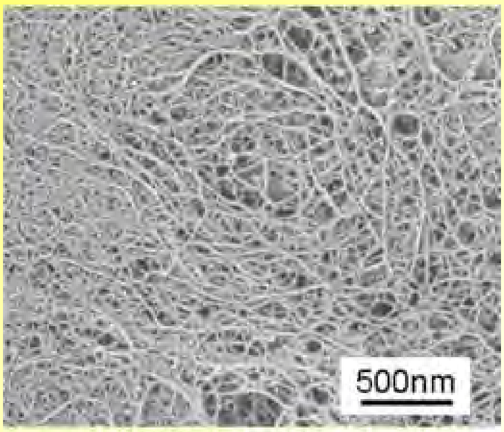
A Paradigm in Nanocellulose Materials

- From nanofibers to nanostructured fibers -

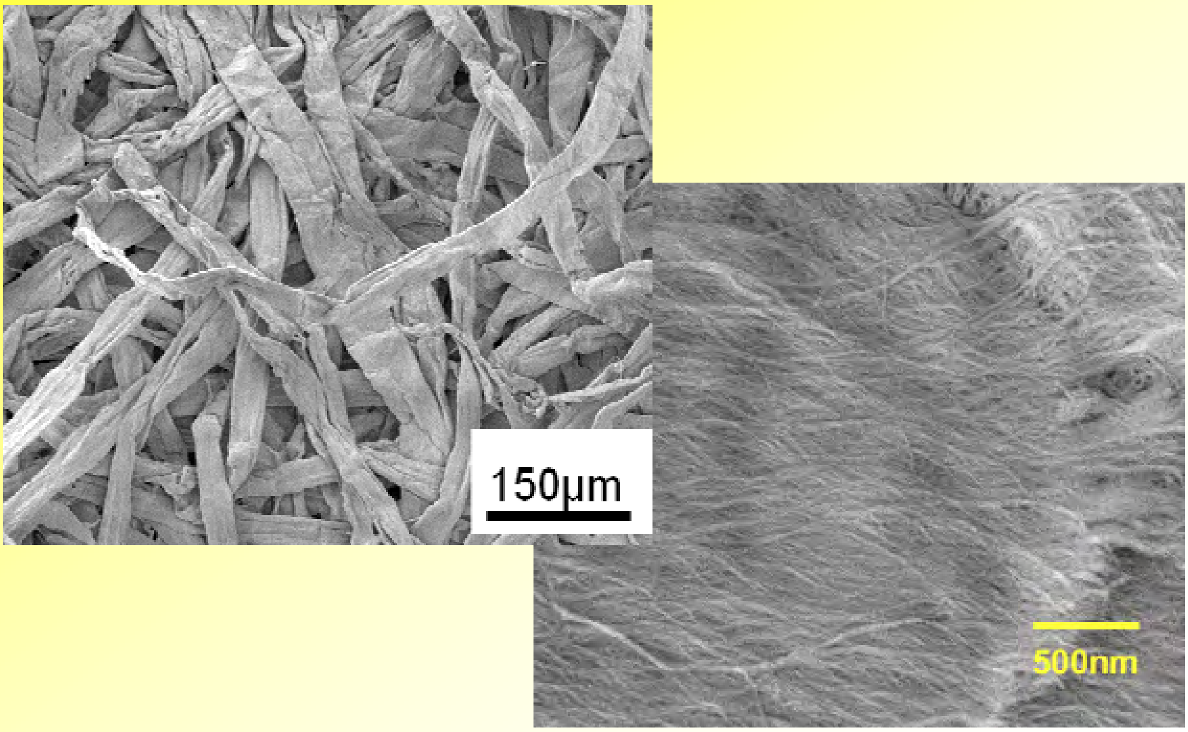


Hiroyuki Yano

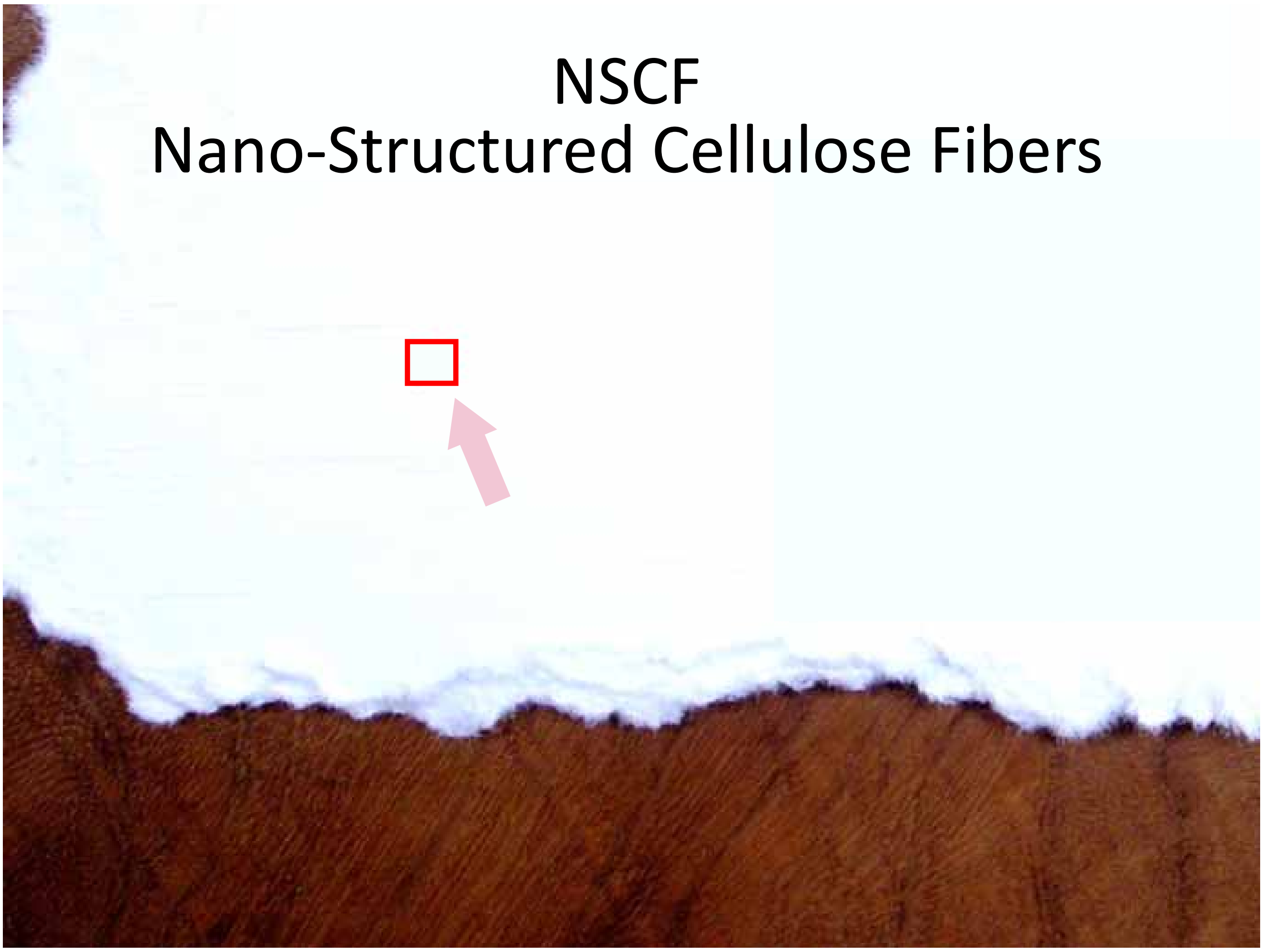
Research Institutes for Sustainable Humanosphere,

