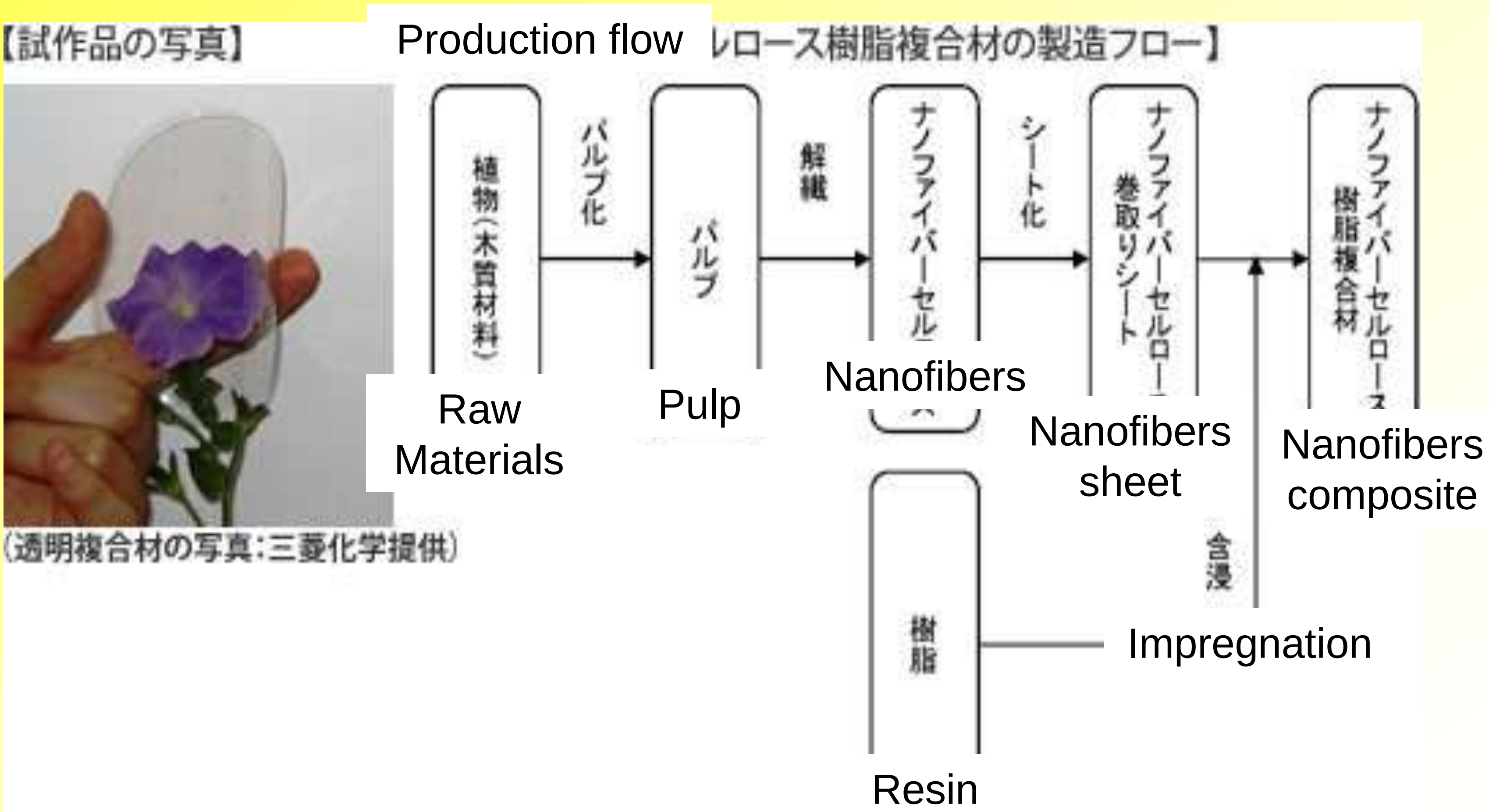


Y. Okahisa, *et al., Comp. Sci. Technol*. (2009)

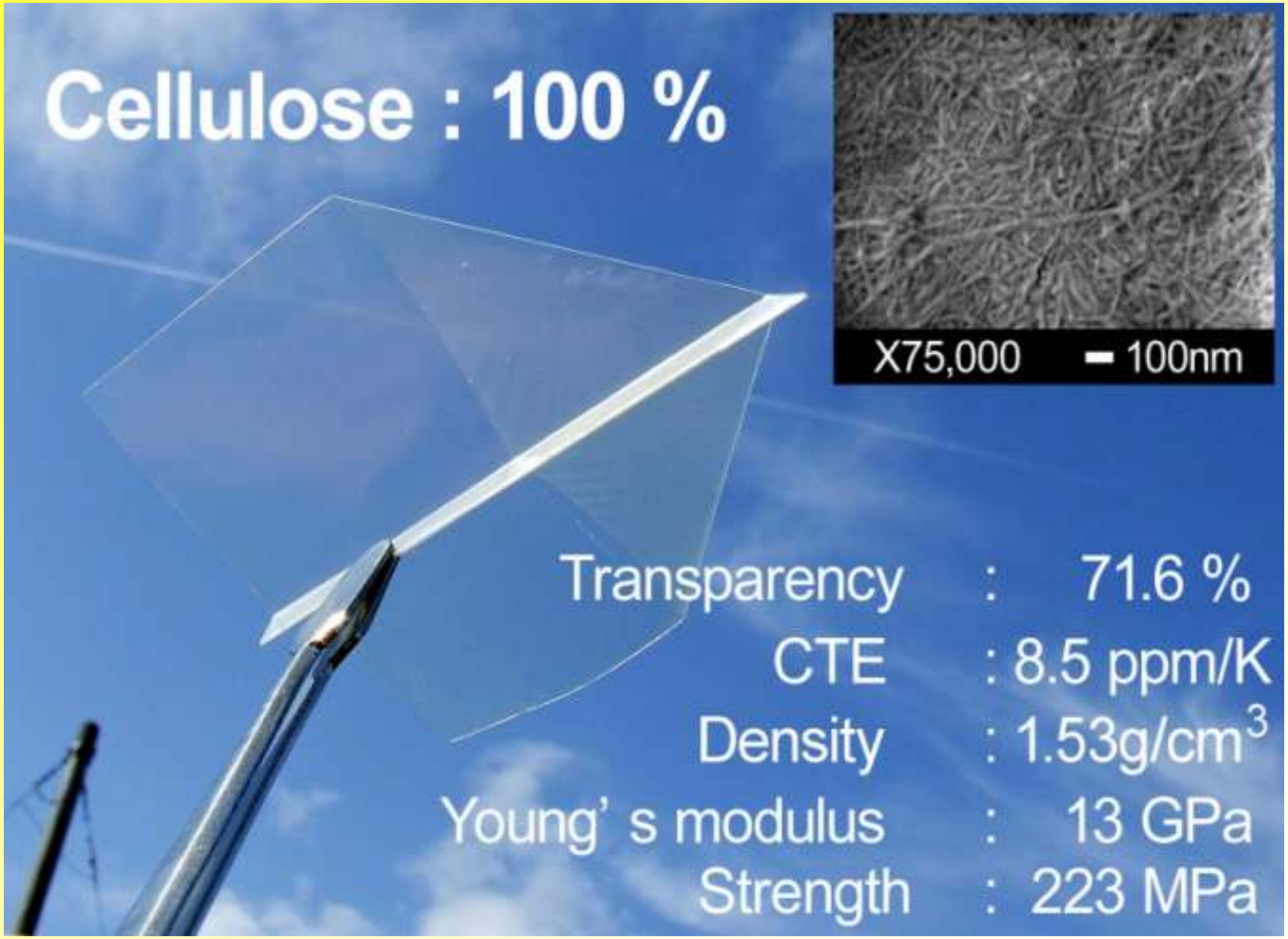
Joint Research Between Oji paper and Mitsubishi Chemical Aiming the Commercialization of Optically Transparent Cellulose Nanofiber Film

2010.Jan.7 http://www.ojipaper.co.jp/release

Joint Research work on the production of cellulose nanofibers reinforced composites



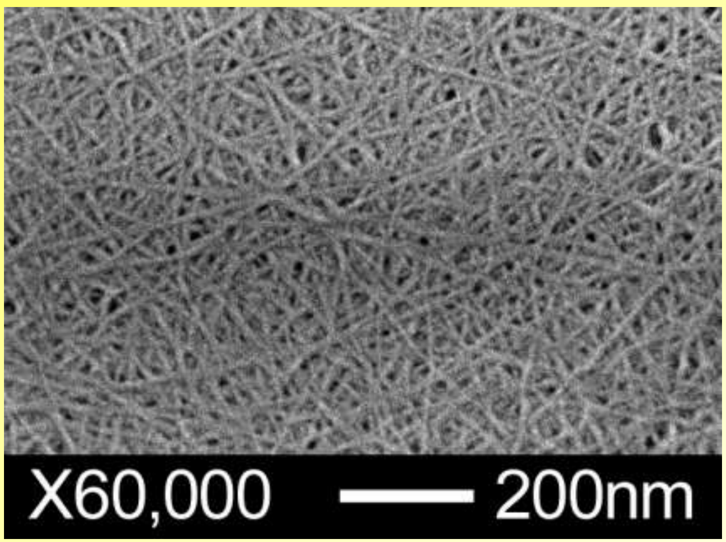
Optically Transparent Sheet, as foldable as paper !



