Nano Cellulose Composite with Various type of Thermoplastic Resins and Their Enhanced Mechanical Strength and Thermal Properties

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Branch and Factory : Kawanishi Factory, Tada Factory, Kamo Factory, Shizuoka Factory, Tokyo Sales Office, Europe Office (Germany)

Number of Employees : approximately 100

Established in 2007 as startup company within Fuji Pigment Co.,Ltd (color business, established in 1938) who research and develop cutting edge technology in the field of energy and environmental green science

Our motivation

Environmental Problem
Global Warming
Depletion of Natural Resources
Lack of Energy
Damaging Environment
Lack of Water
Human Population Explosion
Extinction of Biological Species

Imminent serious problem for Earth caused by Human

Battery, Fuel Cell, Solar Cell

A. Materials for Dye Sensitized Solar Cell, Perovskite Solar Cell

B. Materials for Solid Oxide Fuel Cell (SOFC), Polymer Electrolyte Fuel Cell (PEFC)

C. Lithium Ion Battery for next generation (new cathode, anode, solid electrolyte)

D. Rechargeable Aluminium Air Battery, Aluminium Ion Battery

Bioethaol made from non-edible plant such as wood, bamboo, paper waste, food waste etc…

Various type of Cutting Edge Advanced Functional Materials

Quantum dot, Ionic liquid
MOF : Metal Organic Framework
material for
visible light response type photocatalysis
artificial photosynthesis
thermoelectric materials
oxide nanocolloid
metal nanocolloid
silver nanoink
silver nanowire

conductive ink
carbon nanotube ink
hetero catalyst
hydroxy apatite
chitin, chitosan nanofiber

Biodegradable Materials

1. starch based biodegradable

2. paper, waste paper based biodegradable

3. wood, waste wood, bamboo based biodegradable plastic

4. stone ($CaCO_3$, Clay, Talc, Mica etc…) based biodegradable plastic

(100% nature derived material, no petroleum)

Cellulose nanofiber materials

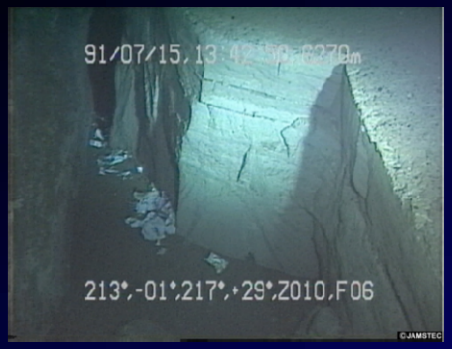
cellulose nanofiber composite material with biodegradable plastic, general plastic, recycle plastic.

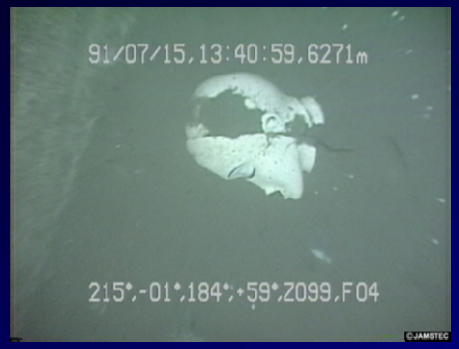
cellulose nanofiber composite color masterbatch material with biodegradable plastic.

cellulose nanofiber in water, various type of organic solvent

chemically modified cellulose nanofiber

plastic garbage problem, micro plastic problem in the ocean

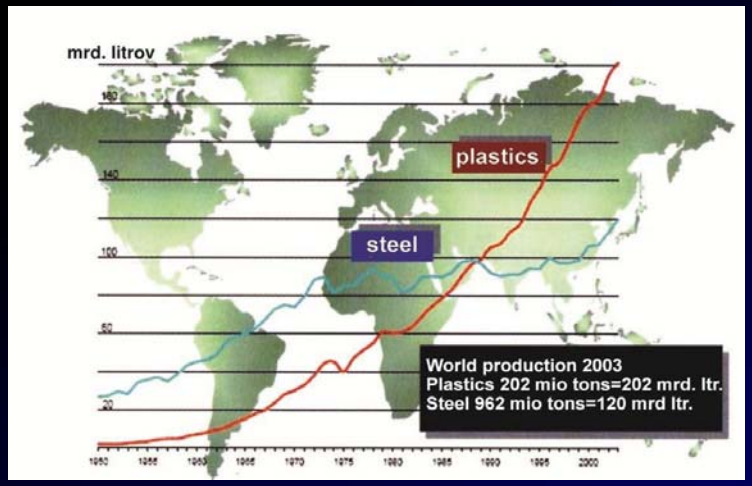




you can find plastic garbage even at the depth of 6270 m !!