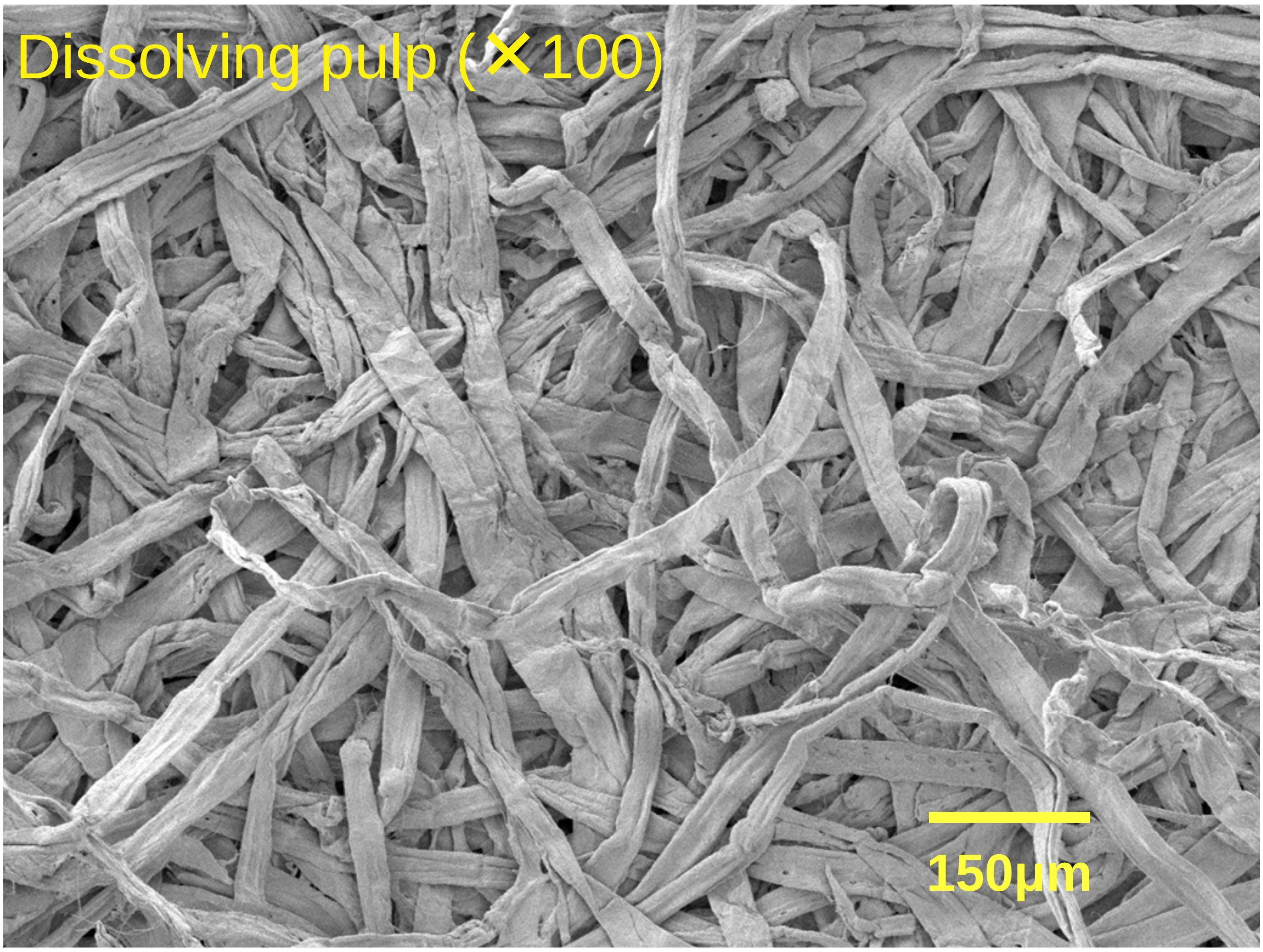
Kyoto University

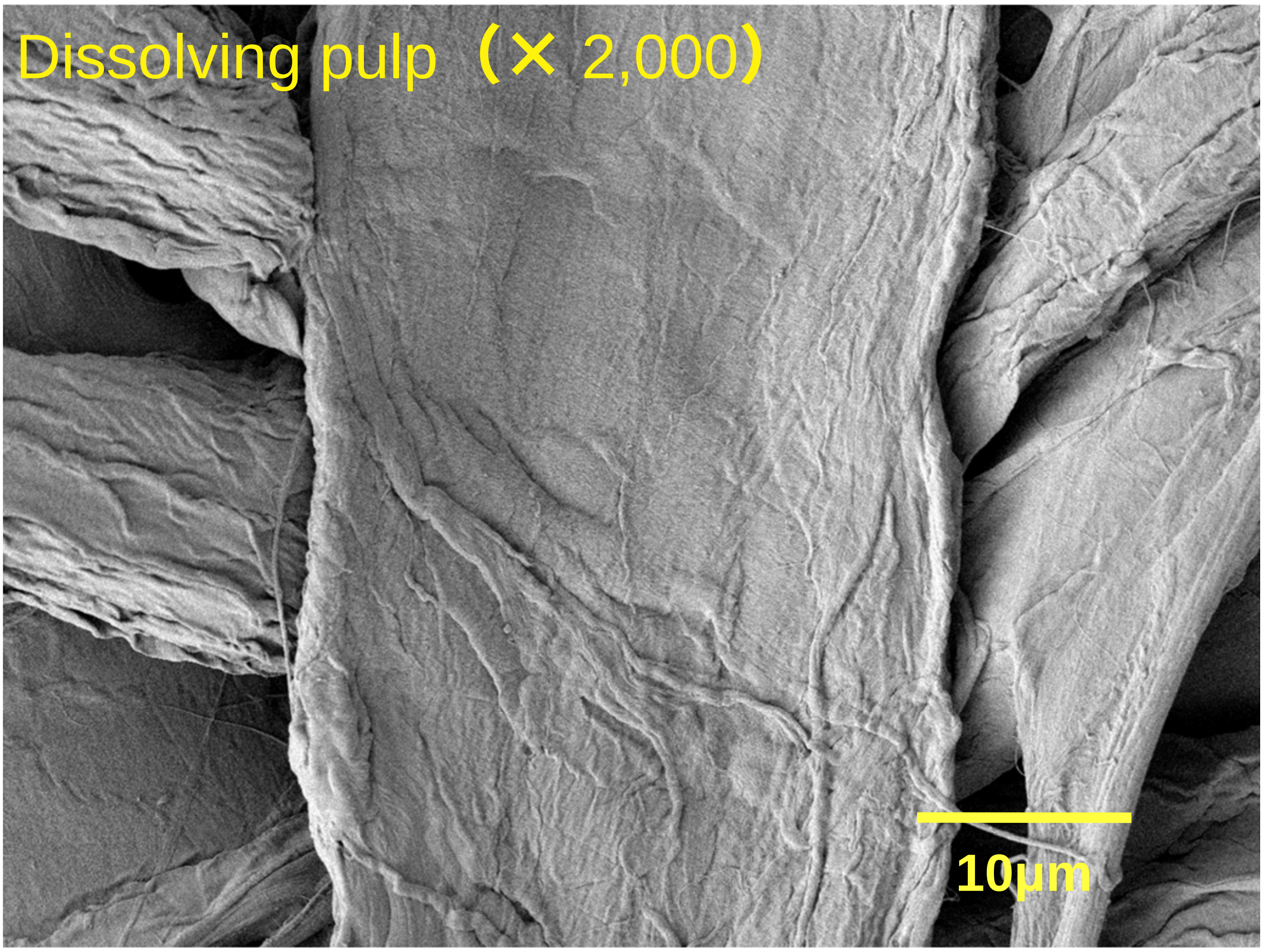
NSCF
Nano-Structured Cellulose Fibers

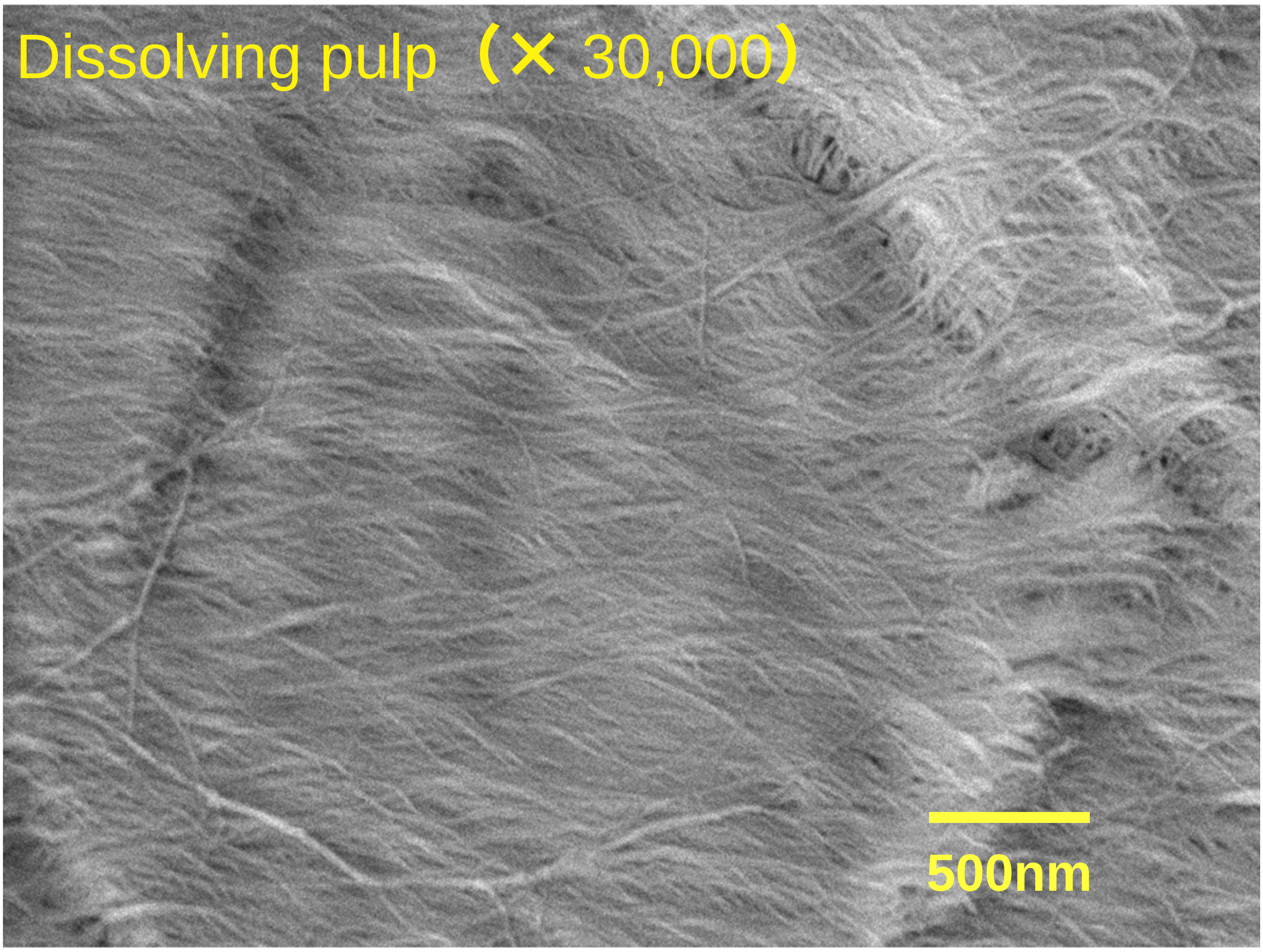


NSCF
Nano-Structured Cellulose Fibers

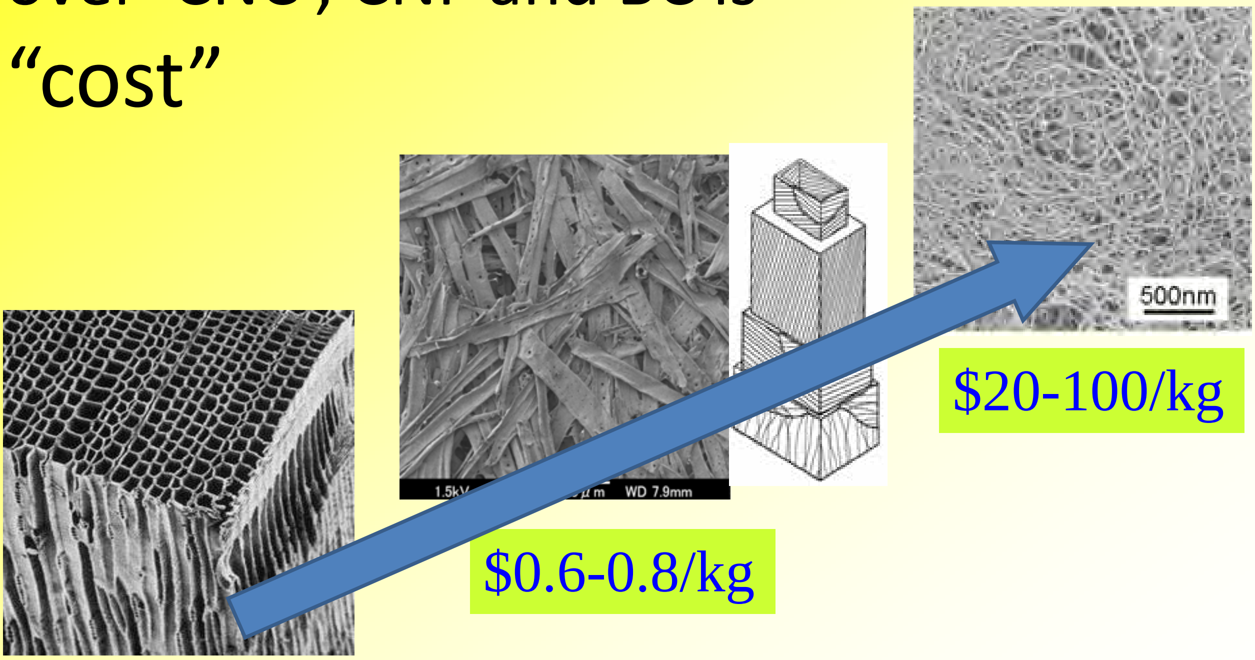





Dissolving pulp（× 2,000）
10μm


Dissolving pulp（× 30,000）
500nm

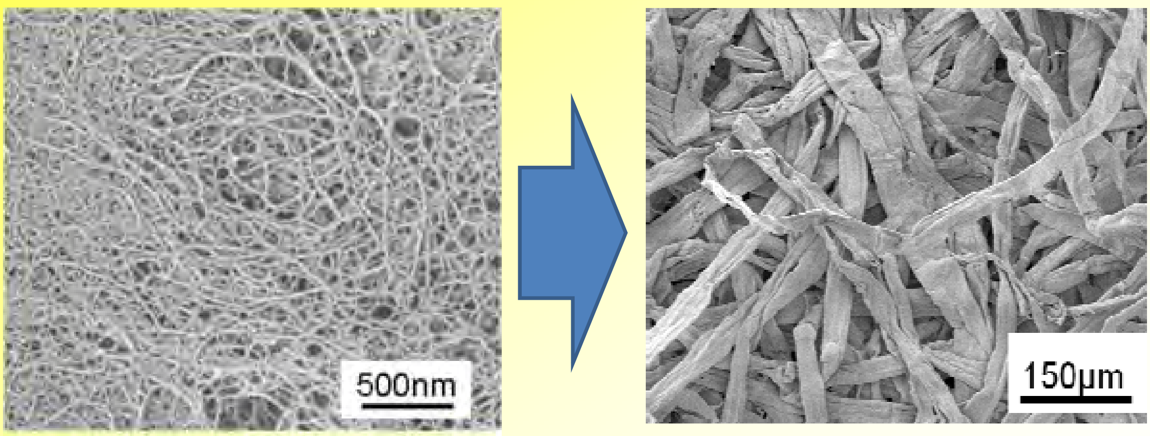
The advantage of pulp: NSCF over CNC , CNF and BC is "cost"



$0.1-0.2/kg

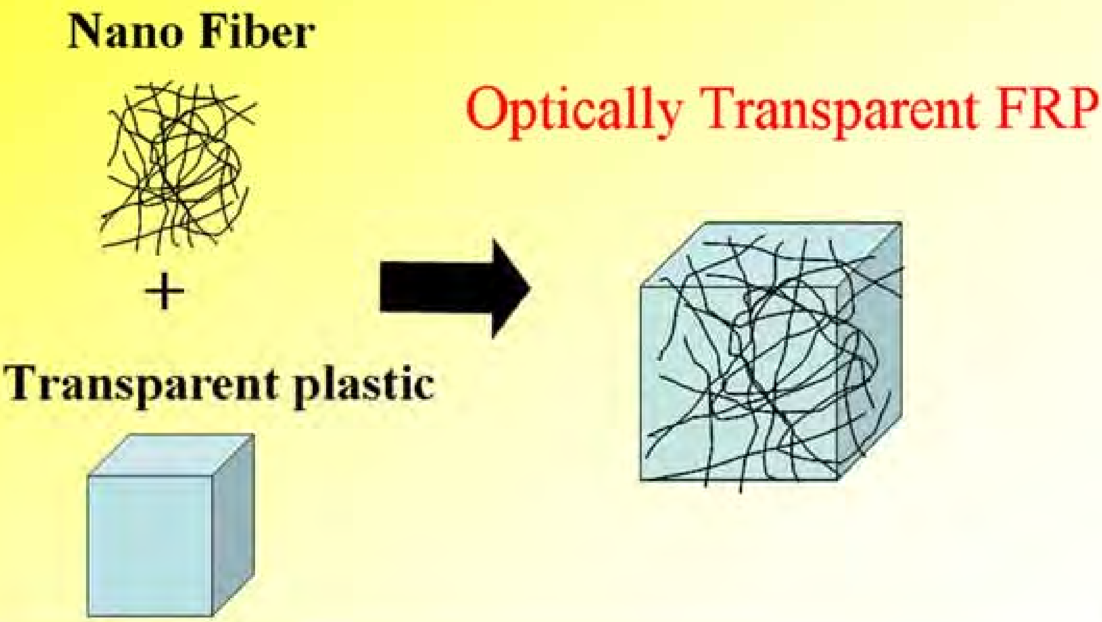
A Paradigm in Nanocellulose Materials

- From nanofibers to nanostructured fibers -



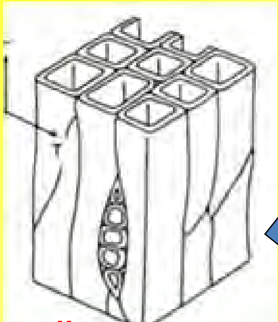
Optically transparent nanocellulose

Mechanical Reinforcement of Transparent Plastic

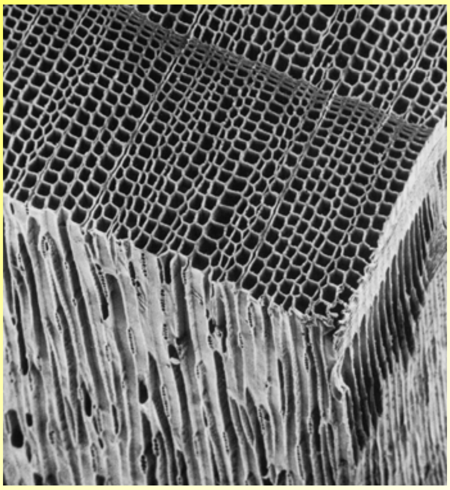


A component less than one-tenth the size of the optical wavelength can eliminate scattering