M. Nogi, *et al., Advanced Materials* (2009)

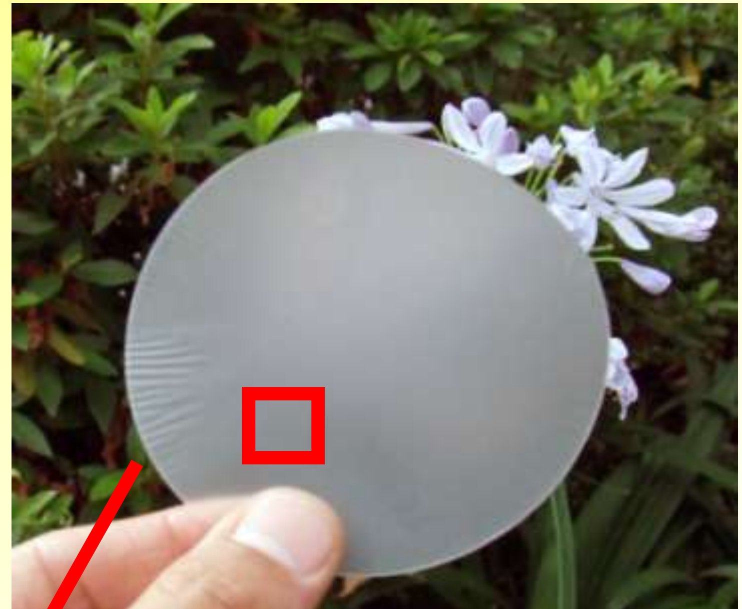
Densely Packed Cellulose Nanofiber Sheet

1wt% nanofiber suspension

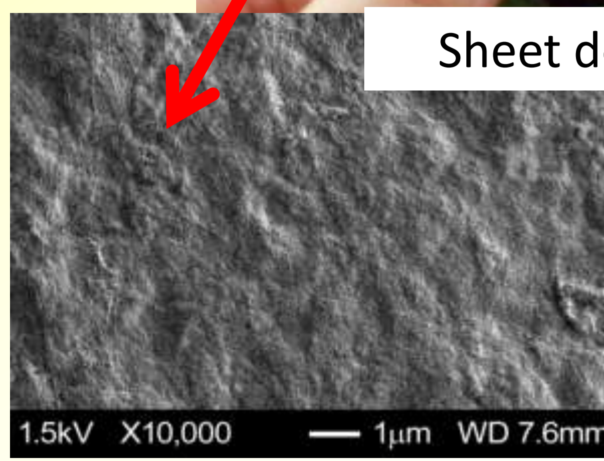


Cellulose nanofibers
(15nm width)

Cellulose nanofiber sheet prepared by filtration and hot pressing



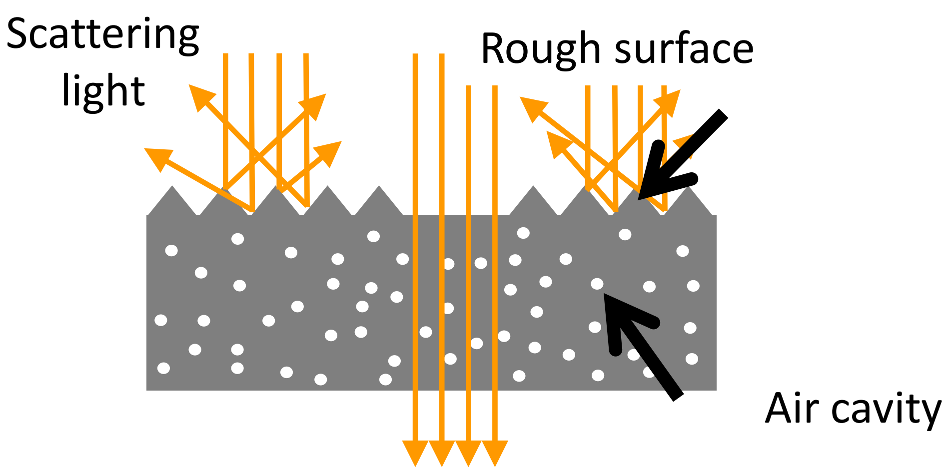
Sheet density : 1.53g/cm^3

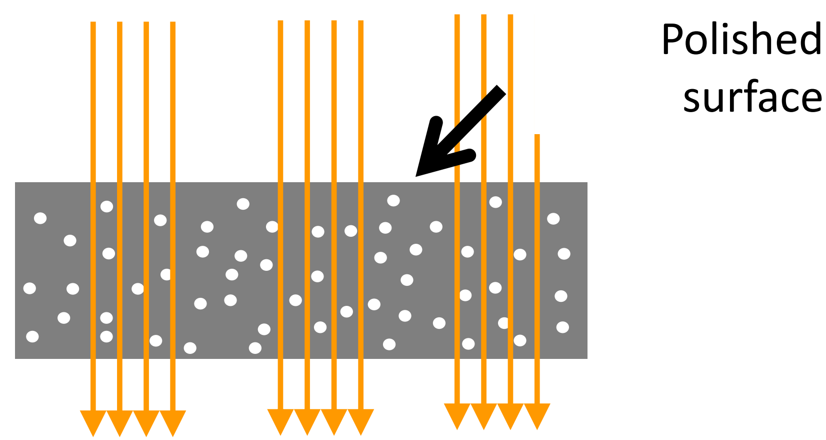


Surface smoothing by polishing

Translucent nanofiber sheet

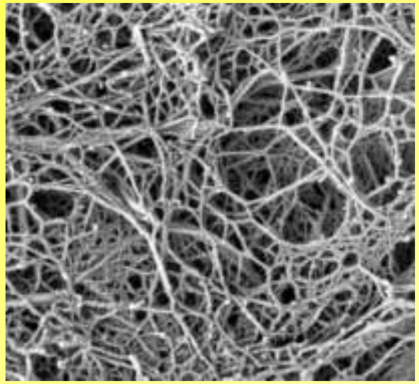
Transparent nanofiber sheet

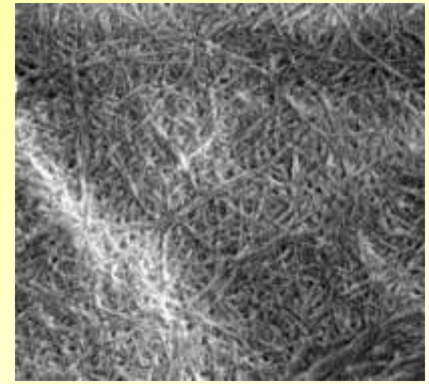


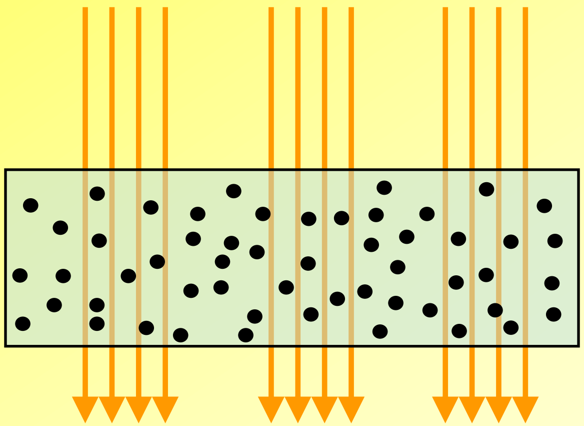
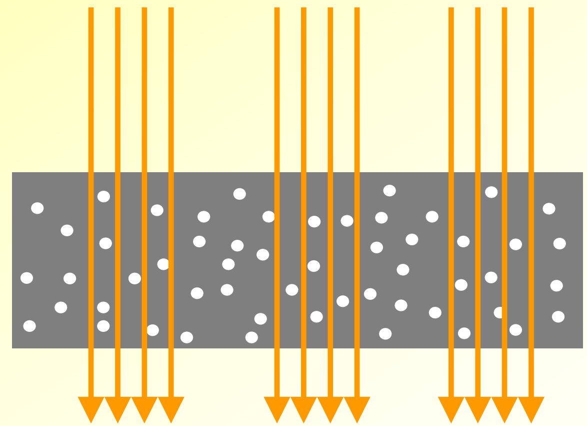


Cavities are small enough to avoid light scattering

Nanocomposite and Nanofiber sheet



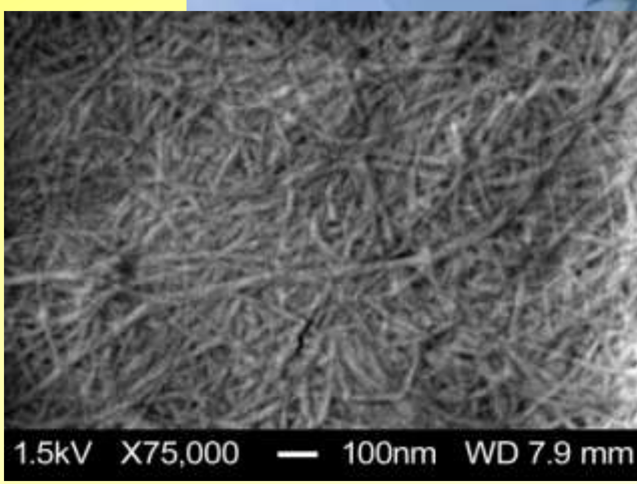
Fibers are small enough to avoid light scattering

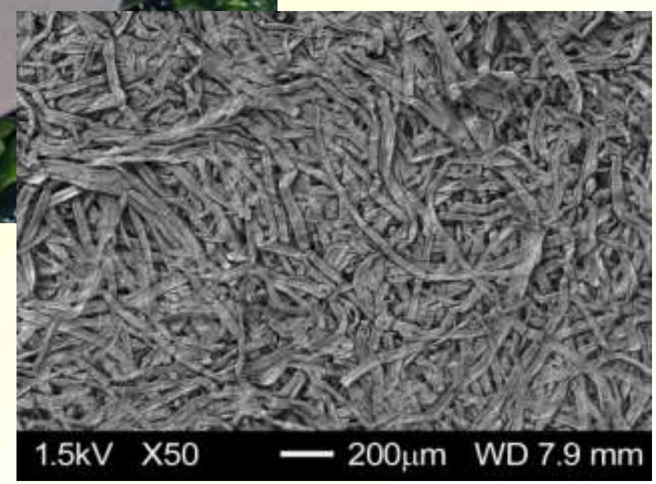
Cavities are small enough to avoid light scattering

Transparent Nanofiber Paper

Nanofiber sheet
“21st century paper”

Pulp sheet
“Traditional paper”