large corporation such as Starbucks, Mcdonald's start prohibiting usage of plastic straw, cups etc…

increase of plastic production in the world



the amount of plastic production is more than production of steel.
the amount of plastic production is increasing every year and
the amount of plastic consumption is also increasing every year.

biodegradable plastic application

Film

Shopping bag

Garbage bag

Agricultural multi film

Plant pot

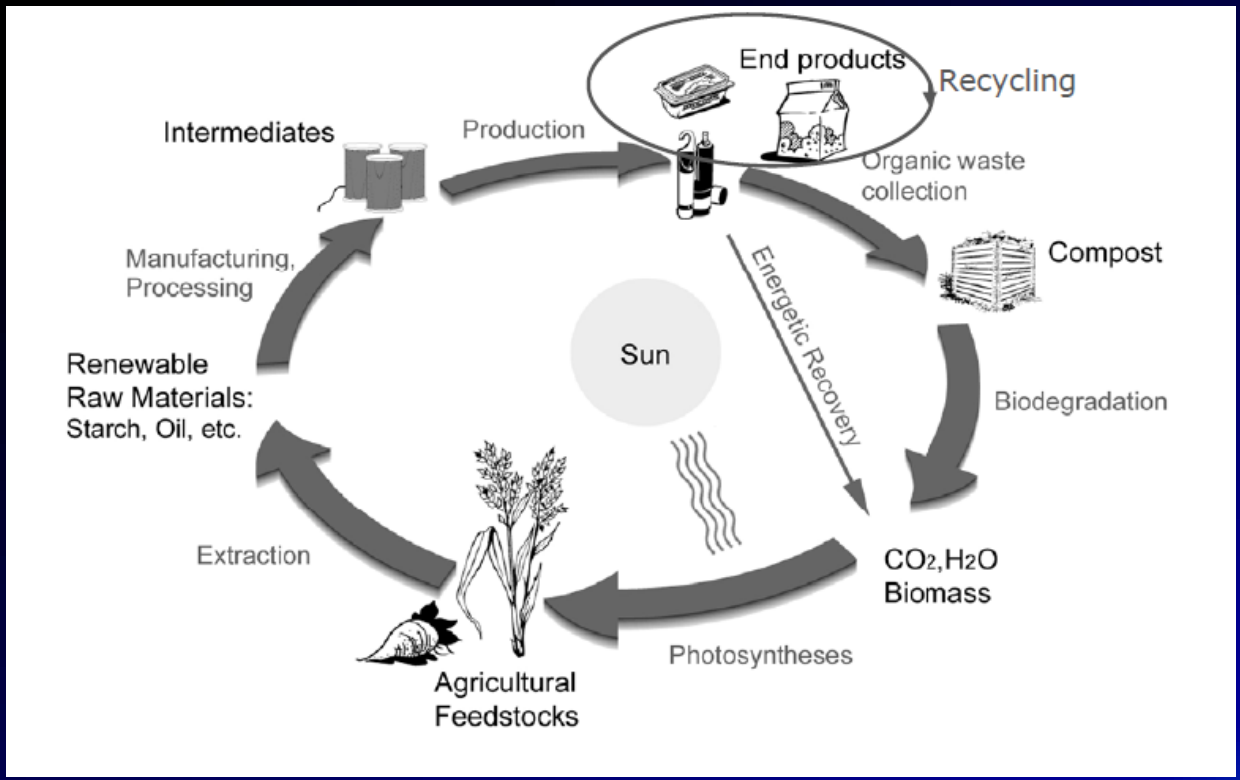
Fishing net

cup

Air cushion

Spoon
Knife
fork

biodegradable plastic



solar Energy + CO_2 = raw material for plastic
(sustainable organic natural resource + CO_2)

biomass base

Bio Plastic

Bio PE(polyethylene)
Bio PP (polypropylene)
Bio PU (polyurethane)
Bio PA (polyamide) etc…