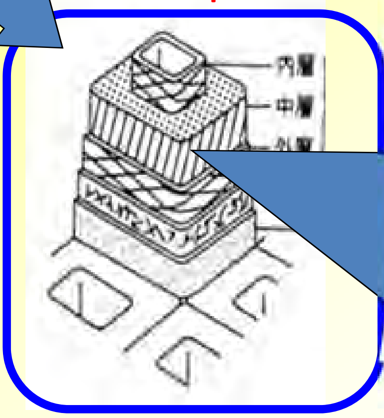
Hierarchical Structure of Wood



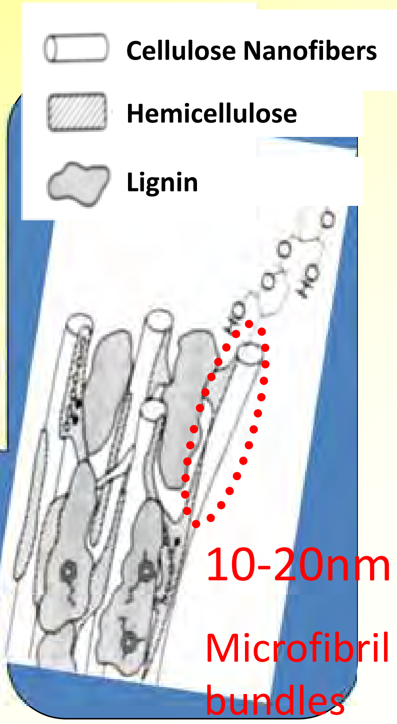
Cell Structure



10-50µm

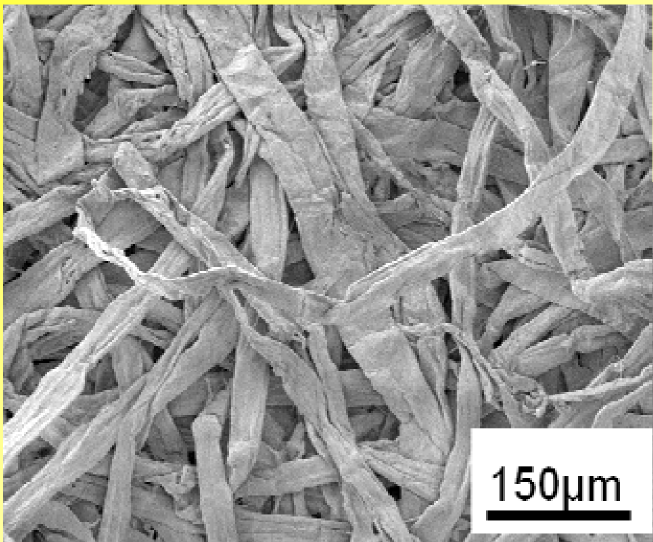


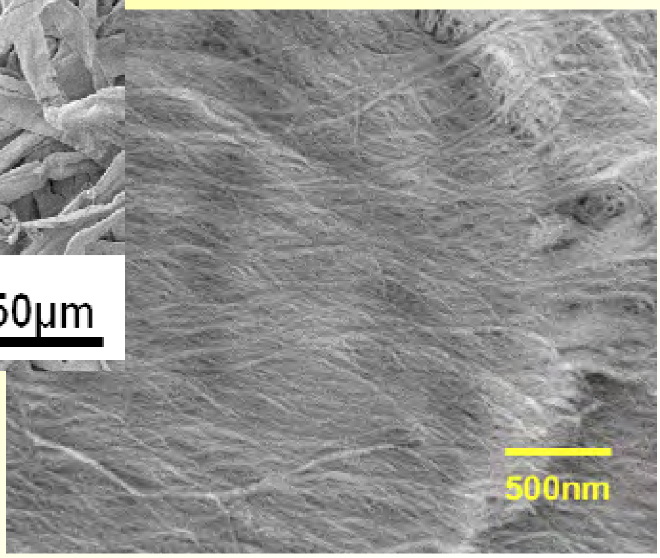
Cell Wall Structure



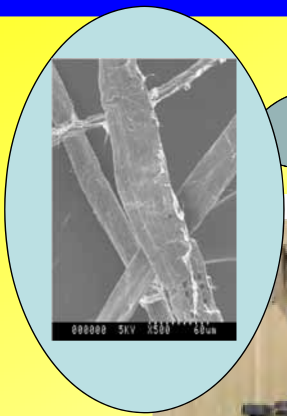
Nano fibers and Matrix

Nano-Structured Cellulose Fibers

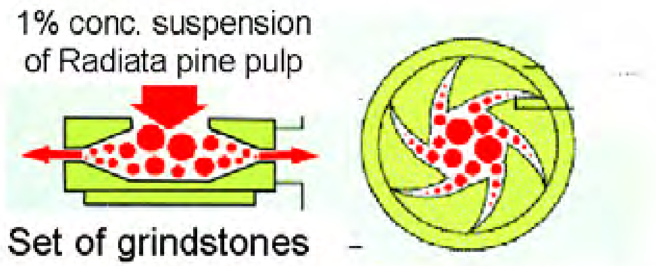


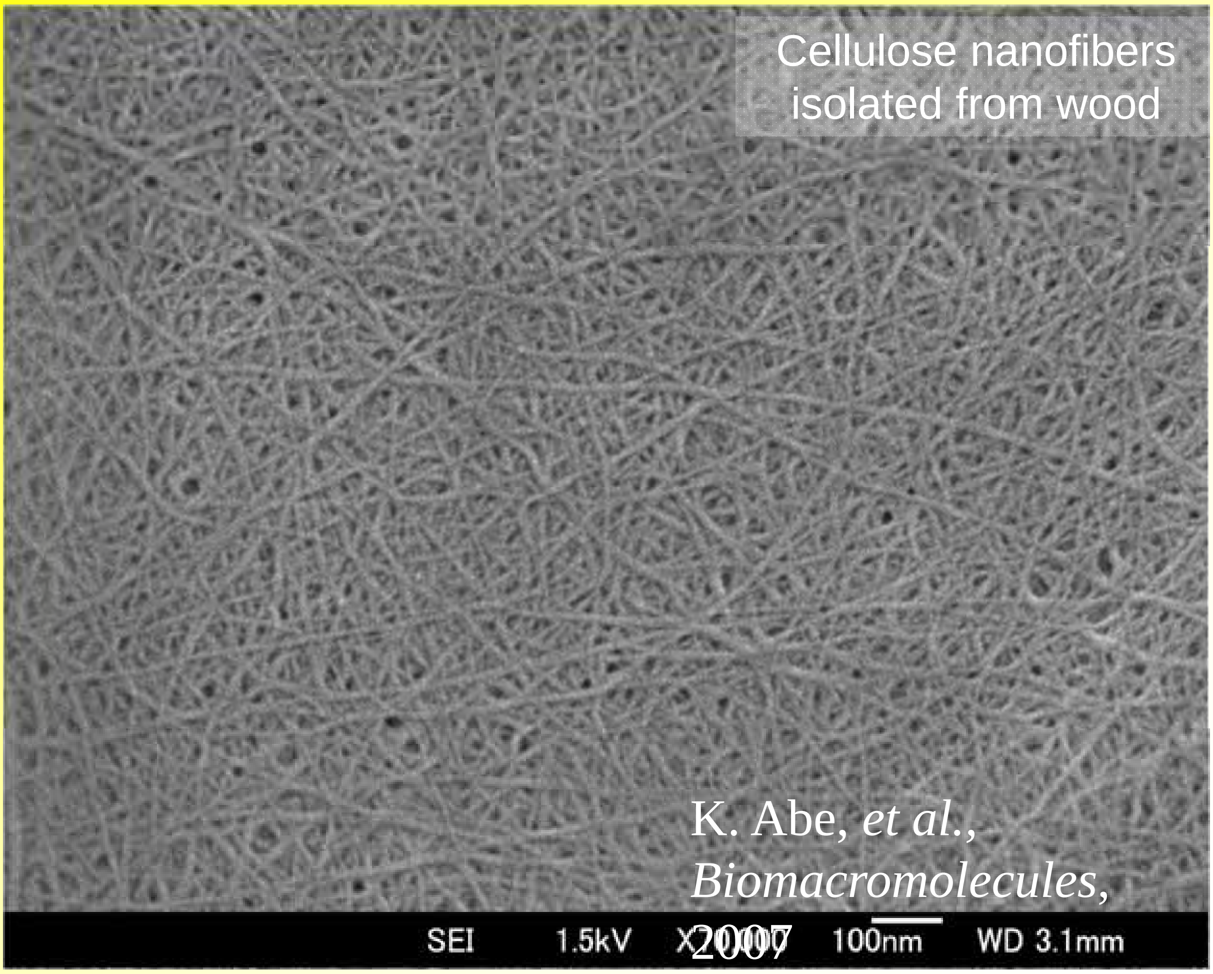


Fibrillation by a Grinder



Never- dried pulp





Cellulose nanofibers
isolated from wood

K. Abe, *et al.*, *Biomacromolecules*, 2007

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%

Cellulose Nanofibers:CNF

- Semi-crystalline extended chains

✓ Tensile strength:3GPa → aramid fibers

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

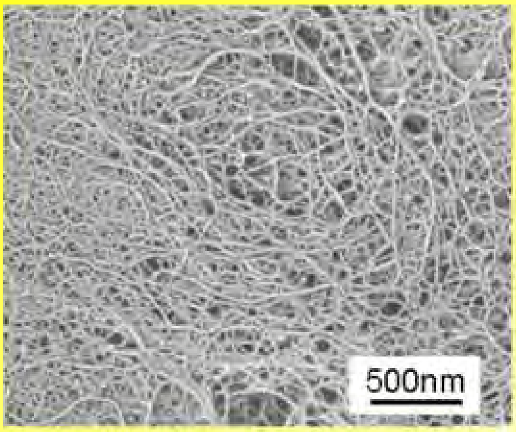
✓Young's modulus:138-141GPa （-200~+200℃）

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

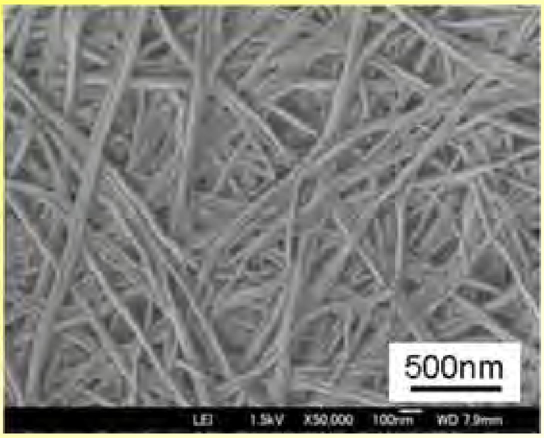
✓Thermal expansion coefficient：0.1 ppm/K → quartz glass

(T. Nishino, Personal communication, 2004)

✓High specific surface area



Wood Nanofiber



Bacterial Cellulose

	Density (g/cm^3)	Light Transmittance[1] (%)	CTE[2] (10^{-6} °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)

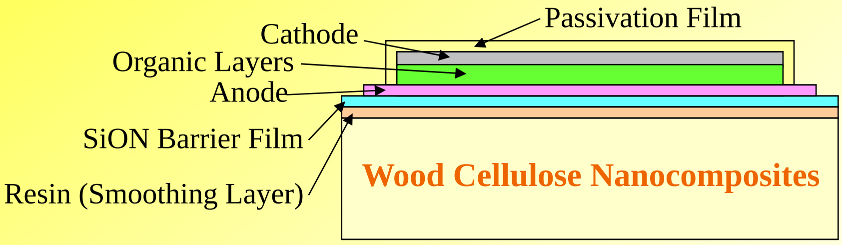
[1]600nm、[2]20～150℃

Optically Transparent Cellulose Nanofiber Reinforced Composite

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

Luminescence of an OLED deposited on the wood nanofiber-composite

Device structure

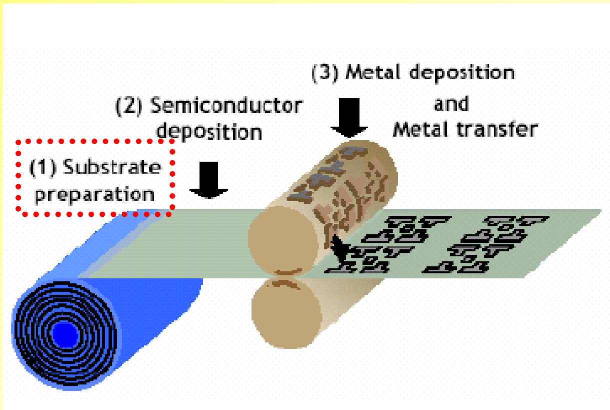


Y. Okahisa, *et al., Comp. Sci. Technol*. (2009)

A future FPD processing; Continuous "Roll to Roll"

R2R process：simple and inexpensive.