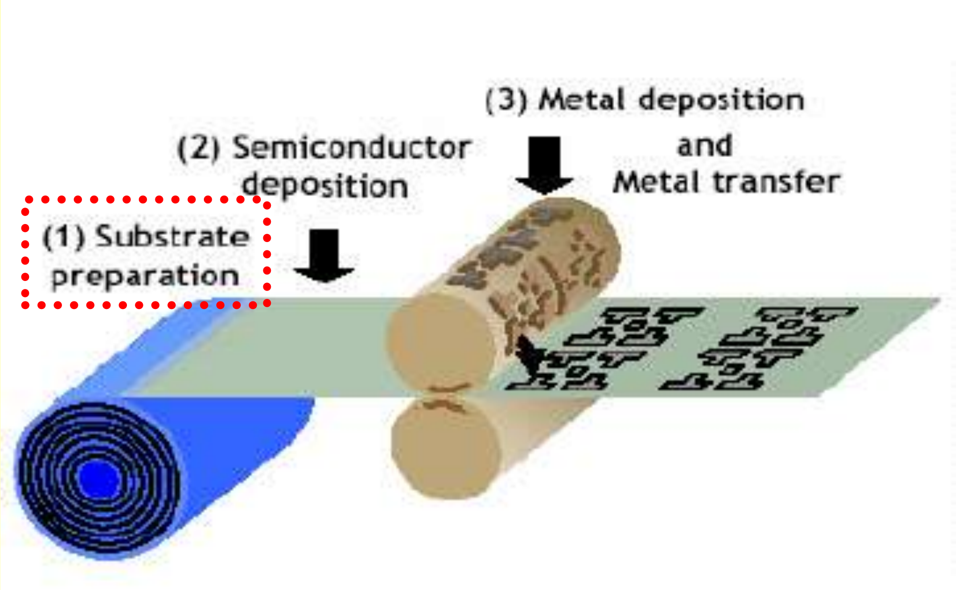


M. Nogi, *et al.*, *Advanced Materials* (2009)

A future FPD processing; Continuous “Roll to Roll”

R2R process : simple and inexpensive.

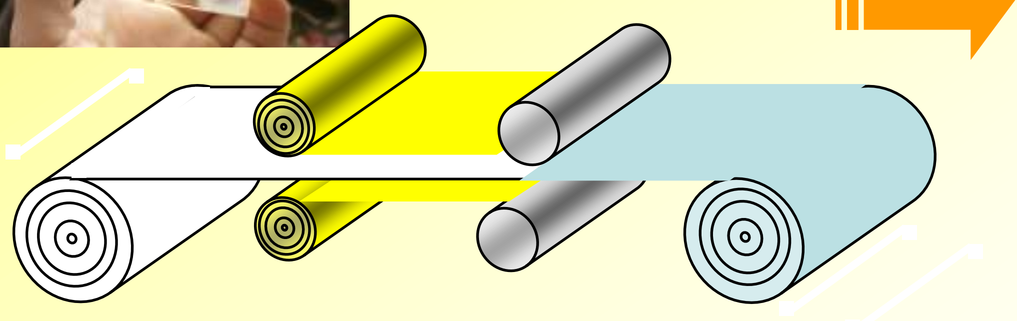
R2R processing enables the continuous deposition of functional materials such as semiconductor, transparent conductive films and gas barrier films on a roll of substrate.



A demonstration of
production of OLED by R2R process

(GE, USA, Press Release, 13 March, 2008)

In future, electronic devices will be printed by like a newspaper printing process on cellulose nanofiber papers, and information will be taken out from cellulose nanofibers paper



Topics

1. Extraction of cellulose nanofibers
2. Optically transparent materials
3. <u>Structural materials</u>

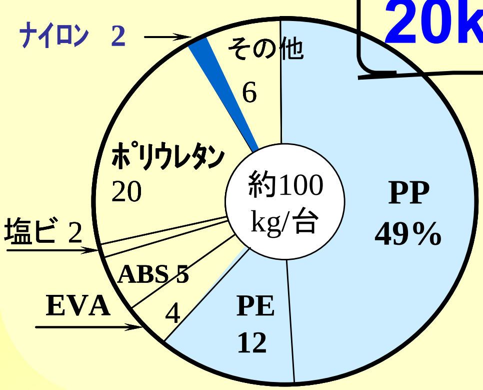
Challenge：Green Nanocomposites for Automotive Parts
- Reduction of CO2 emission -

Average weight：1200kg

Interior

Green Nanocomposites

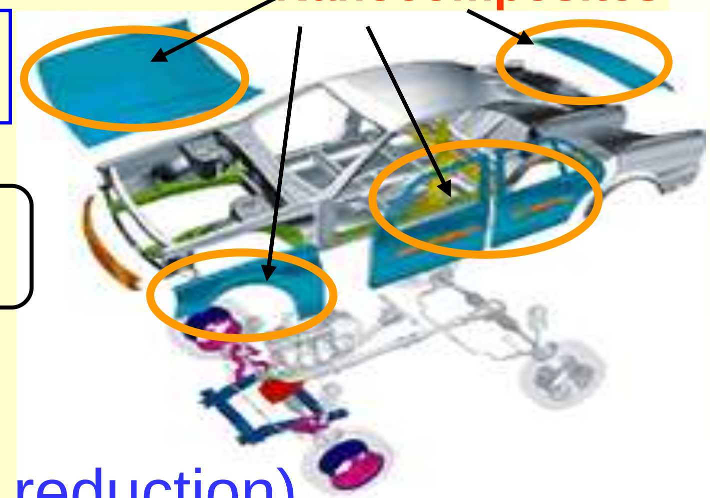
20kg↓



Exterior

100kg↓

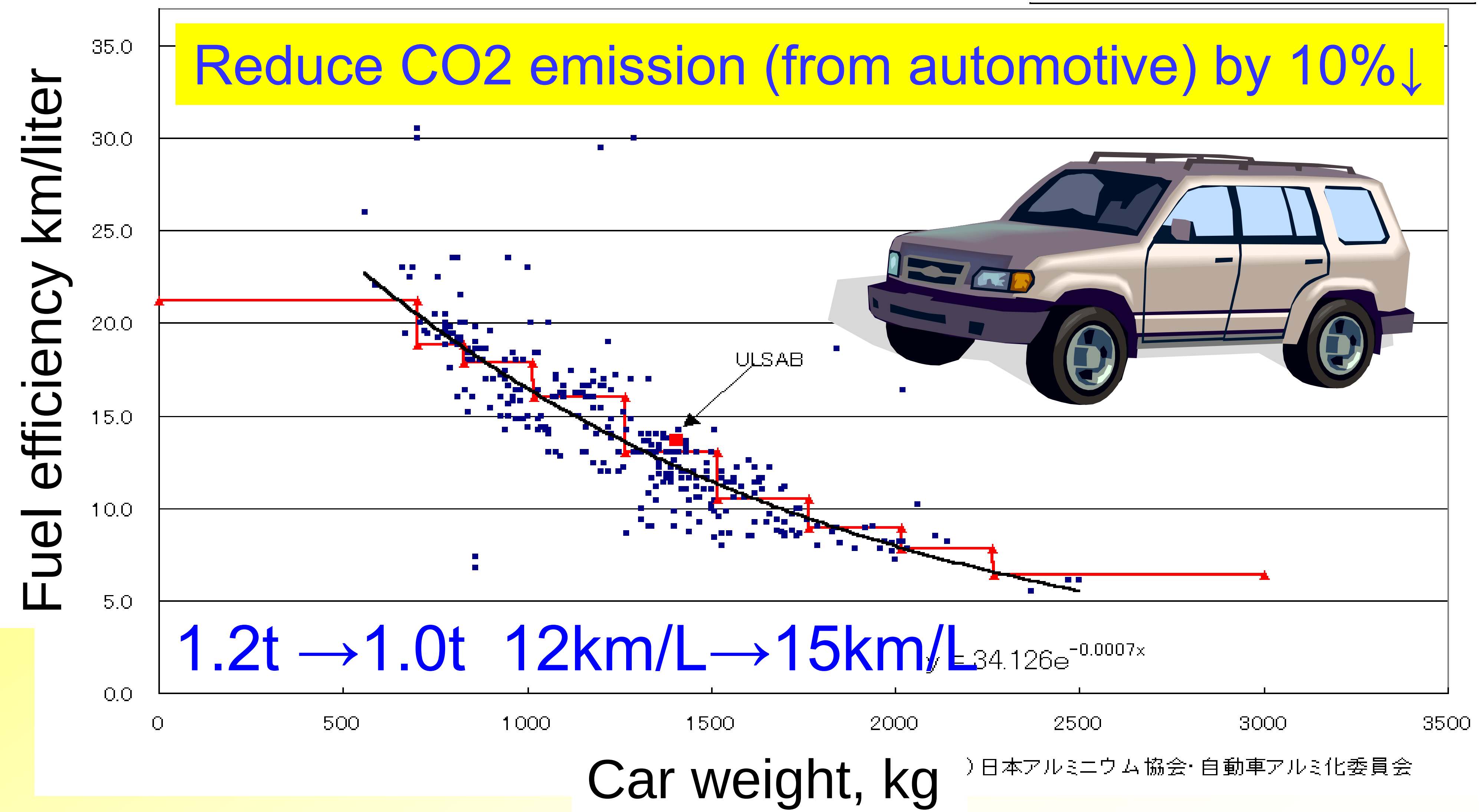
Green Nanocomposites



Total 120kg↓ (10% weight reduction)

The Reduction of Body Weight Improves Fuel-efficiency

10% weight reduction improves fuel efficiency by 10%



Structural purpose

1. CNF Reinforced Thermosetting Resin

2. CNF Reinforced Thermoplastic Resin

Preparation of Cellulose NF/PF composites: Sheet molding

Stirring with water
(0.2% in weight)