Biodegradable Plastic

PLA(poly lactic acid)
PHA(polyhydroxyalkanoate)
Starch base
Cellulose base etc…

not biodegradable

PE(polyethylene)
PP(polypropylene)
PVC(poly vinyl chloride)
PS(polystyrene)
PET(polyethylene terephthalate)
ABS etc…

biodegradable

PCL(poly caprolactone)
PVA(polyvinyl alcohol)
PBS(polybutylene succinate)
PBAT(polybutadiene adipate terephthalate)
PETS(polyethylene terephthalate succinate) etc…

petroleum base

biomass base

cellulose nanofiber composite : Nano Sakura

Bio Plastic	**Biodegradable Plastic**
Bio PE(polyethylene) Bio PP (polypropylene) Bio PU (polyurethane) Bio PA (polyamide) etc…	PLA(poly lactic acid) PHA(polyhydroxyalkanoate) Starch base Cellulose base etc…
not biodegradable	**biodegradable**
PE(polyethylene) PP(polypropylene) PVC(poly vinyl chloride) PS(polystyrene) PET(polyethylene terephthalate) ABS etc…	PCL(poly caprolactone) PVA(polyvinyl alcohol) PBS(polybutylene succinate) PBAT(polybutadiene adipate terephthalate) PETS(polyethylene terephthalate succinate) etc…

petroleum base

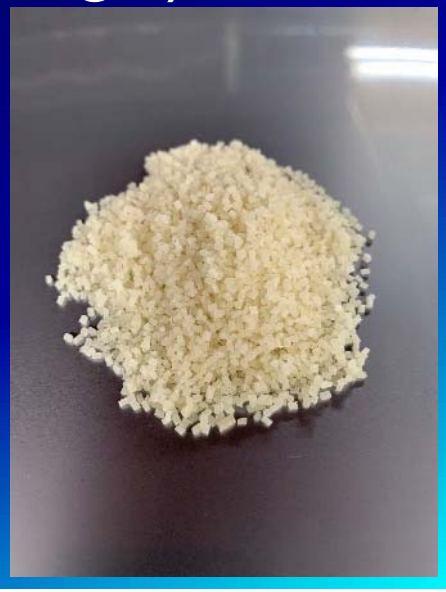
starch based biodegradable plastic (100% nature material)

should be biodegradable even in the ocean
(under biodegradability testing)

100% nature derived material, no petroleum usage)

cellulose nanofiber composite with starch based biodegradable plastic

tensile strength 3 - 9 MPa



paper, paper waste based biodegradable plastic (100% nature derived material)

we are cling to the idea of creating biodegradable plastic with 100 % natural material

no petroleum origin raw material

paper, waste paper, paper scrap, recycle paper, news paper etc… can be used.

promote paper recycling

harmless to the environment as much as possible

left : paper based biodegradable plastic pellet

right : test specimen molded with paper based biodegradable plastic pellet

wood, wood waste, bamboo based biodegradable plastic (100% nature derived material)

we are cling to the idea of creating biodegradable plastic with 100 % natural material

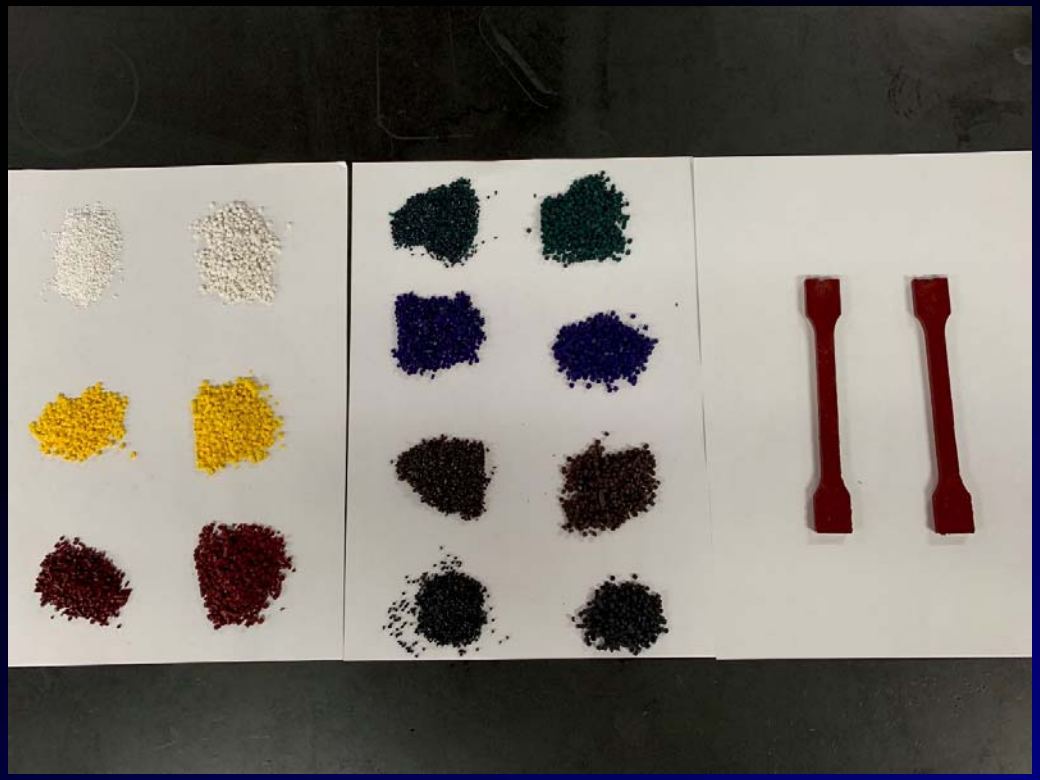
no petroleum origin raw material

wood, wood waste, bamboo etc…,
all kind of plant based material
can be used as raw material.