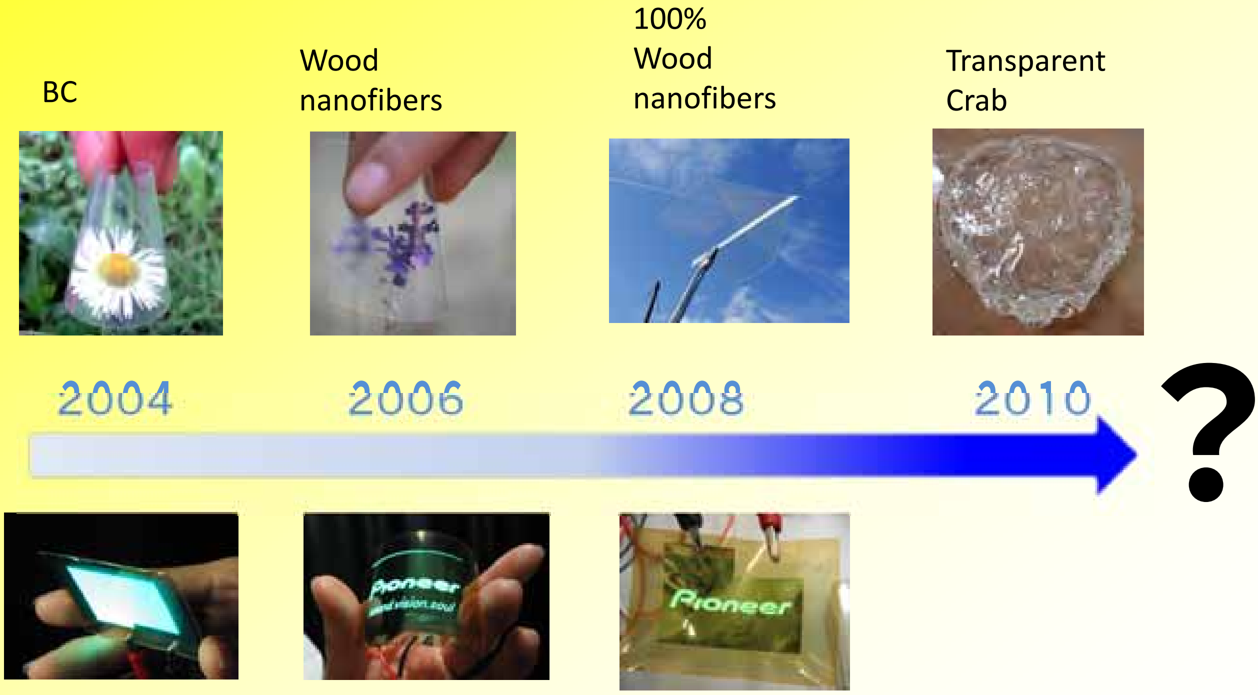
R2R processing enables the continuous deposition of functional materials such as semiconductor, transparent conductive films and gas barrier films on a roll of substrate.



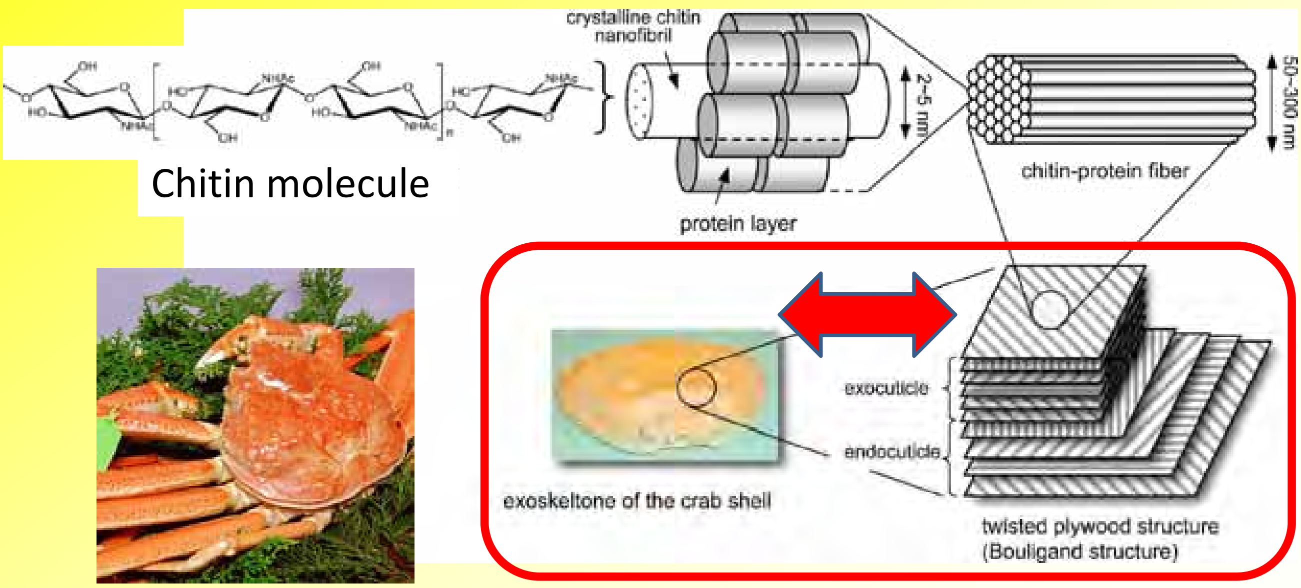
A demonstration of production of OLED by R2R process

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

Transparent materials developed in Kyoto Uni.



Micro to Nano Structure of Crab



Schematic presentation of the exoskeleton structure of crustacean shell. **(Ifuku, et al. Biomacro, 2009)**