Vacuum filtering

Oven-drying: 70°C

PF resin Impregnation (MW=3,351) at 20°C

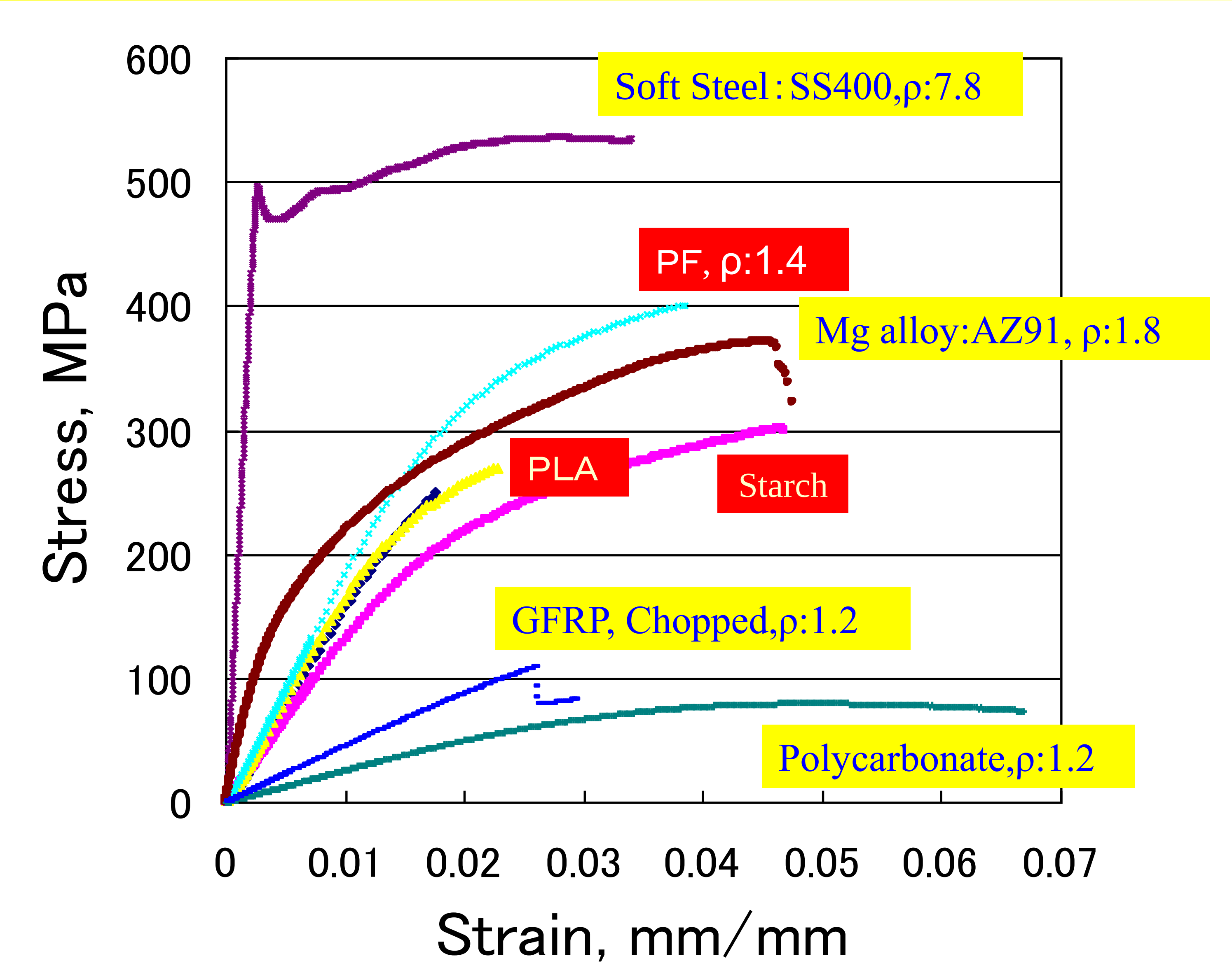
Air drying – Vacuum drying: 50°C

Hot pressing
160°C, 30min,50MPa.

Finished sample

AN. Nakagaito, *et al.*, Applied Physics A (2005)

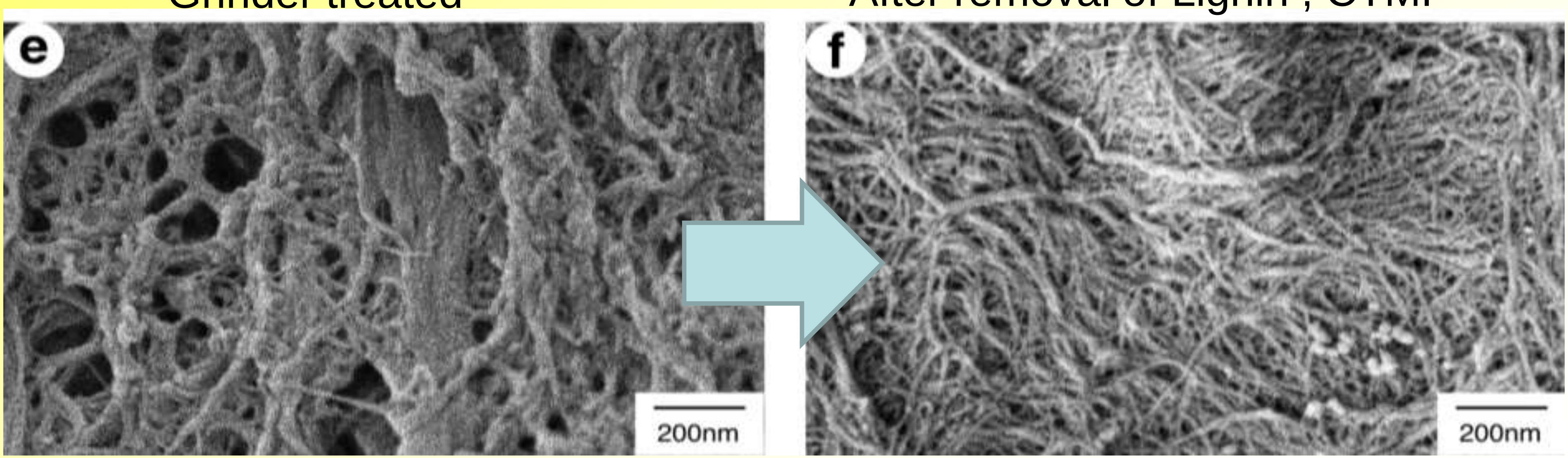
Cellulose NF-based Composites vs Conventional Materials



Chemi-Thermomechanical pulp, CTMP with a lignin content of 28%

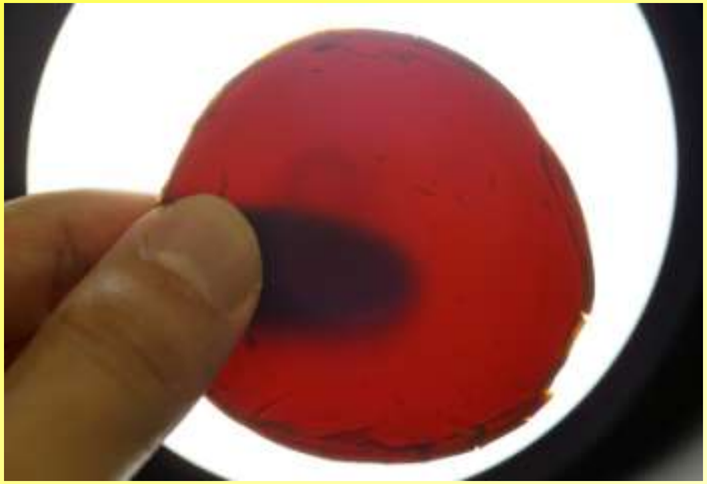
Grinder treated

After removal of Lignin , CTMP

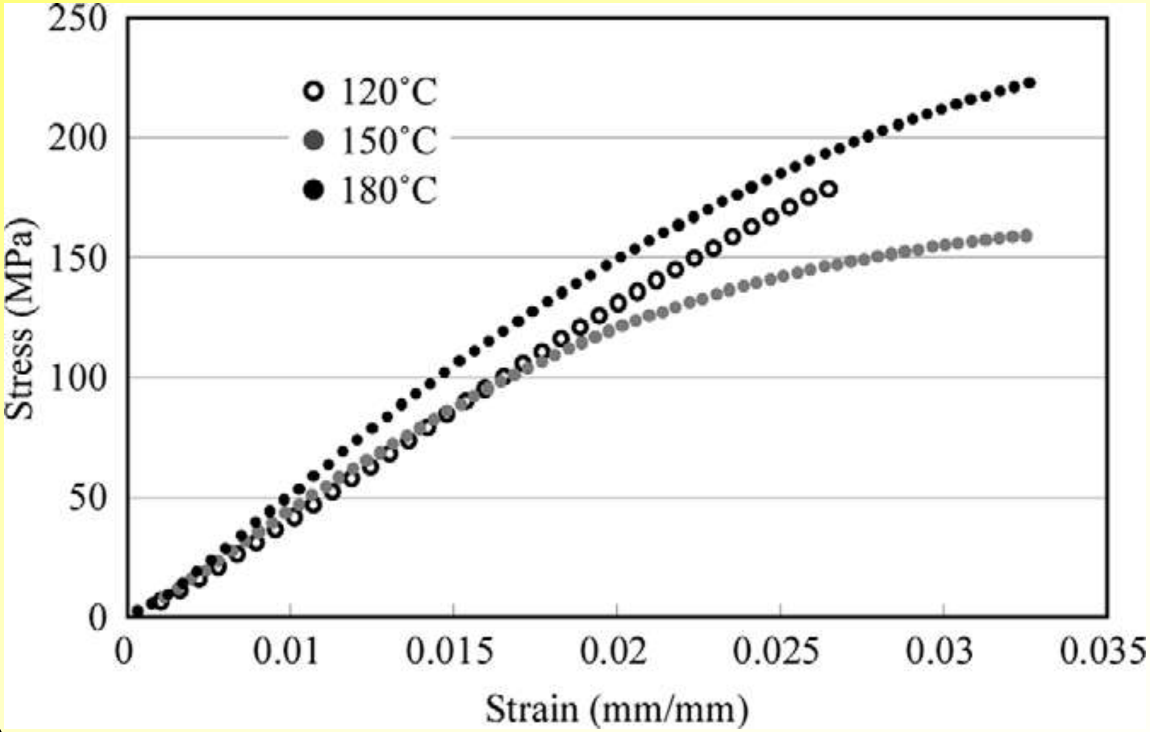


(Abe, *et al.*, *Comp. Sci.Technol*, 2009)