promote paper recycling

harmless to the environment
as much as possible

nano cellulose + biodegradable plastic color masterbatch



White(Pigment White 6)

Yellow(Pigment Yellow 120)

Red (Pigment Red 57:1)

Green (Pigment Green 36)

Blue (Pigment Blue 15)

Brown (Pigment Brown 25)

Black (Charcoal)

nano cellulose + biodegradable plastic color masterbatch

Nano Cellulose

Nano Cellulose

Width 4～100nm　length more than 5μm

High aspect ration

Manufacture by physical breakdown by machine

Component of Plant

Cellulose : 50 - 60 % %

Hemi Cellulose : 20 - 30 %

Lignin : 20 - 30 %

Plant cell wall structure is similar to concreate structure

Nano cellulose (iron reinforcing bar)

is embedded in lignin (concrete)

our focus of nano cellulose property

1. sustainable, recyclable and environmentally friendly material

2. low thermal expansion coefficient (1 / 50 of glass).
useful property at plastic molding due to its dimensional stability.

3. nano cellulose can be made from plant, tree, paper, waste wood, paper scrap etc…

4. nano cellulose can be used as reinforced material. Next generation fiber material next to glass fiber, carbon fiber. strong and light weighted.

5. biodegradable

Application of Nano Cellulose

Next generation fiber reinforced material next to glass fiber, carbon fiber.
Material can be stronger and light weighted. Can be apply to
Automotive, airplane, building material etc…

Various type of film, filter.

Cosmetic

Scaffold for catalyst

Viscosity thickener, adhesive, gelling agent, emulsion, suspension etc…

Battery separator

Bio, medical use (for human body tissue, ligaments, artificial blood vessel,
DDS (Drug Delivery System) etc…

Paint, food additive, pesticides, wrapping material etc…

Flexible substrate for solar cell, LED, display etc…

Etc…

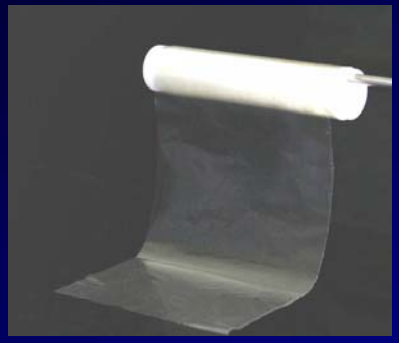
flexible electronic device film

shoe bottom

automotive parts

diapers

stationery ink



nano cellulose sheet

nano cellulose gel

diaphragm (acoustics)

application of nano cellulose

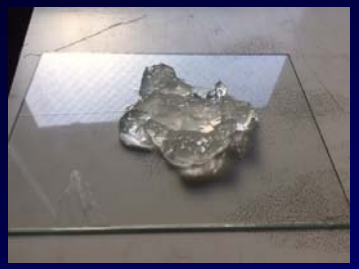
nano cellulose (Cellulose Nanofiber : CNF) products

1. nano cellulose in water

2. nanocellulose in various types of organic solvent
(Alcohol, ketone, ethyl acetate, butyl acetate, glycol ether, glycol ether acetate, toluene, NMP, phenyl glycol and all other organic solvent etc…)