Crab shell powder, Red king

↓

Demineralization ($CaCO_3$) by HCl

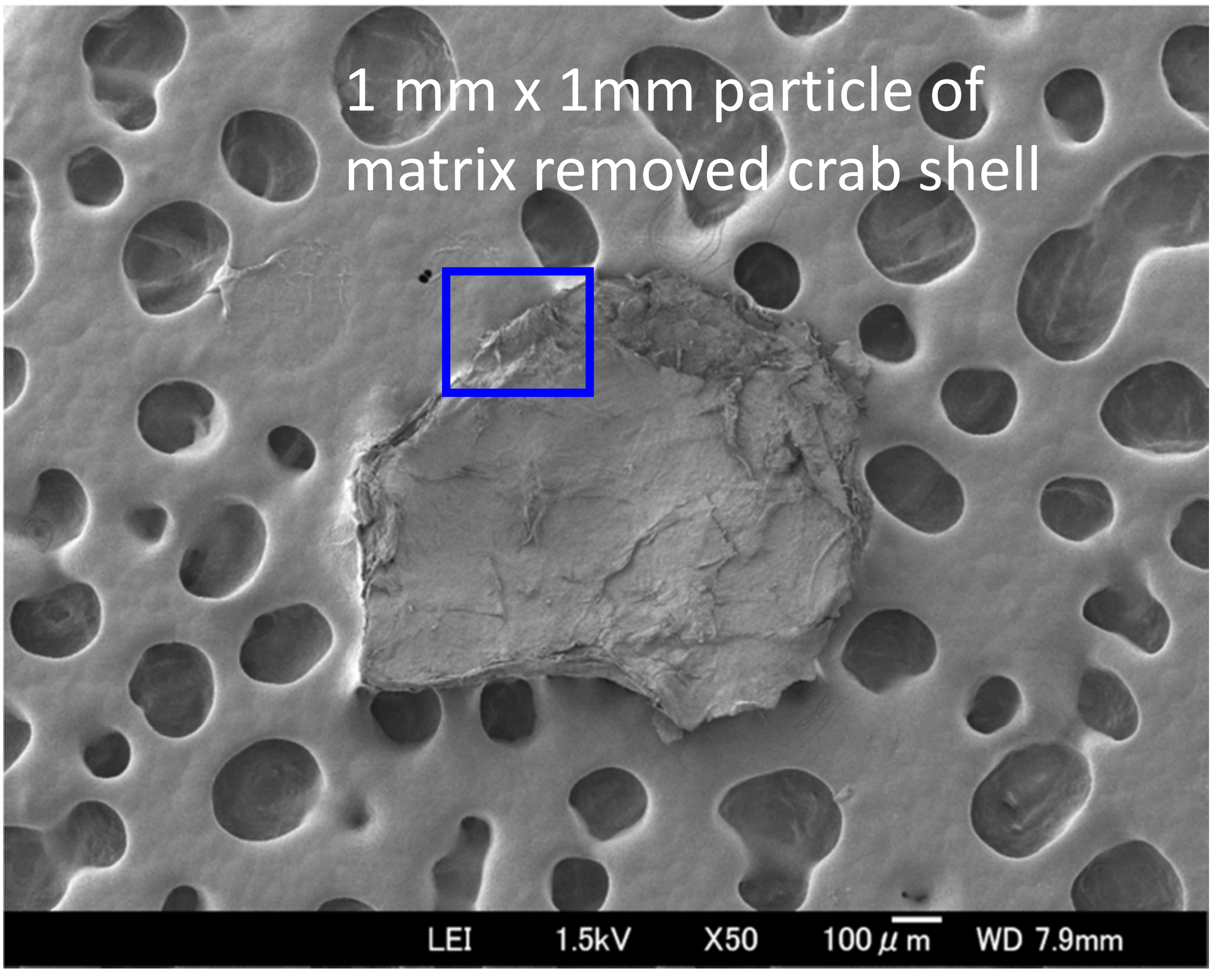
↓

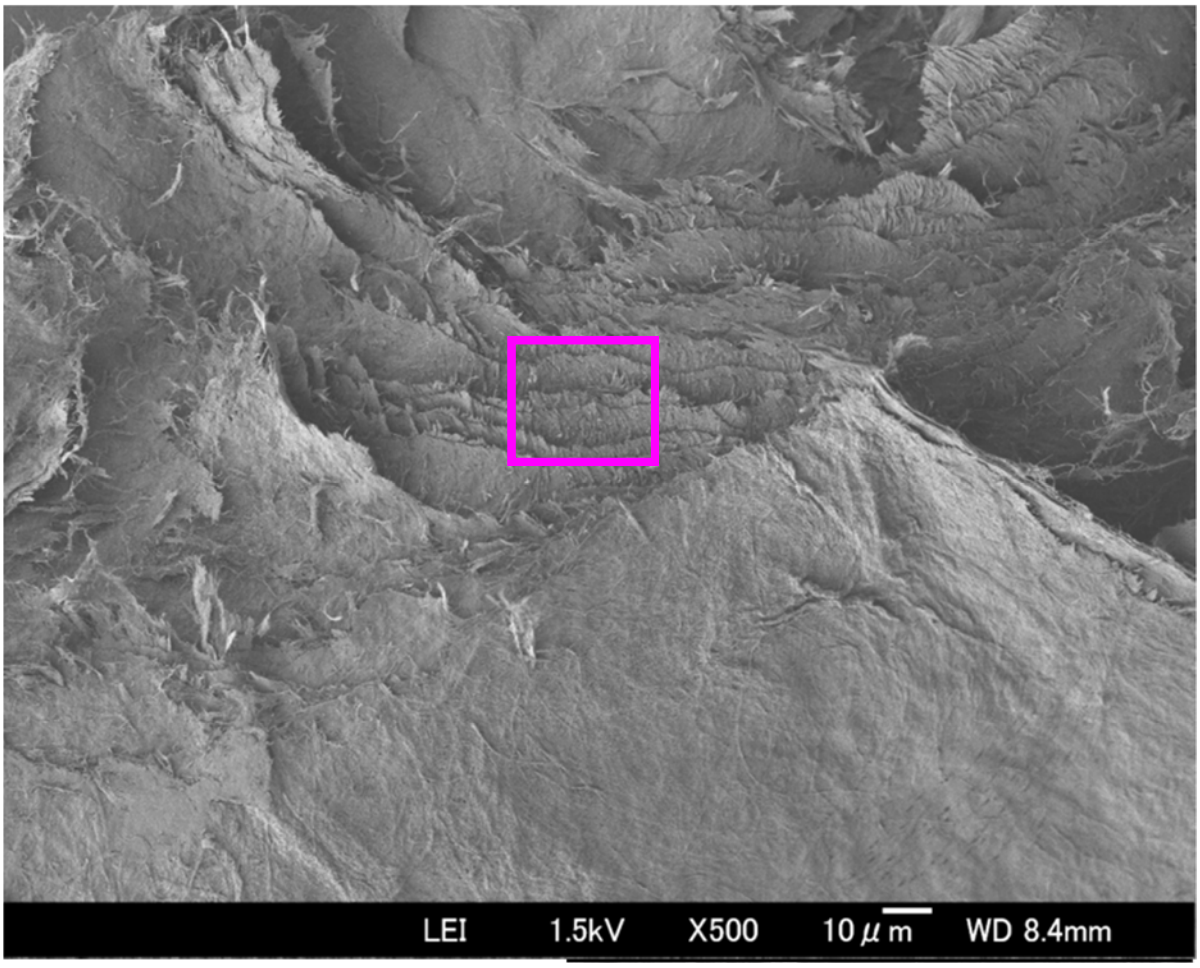
Deproteinization by NaOH

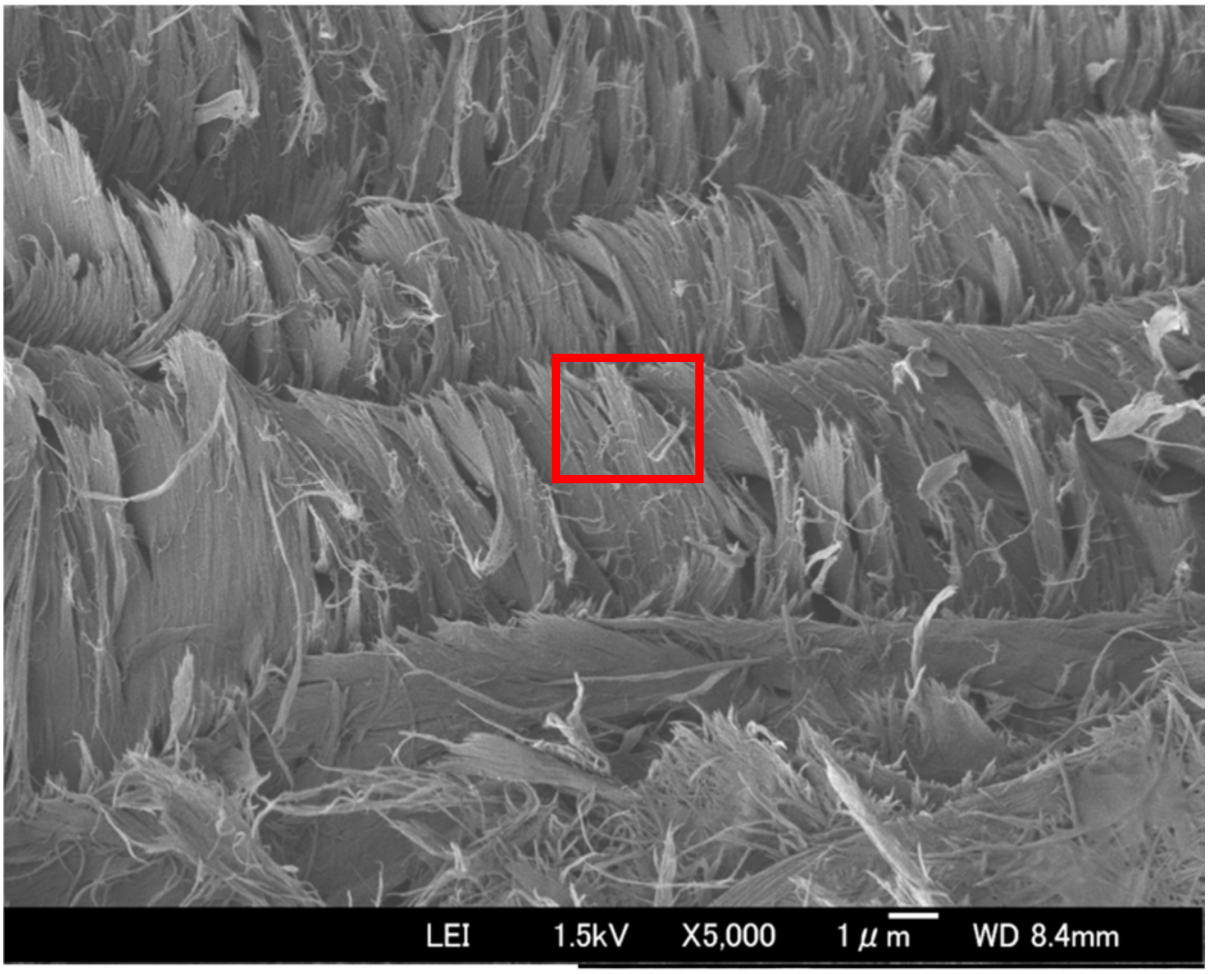
↓

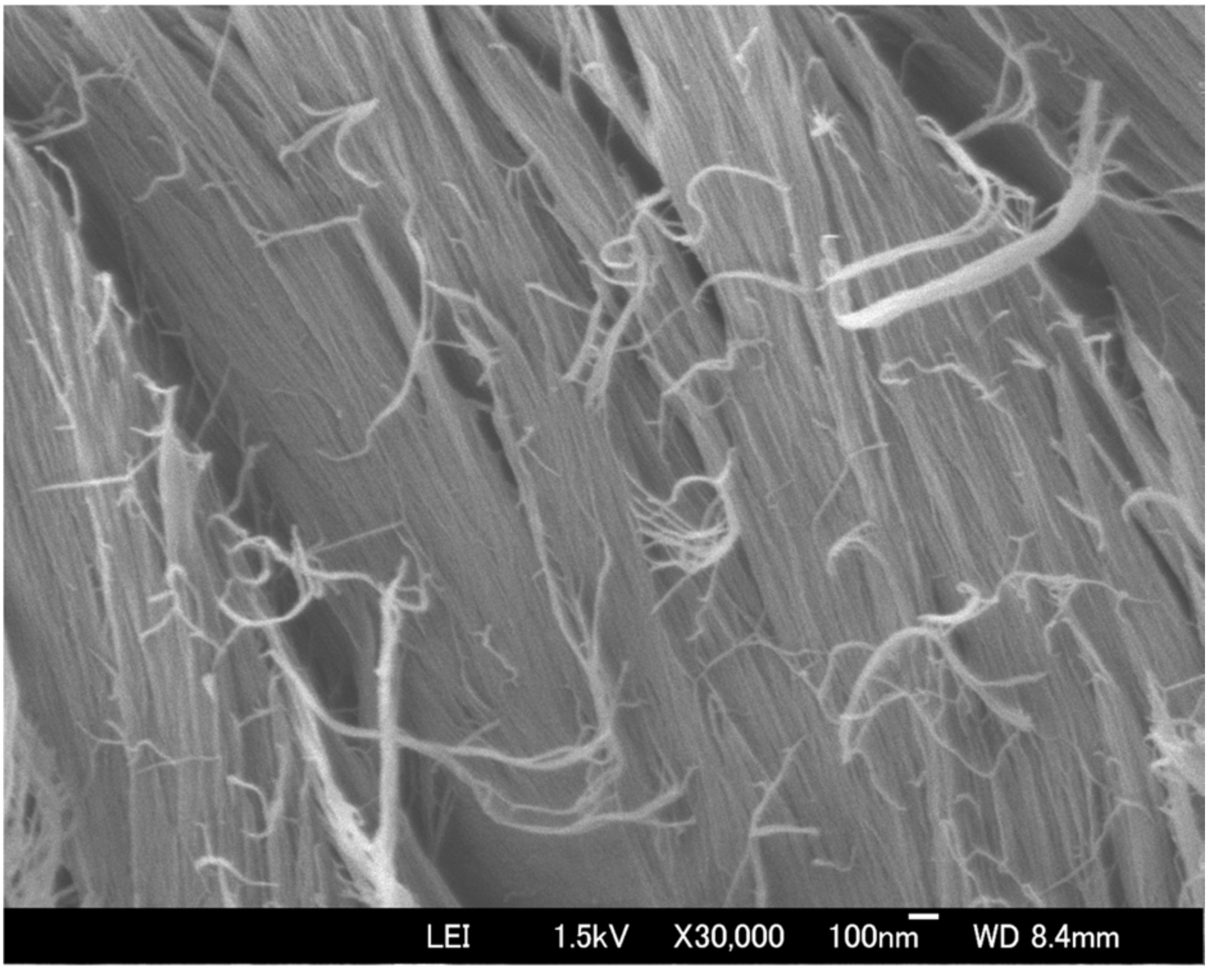
Pigment removal by ethanol

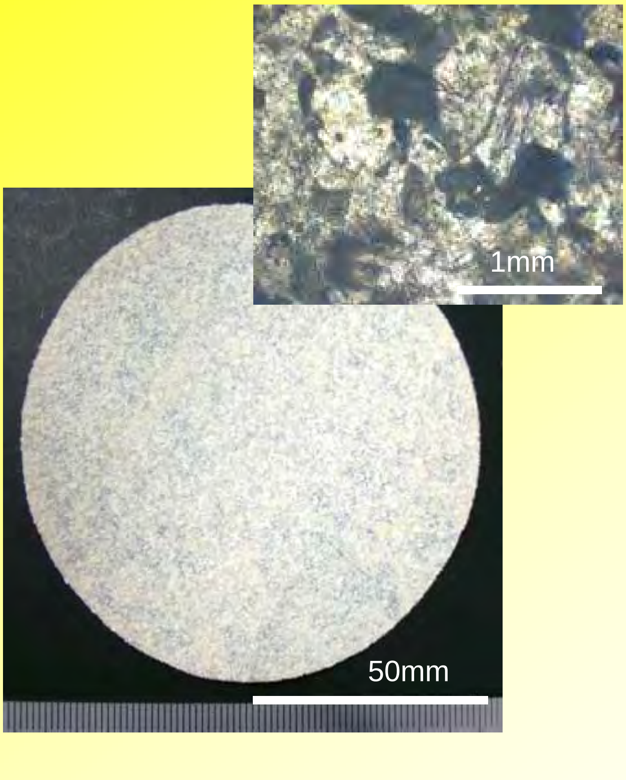
I. Md. Shams and Yano, 2009

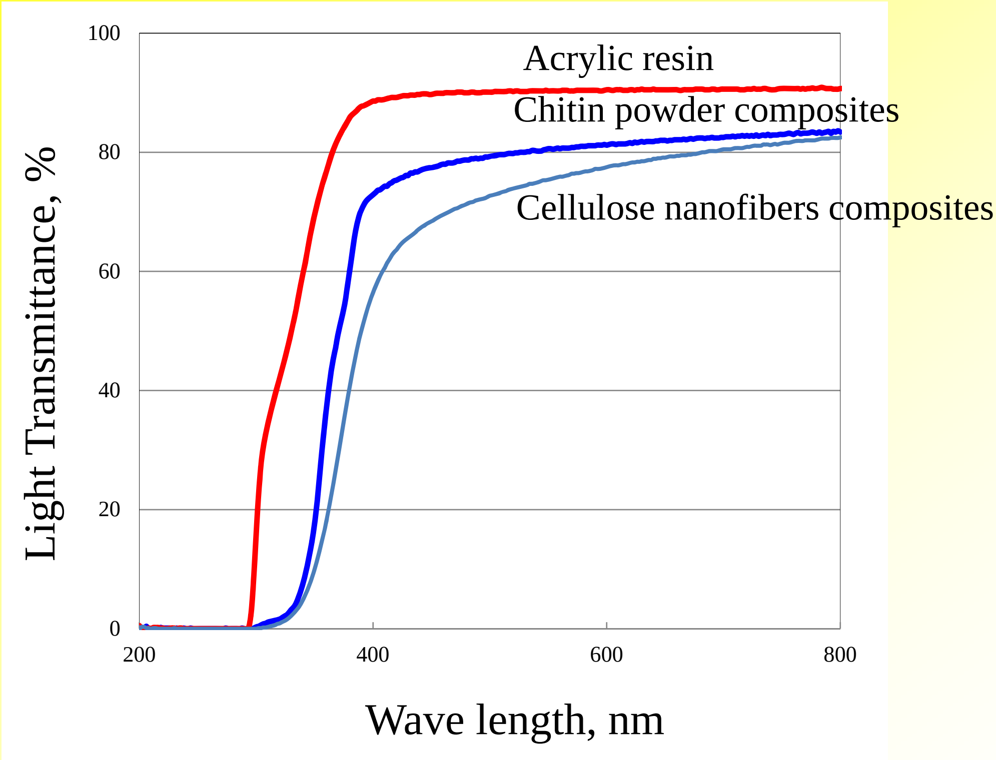



LEI
1.5kV
X500
10 μm
WD 8.4mm


LEI
1.5kV
X5,000
1 μm
WD 8.4mm

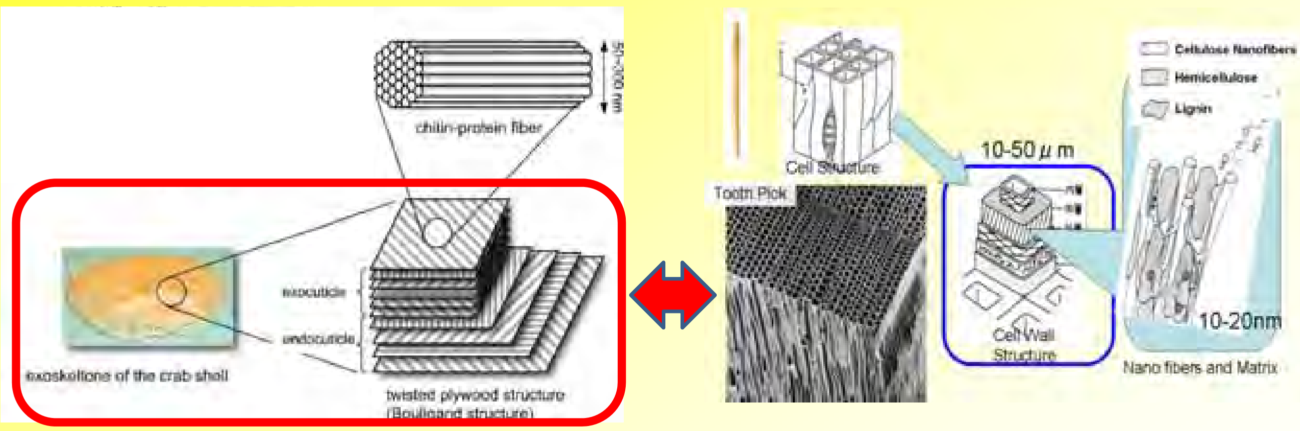

LEI
1.5kV
X30,000
100nm
WD 8.4mm


1mm
50mm



(a) Light transmittance of the chitin powder reinforced acrylic resin sheet (thickness 190 µm, Powder content: 22wt%) and cellulose nanofibers reinforced acrylic resin sheet (thickness 100 µm and Fiber content: 60wt%).

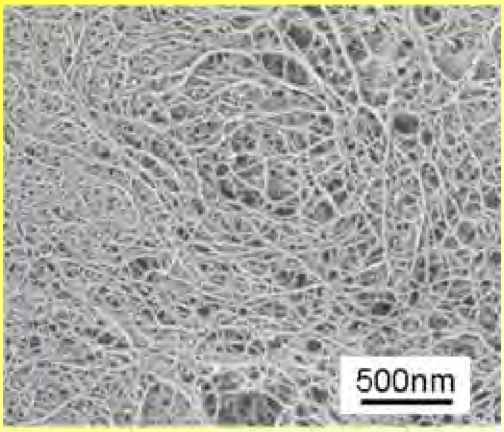
Comparison of Micro to Nano structures

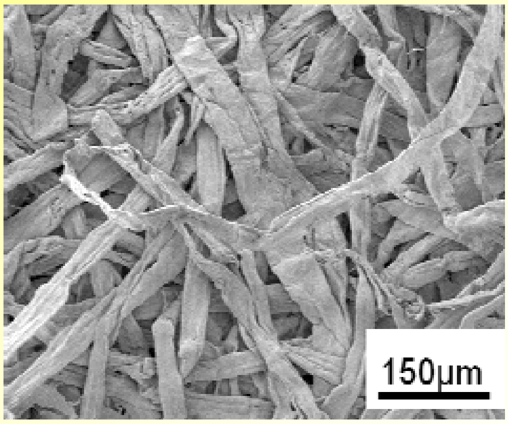