100% wood nanocomposites



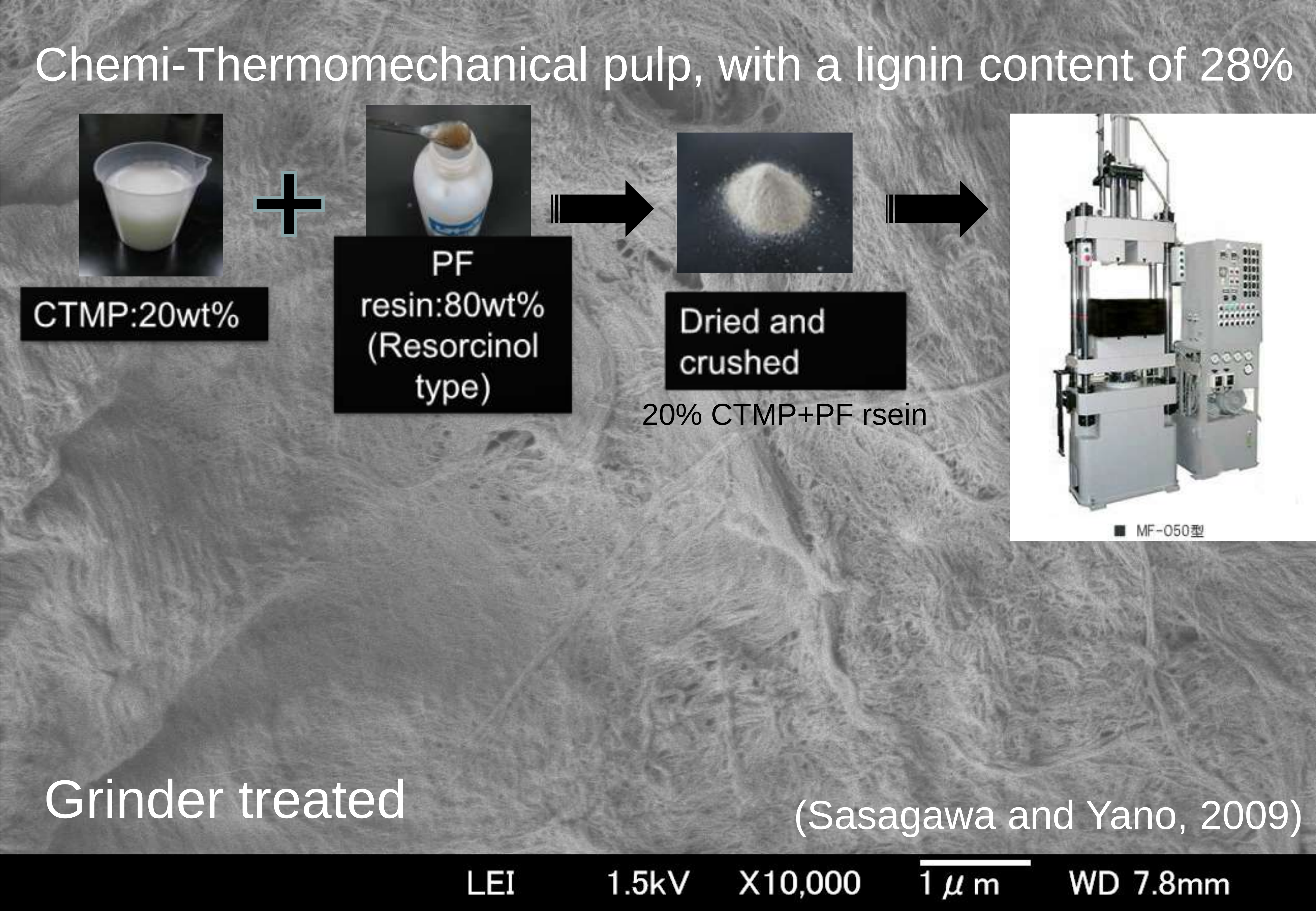
Visible light transmittance of the CTMP molded product pressed at 180 °C.



Stress–strain curves of CTMP molded products pressed at 120, 160, 180 °C.

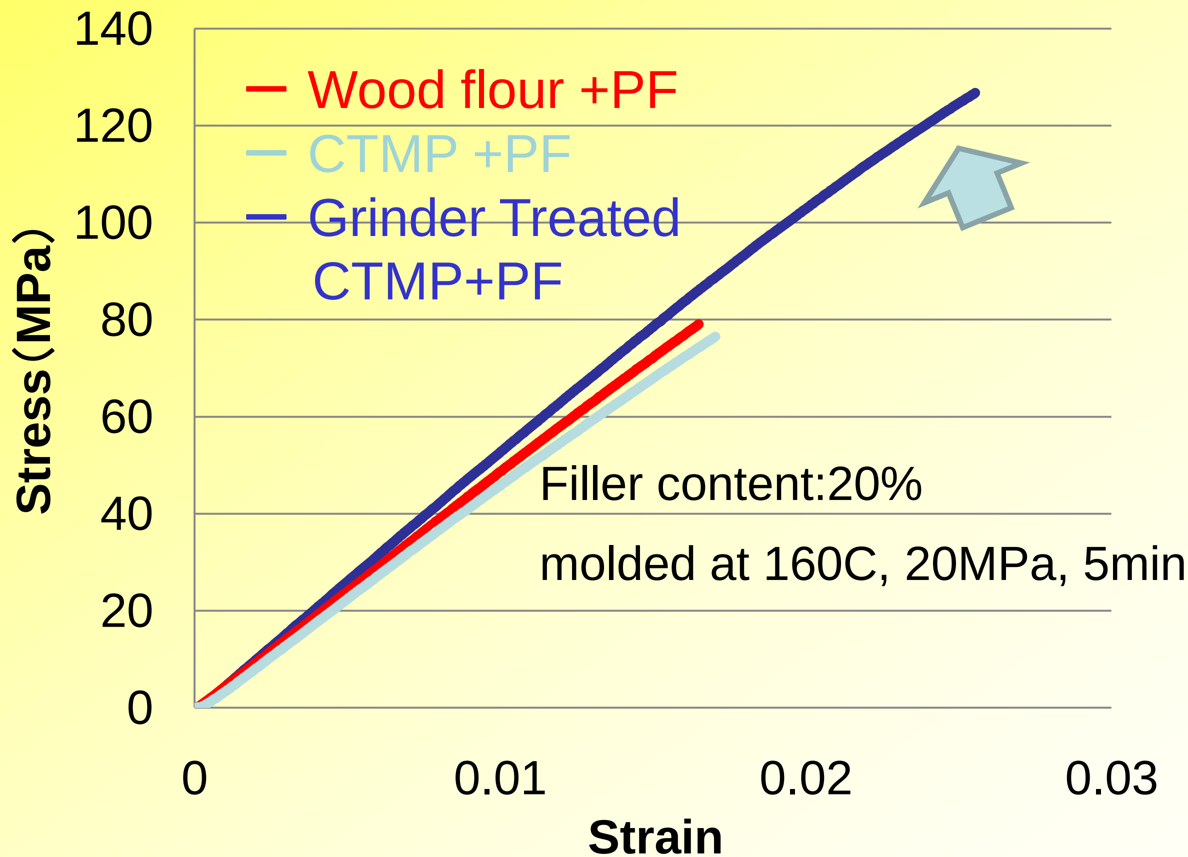
Chemi-Thermomechanical pulp, with a lignin content of 28%

(Abe, *et al., Comp. Sci.Technol*, 2009)


Chemi-Thermomechanical pulp, with a lignin content of 28%
CTMP:20wt%
PF resin:80wt% (Resorcinol type)
Dried and crushed
20% CTMP+PF rsein
■ MF-050型
Grinder treated
(Sasagawa and Yano, 2009)
LEI 1.5kV X10,000 1 μm WD 7.8mm

transfer molding

Bending Test



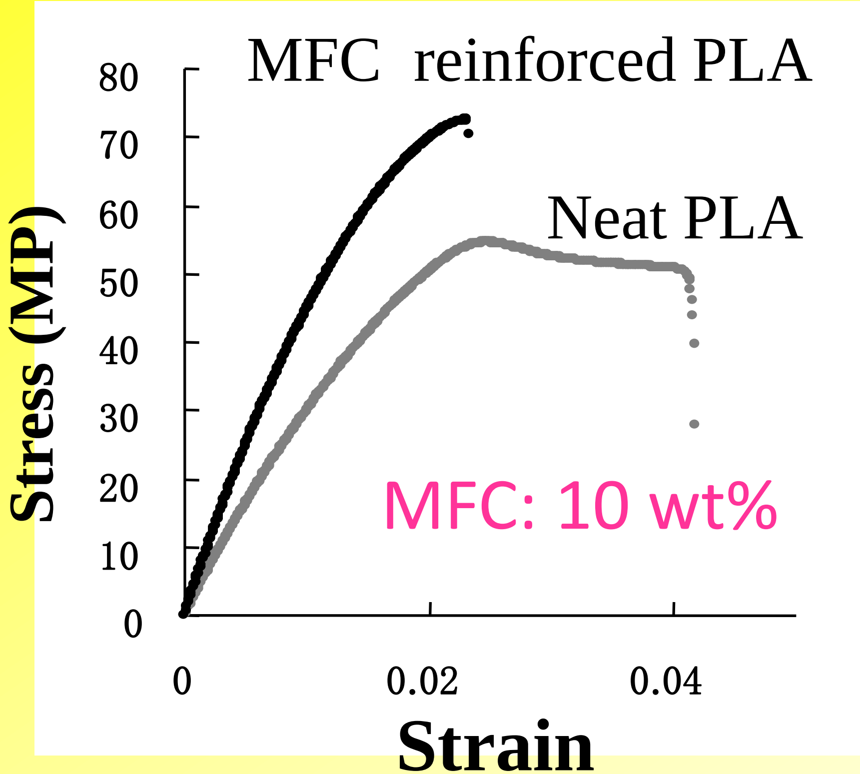
Filler	Density (g/cm3)	Young's modulus (GPa)	Bending strength (MPa)
Wood Powder	1.33	4.7	73.5
CTMP	1.33	4.5	69.5
Grinder treated CTMP	1.35	5.3	115.3