Crab

Wood

The transition from nanofibers to nanostructured fibers



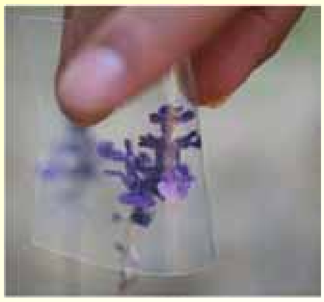


- Encouraged by the transparent crab powder sheet, we undertook the preparation of optically transparent pulp-fiber composites.

Difficulty in the production of nanocellulose reinforced composites

Nanofibrillation of Pulp

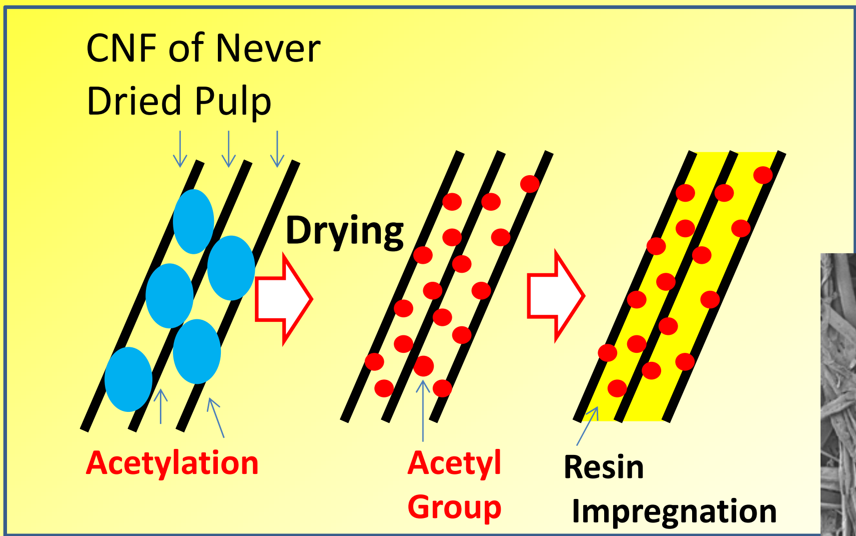
Slow Dewatering Speed



Low Productivity

Optically transparent pulp sheet

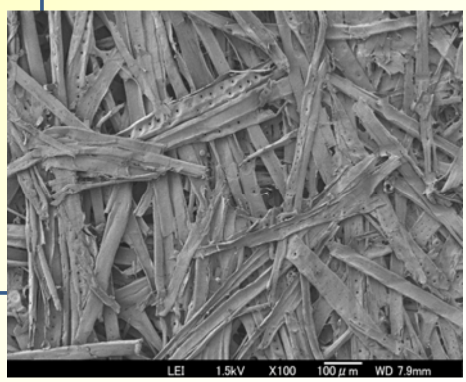
The pulp-fiber sheet was acetylated, with care taken to maintain a never-dried condition, and it was then dried and impregnated with acrylic resin.



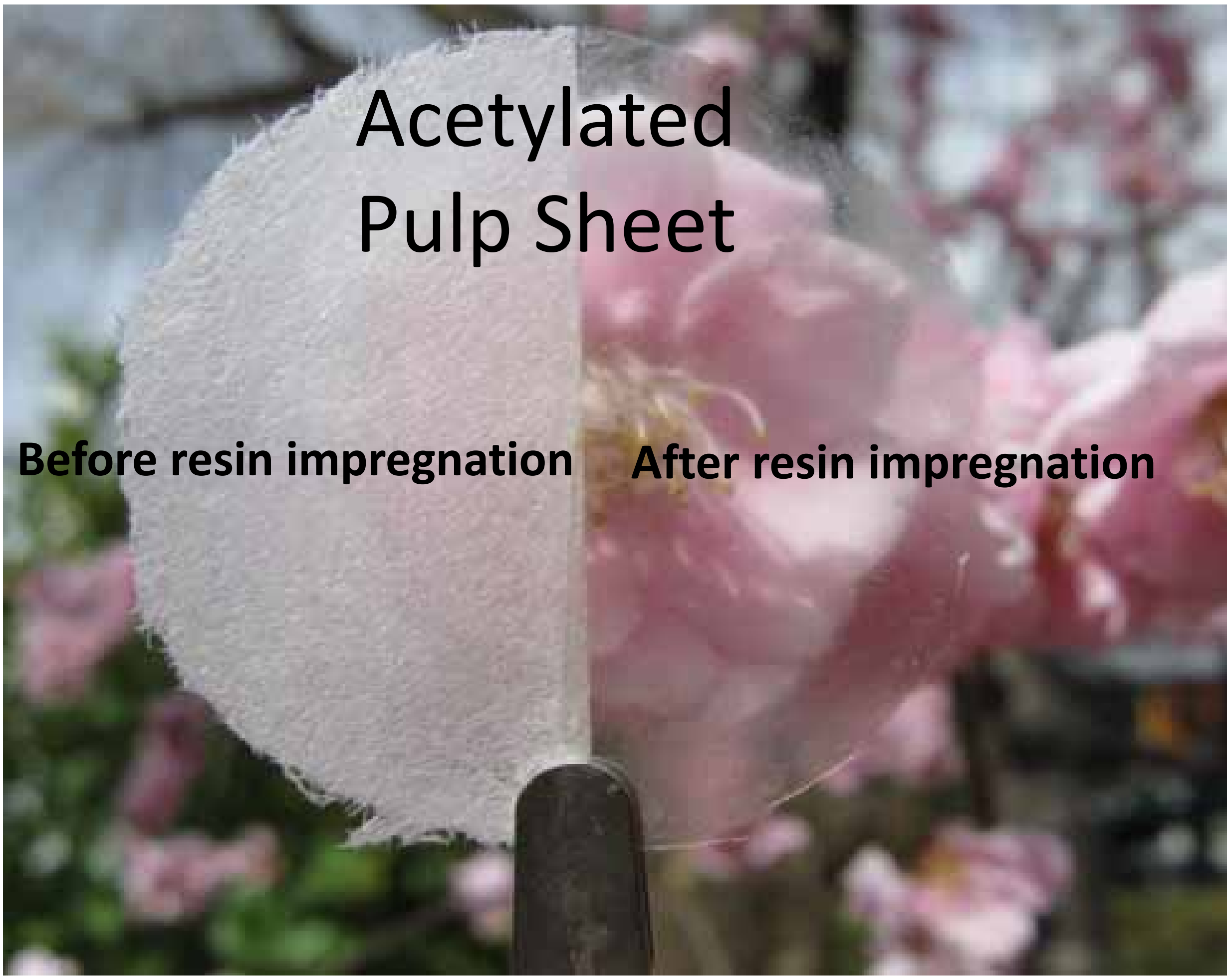
Never dried Pulp

Acetylated dry pulp

Resin impregnated acetylated dry pulp



Acetylated Pulp Sheet



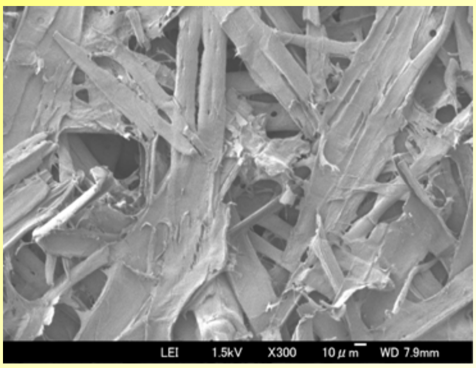
Effect of surface fibrillation using beads mill

Pulp, NBKP

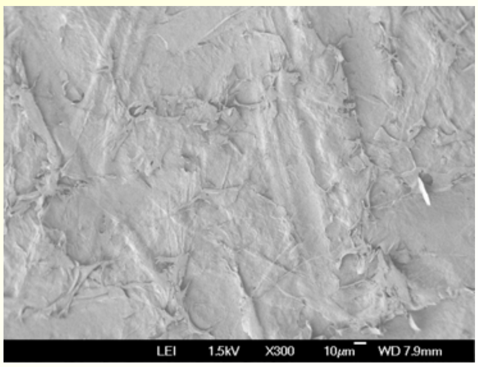
Surface fibrillation

Surface fibrillated pulp

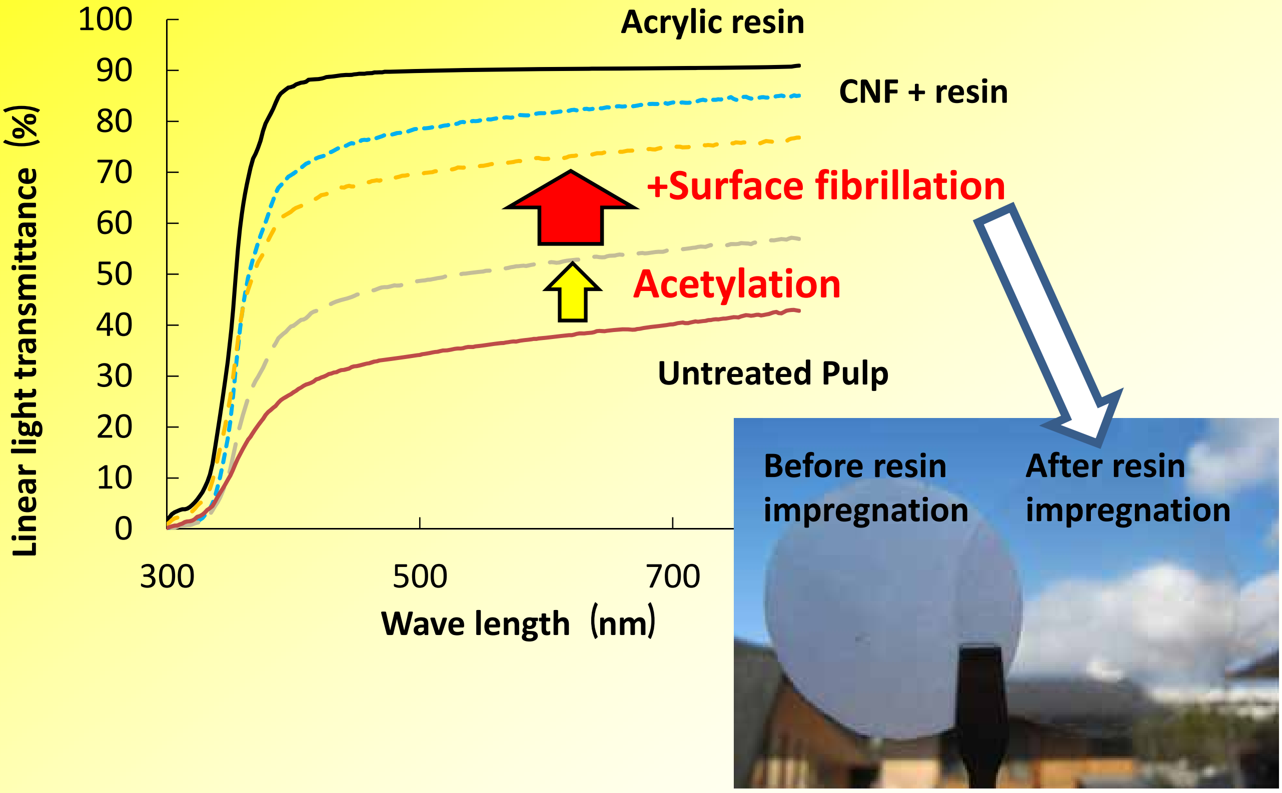
Pulp sheet

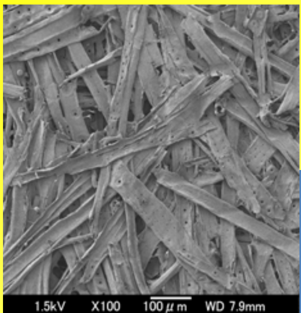


Surface fibrillated pulp sheet



Changes in transparency of acrylic resin impregnated paper

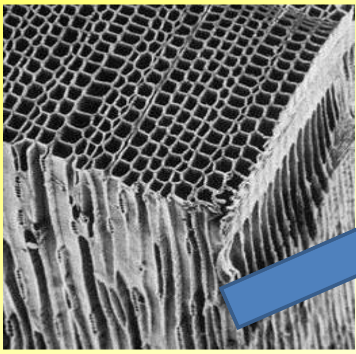




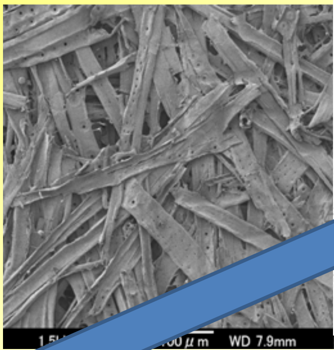
	Thickness (um)	Fiber content (%)	CTE (ppm/K)	Linear Light Transmit. (%)	Total Light Transmit. (%)
Acetylated surface fibrillated pulp	60	18.0	11.9	70.0	88.1
Acetylated pulp	100	26.0	8.30	54.1	87.8
Untreated pulp	100	28.5	3.64	43.7	87.0
Nanofiber[1)]	100	35-40	12.1	82.0	90.0
Resin[1)]	—	0	213.0	91.0	92.0
※CTE:20-150℃					

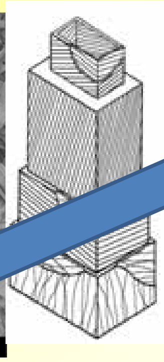
1) Y. Okahisa, et al., Composite Science and Technology ,2009

The advantage of pulp: NSCF over CNC , CNF and BC is "cost & performance"

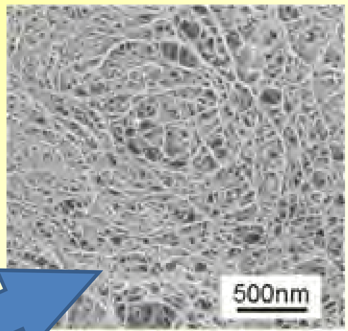


0.1-0.2US$/kg



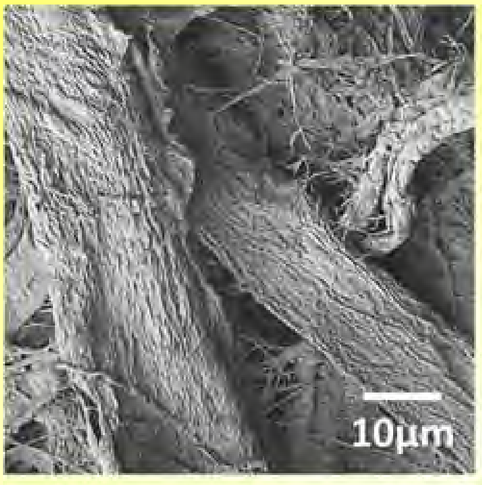


0.6-0.8US$/kg



20-100US$/kg

Another example using NSCF



Chemically modified surface fibrillated pulp
or Chemically modified NSCF

NEDO Green Sustainable Chemical Process Programs from 2009 to 2013

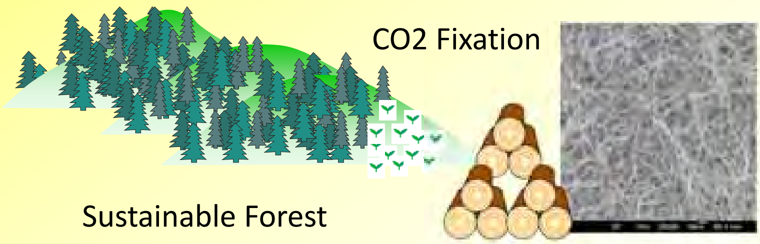
NEDO: New Energy and Industrial Technology Development Organization of Japan

Project Title

Development of high performance cellulose nanofibers reinforced plastics for automotive parts

Organizations: Kyoto University, Kyoto Municipal Institute, Oji Paper, Mitsubishi Chemical , DIC, Seiko PMC

Advisers: Toyota Autobody, Nissan, Suzuki, Denso, Nippon Paint , Panasonic, Japan Steel Works



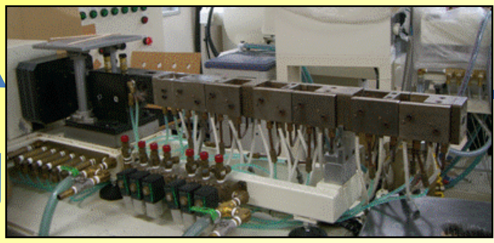
Automotive Parts

Disintegration and well-dispersion of chemically modified pulp in HDPE,PP and PA12 during melt compounding

Chemically modified **dry pulp**

PE, PP, PA pellets + Additives

Twin screw extruder



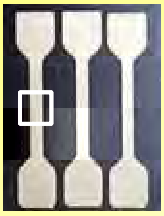
Nanofibrillation & Compounding

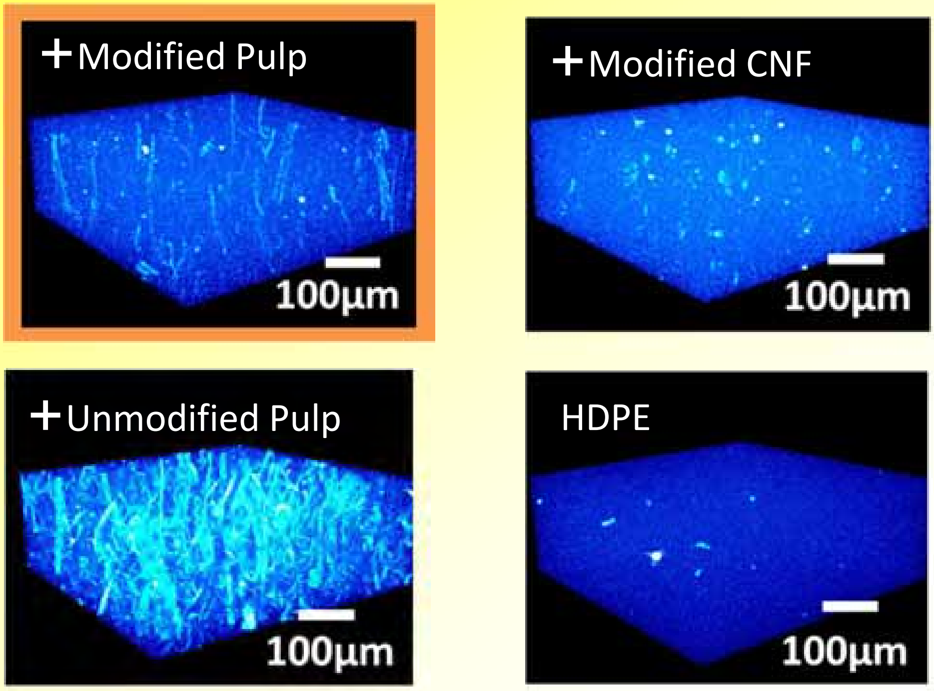
Chemically modified CNF reinforced plastic