Structural purpose

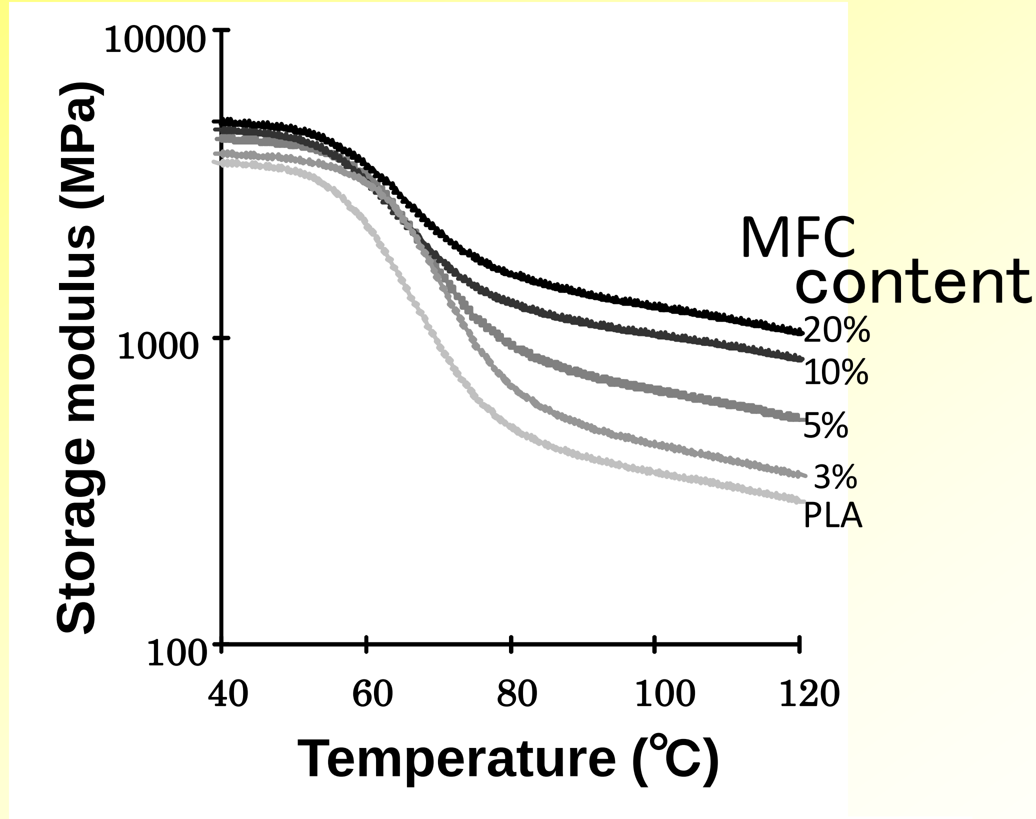
1.CNF Reinforced Thermosetting Resin

2.CNF Reinforced Thermoplastic Resin

CNF Reinforced PLA



Tensile strength of MFC reinforced **amorphous PLA**. MFC:10%

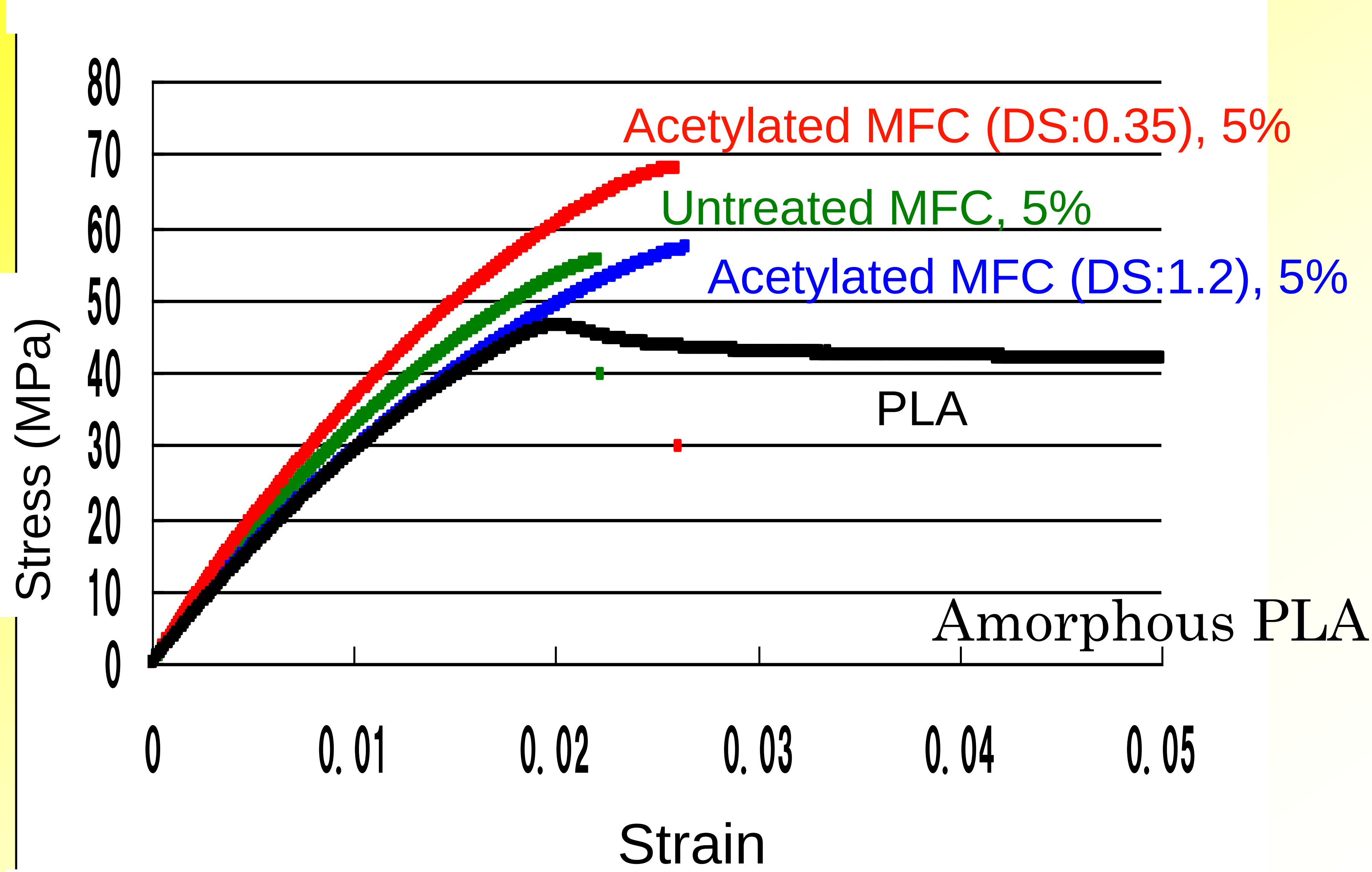


Temperature dependency of strage modulus of MFC reinforced **crystallized PLA**

(Iwatake, *et al., Comp. Sci. Technol*, 2008)

(Lisman, *et al., Comp. Sci.Technol*, 2009)

Acetylated CNF Reinforced PLA



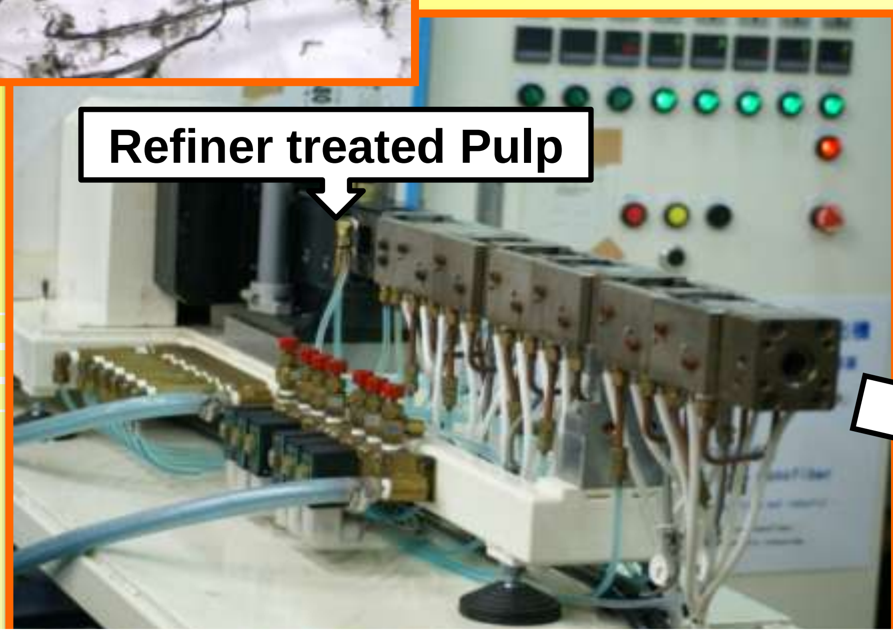
Takagi and Yano, 2006

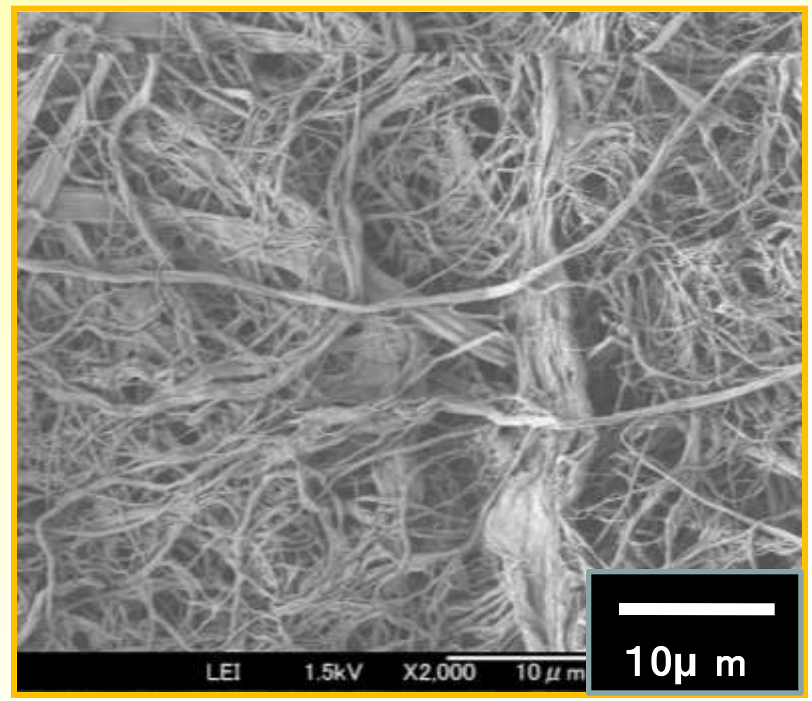
Melt-compounding of PLA powder/MFC using Twin Screw Extruder

No	Sample	Young's Modulus GPa	SD	Max Stress MPa	SD	Strain %	SD
1	PLA	3.56	0.06	58.6	3.1	16.3	4.0
2	PLA/10MFC	3.80	0.04	55.0	1.6	1.9	0.1
3	PLA/20MFC	4.25	0.19	64.2	2.2	2.2	0.2
4	PLA/30MFC	5.13	0.14	66.3	1.7	2.1	0.1

Yano et al., 2006

Nanofibrillation using twin screw extruder





Preparation of Cellulose NF/PP composites: Injection molding

Refiner treated Pulp:NBKP

＋

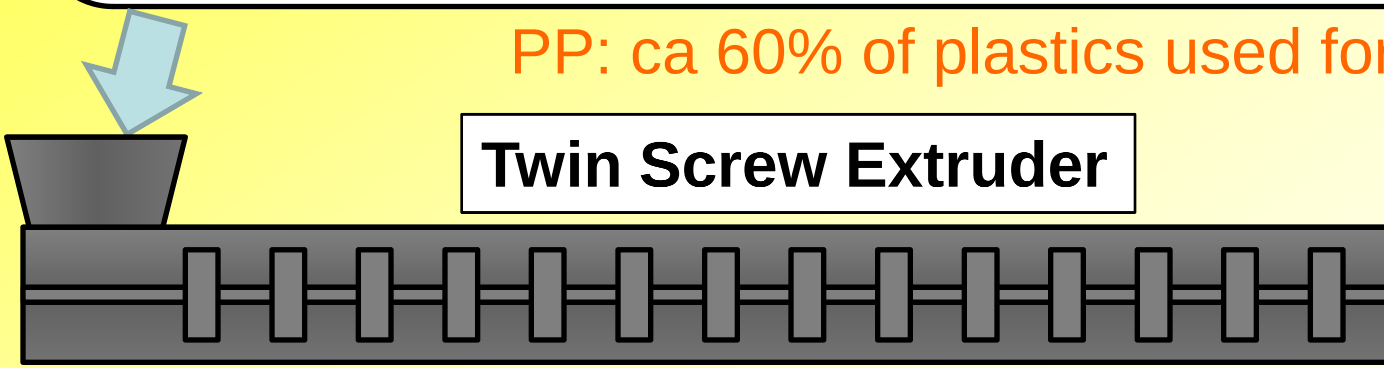
Polypropylene:PP

＋

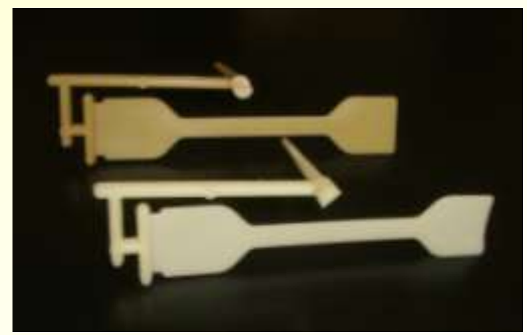
additives

PP: ca 60% of plastics used for automotive parts

Twin Screw Extruder

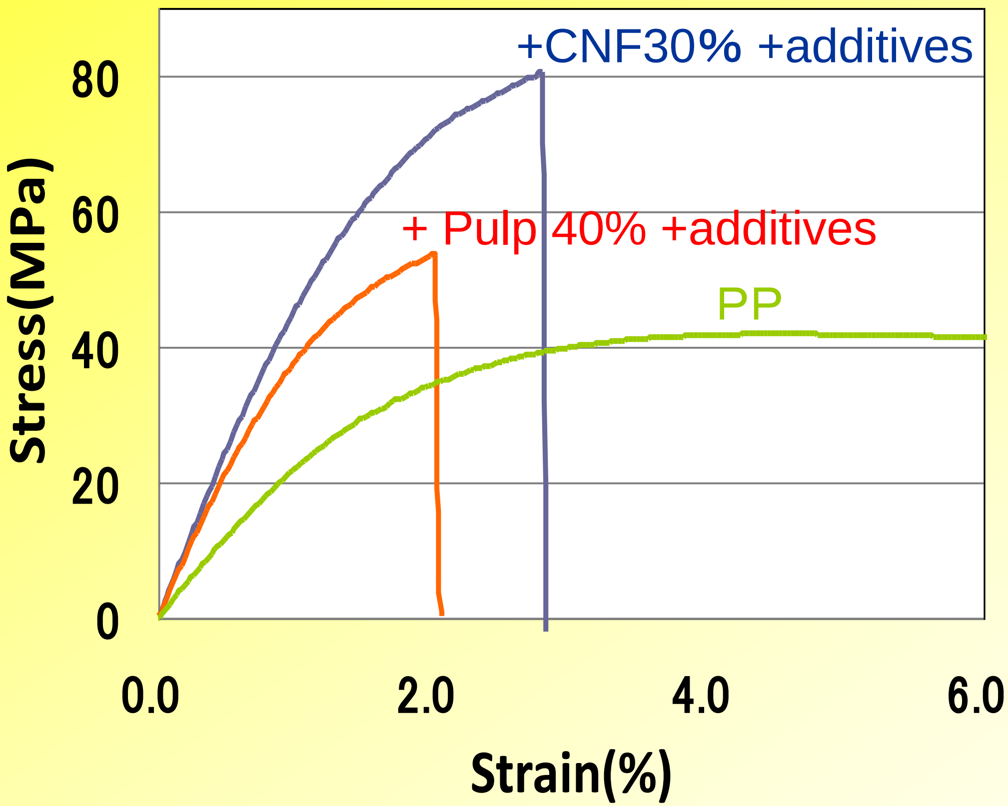


Nanofibrillation & Compounding



Allowing nanofibriilation and well-mixed compounds, ⇒ **Injection Molding**

CNF Reinforced Polypropylene

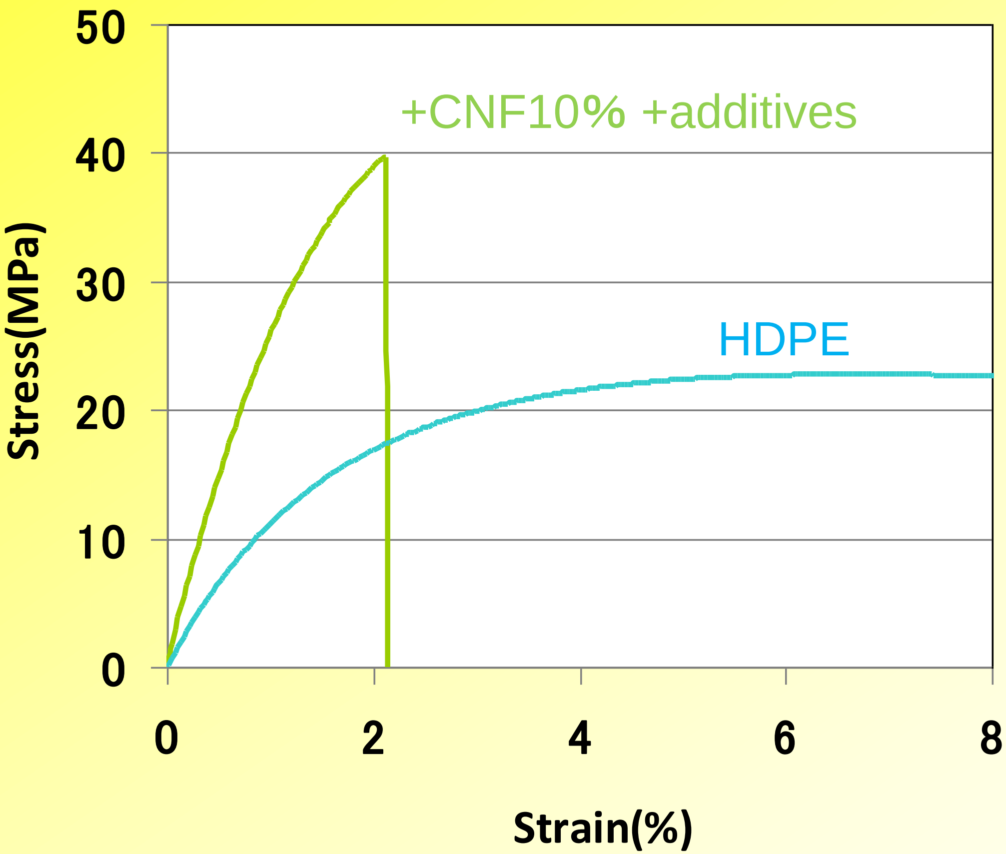


Comparison of CTE (23-100℃)

	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**

Suzuki, Yano, *et al.*, 2010

CNF Reinforced Polyethylene



Comparison of CTE (23-100℃)