Injection molding

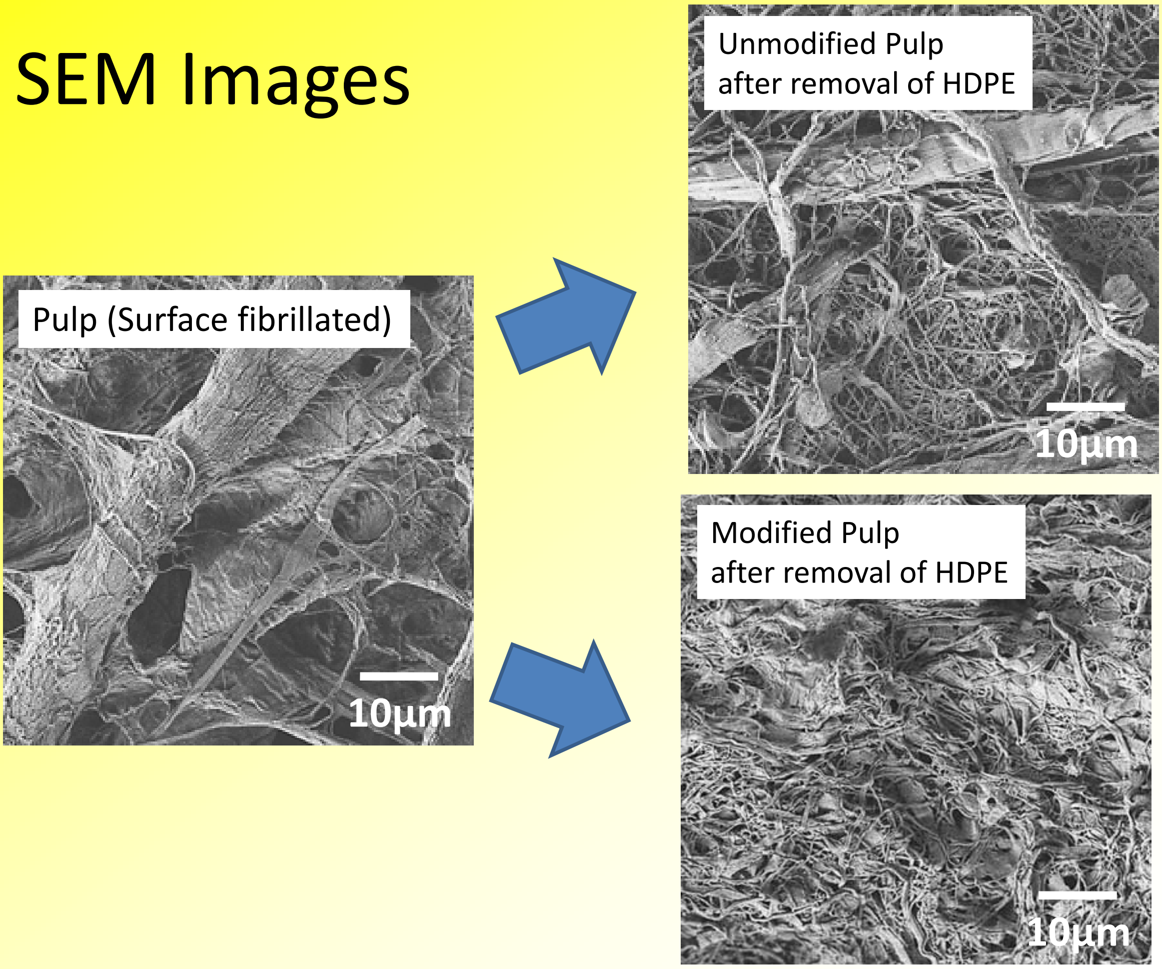
Samples

X-ray tomography of injection molded samples



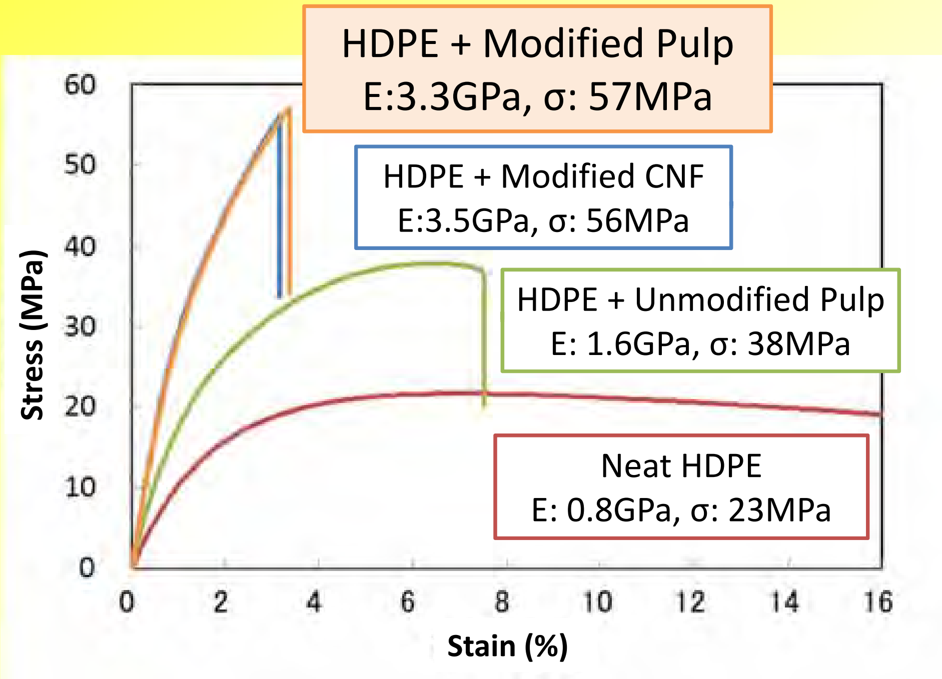


SEM Images



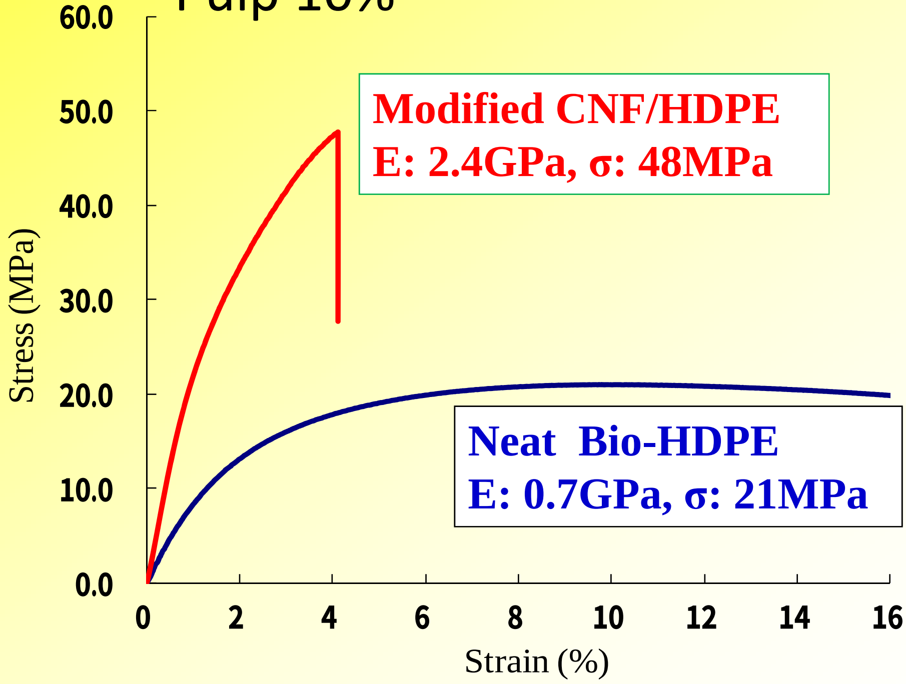
Tensile properties

(Pulp or CNF 10%)

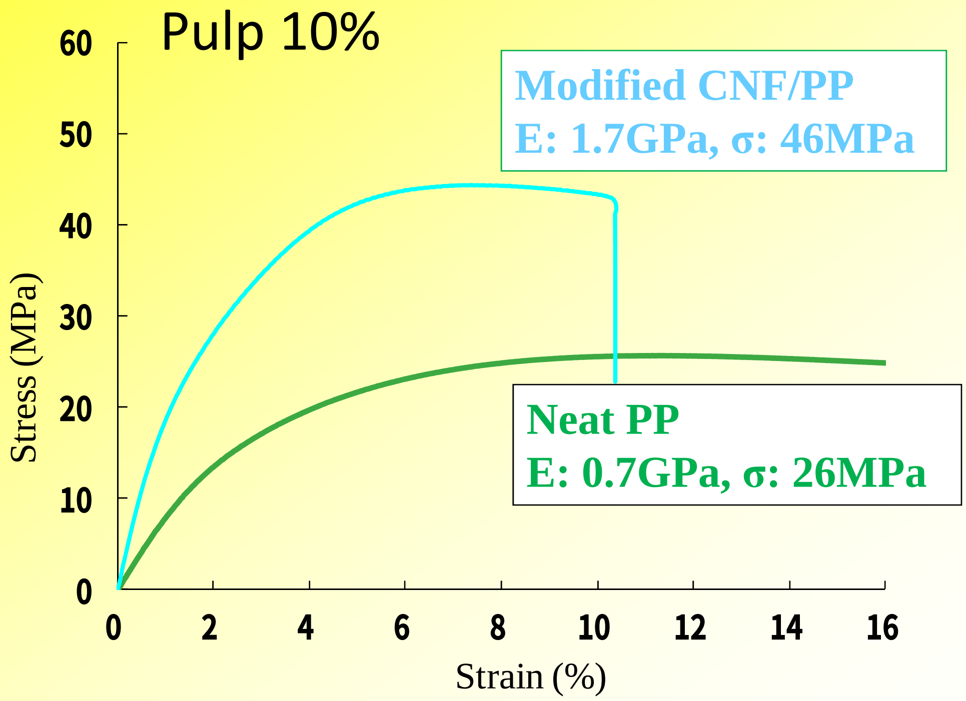


Chemically modified CNF reinforced Bio-HDPE

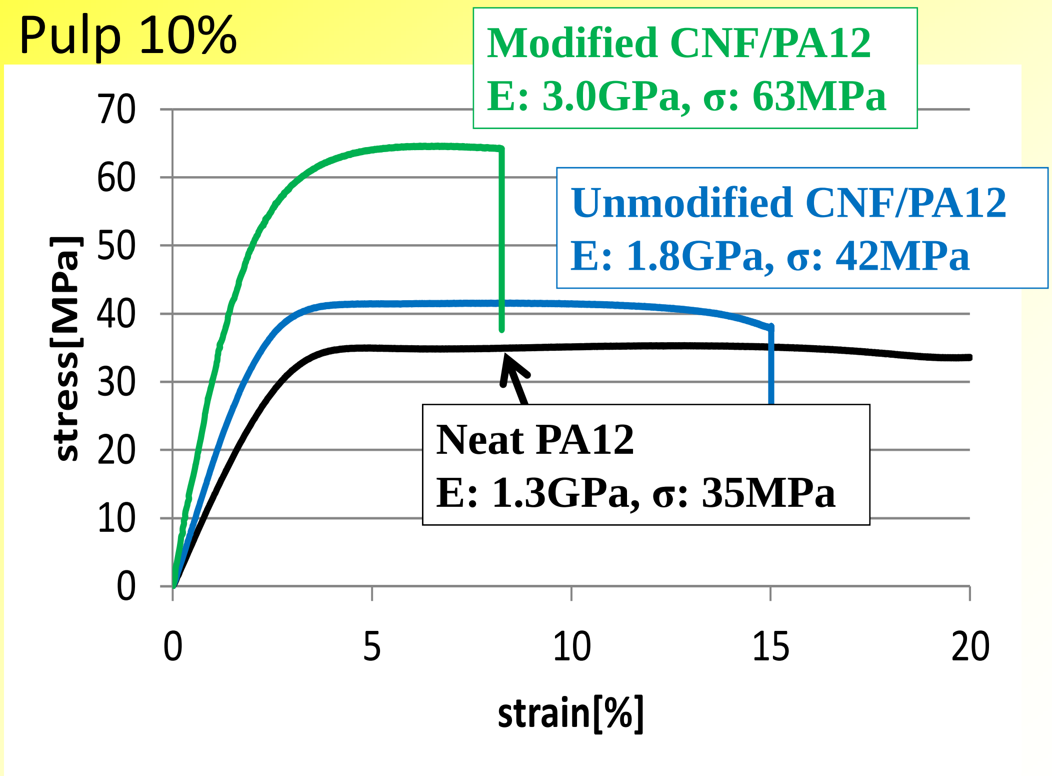
Pulp 10%



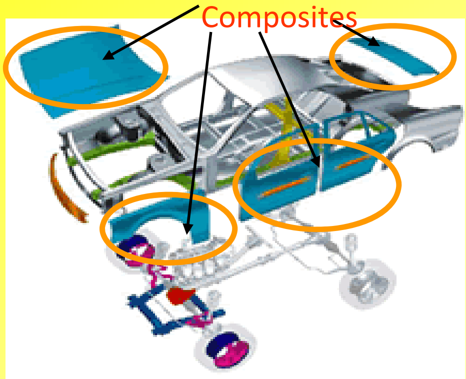
Chemically modified CNF reinforced PP

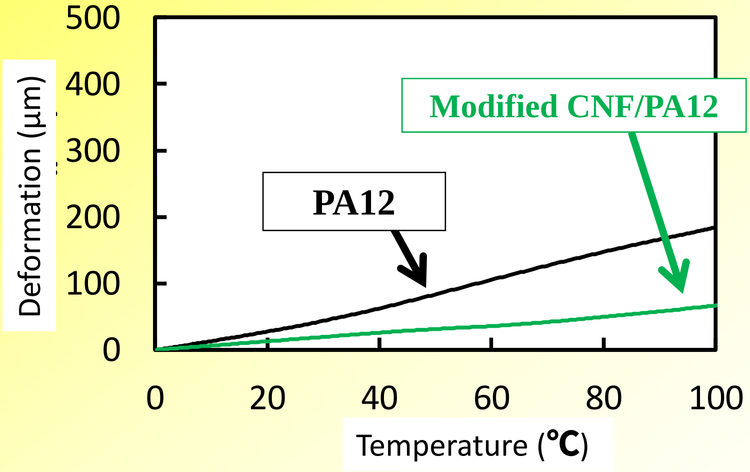


Chemically modified CNF reinforced PA12



Chemically modified CNF reinforced PA12





	CTE (0-100℃) ppm/K
PA12	92
Modified CNF/PA12	24
Aluminum alloy	23

Thank you very much for your kind attention!