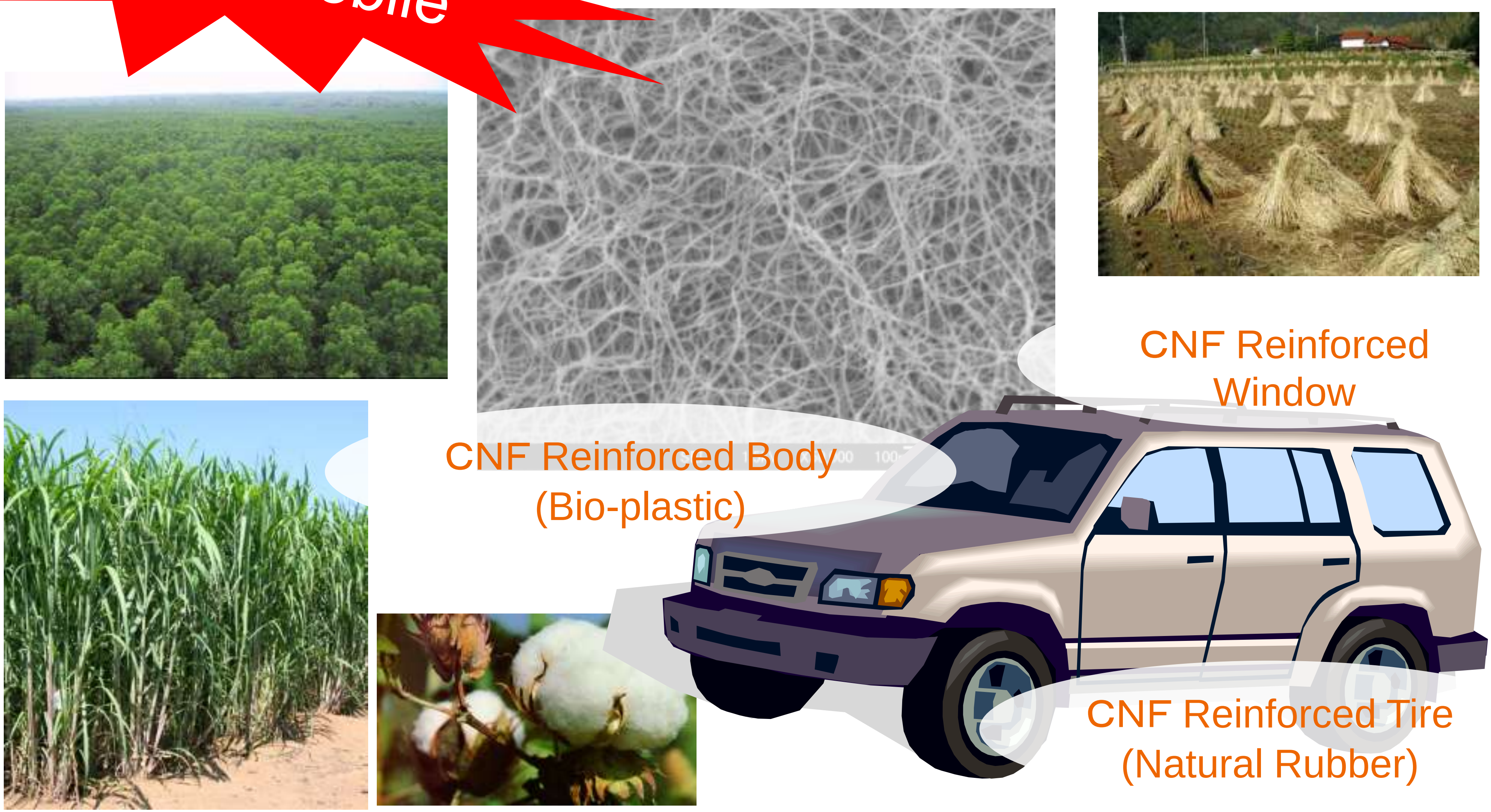
	Density (g/cm3)	CTE (ppm/K)
HDPE	0.96	222.2
HDPE +additives +MFC20%	1.06	26.9

Suzuki, *et al.*, 2010

Future Application of Cellulose Nanocomposites

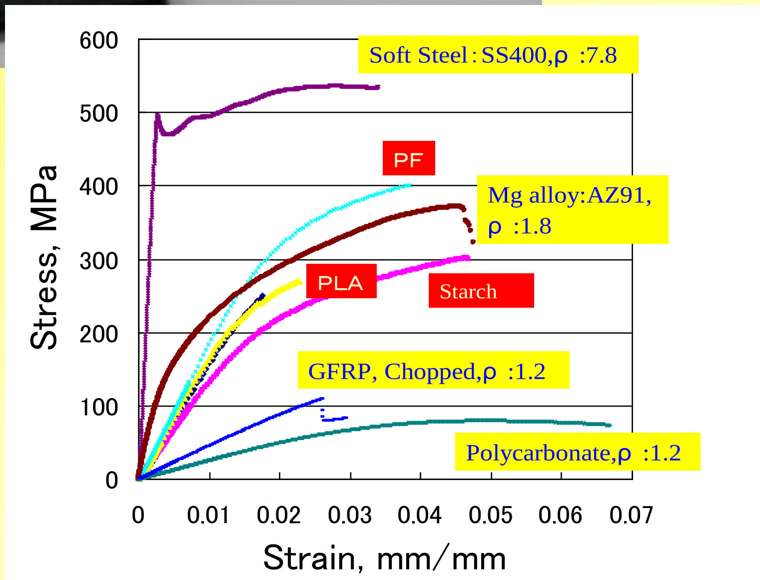
Bio-automobile

300kg reduction of automobile body weight improves fuel consumption by 20%



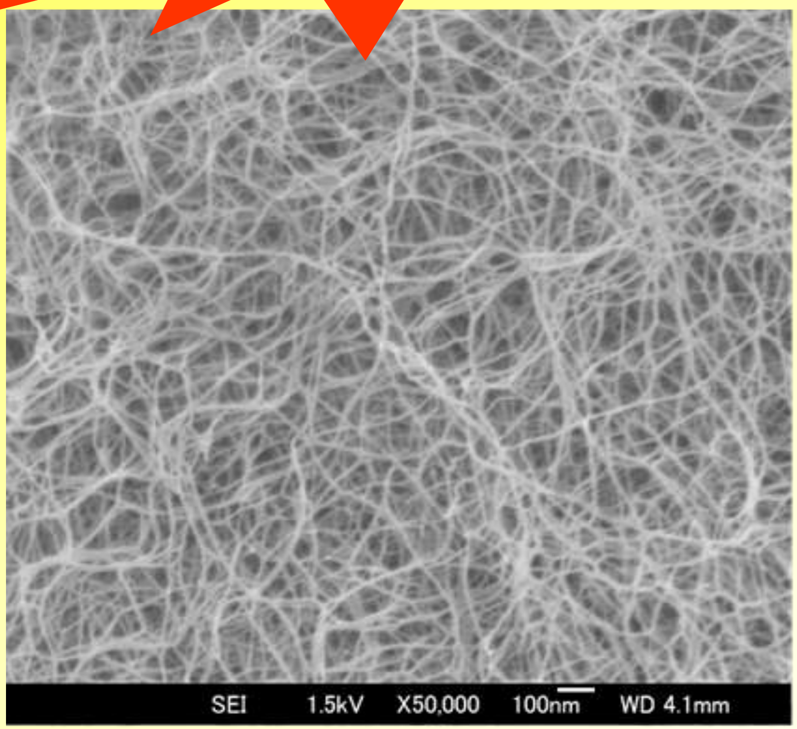
Concluding Remarks

Who made these materials?

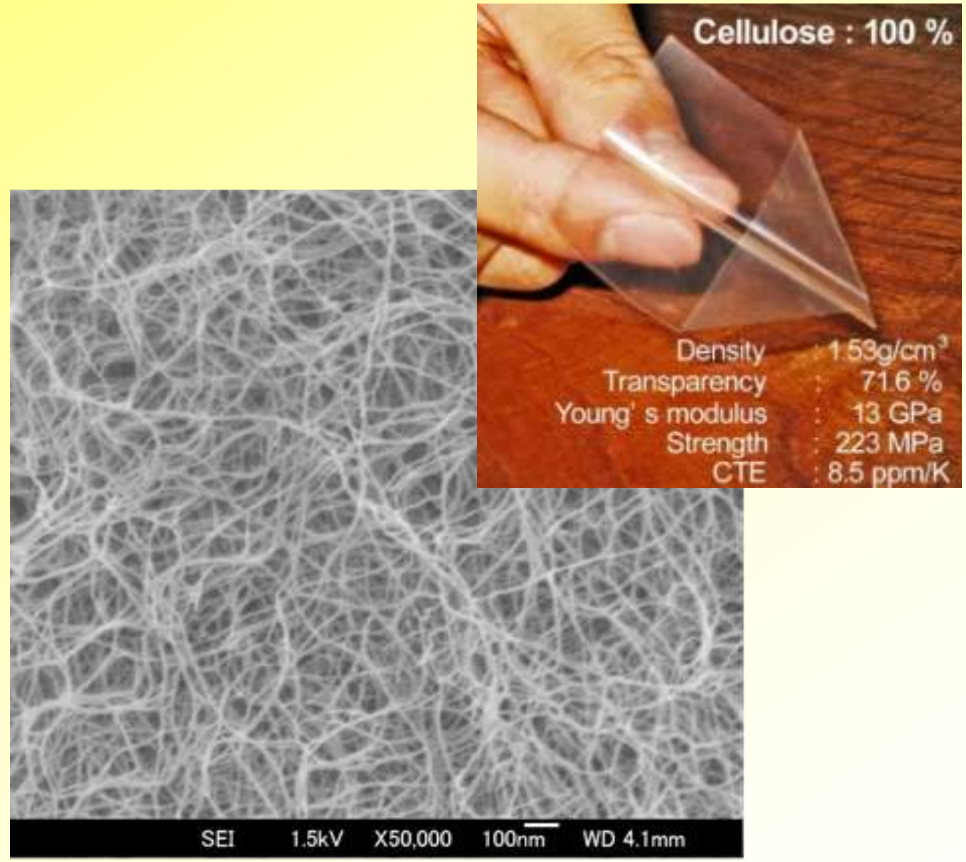


Cellulose Nanofibers

Tree's job!



Green Nanomaterials



To survive this century, we have to create new materials beyond our capability. Combination of 0.1 % human being job and 99.9% tree's job.

http://www.inoues.net/science/war.html

Whenever we want to reach a new world, wood takes us.

by Yano 2010

Acknowledgment: This work was partly supported by
1) Grant-In-Aid from the Integrative Industry-Academia Partnership between Kyoto University and five companies (Nippon Telegraph and Telephone Corporation, Pioneer Corporation, Hitachi, Ltd., Mitsubishi Chemical Corporation, and Rohm Co., Ltd.),
2) Matching Fund of NEDO and five companies (Oji Paper Co., Ltd., Nippon Paper Industries Co., Ltd., Mitsubishi Chemical Corporation, DIC Co., and Sumitomo Rubber Industries Co., Ltd.

Thank you