3. chemically modified Cellulose

4. nano cellulose mixed plastic composite material



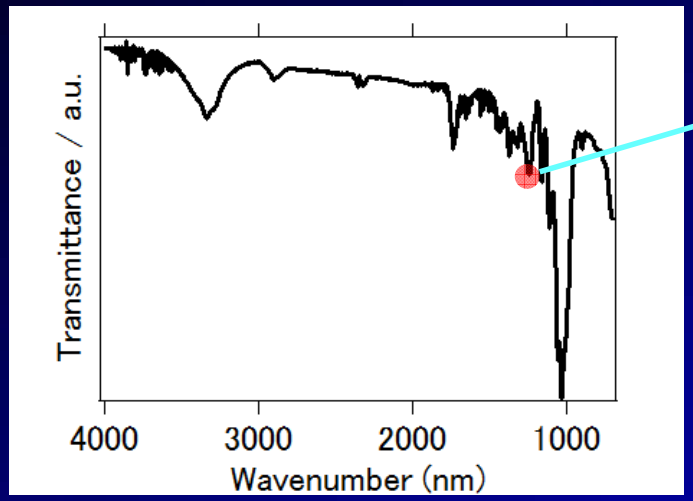
CNF gel in organic solvent

PLA + CNF composite masterbatch

chemically modified cellulose

CNF + plastic composite testing piece

IR spectra of chemically modified nano cellulose



C-H bending mode
of acetyl group

making composite with thermoplastic resin such as PP

It is very meaningful to make composite with thermoplastic resin with nano cellulose as environmentally friendly nature derived material, instead of glass fiber or carbon fiber because they are not nature derived material.

however, it is difficult to make composite with hydrophilic cellulose and hydrophobic thermoplastic resin

chemical treatment

coupling chemical, additive

physical compounding technology.

epoxy, urethane, silicon, ethylene – acryl oligomer emulsion etc…

The Use of Cellulose Nanofillers in Obtaining Polymer Nanocomposites: Properties, Processing, and Applications
Fernanda Abbate dos Santos et. al. Materials Sciences and Applications, 2016, 7, 257-294

esterification by sulfuric acid treatment

esterification by halogen compound

carboxylic sodium group addition by TEMPO treatment.

carboxylic group addition by TEMPO treatment.

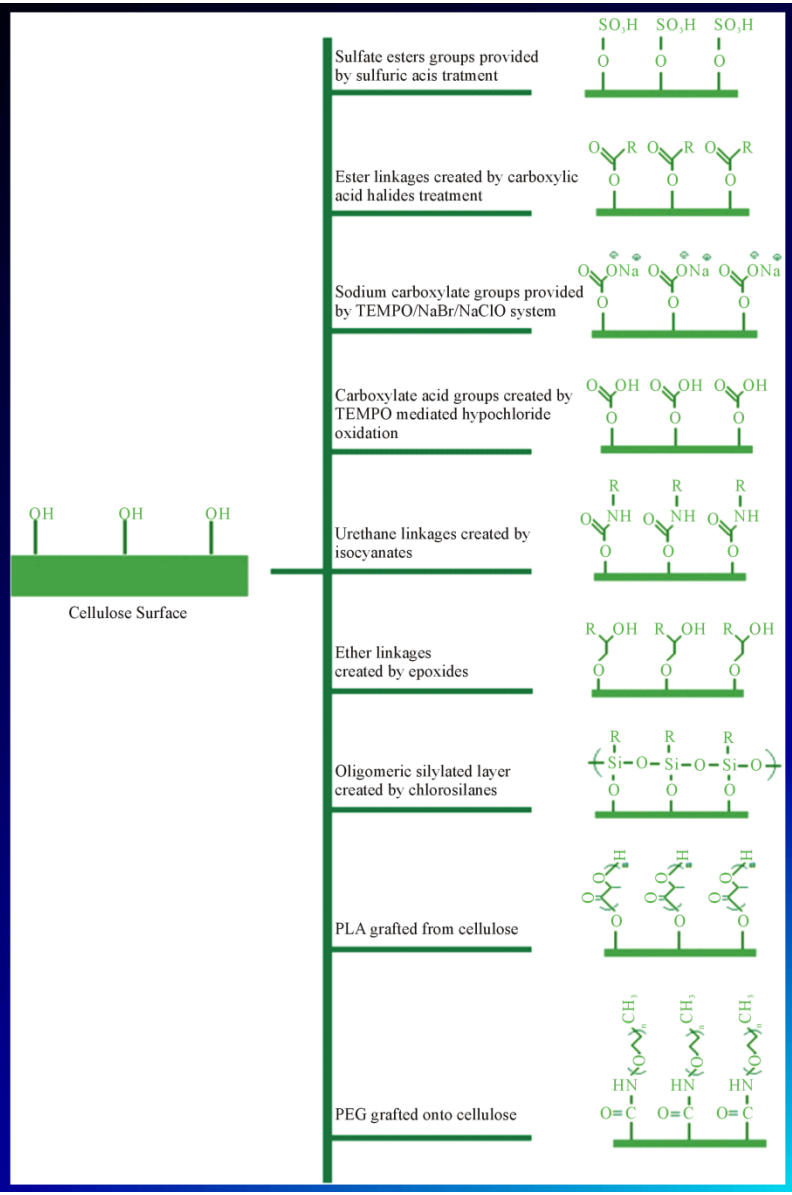
urethane group addition with isocyanate

ether group addition with epoxy

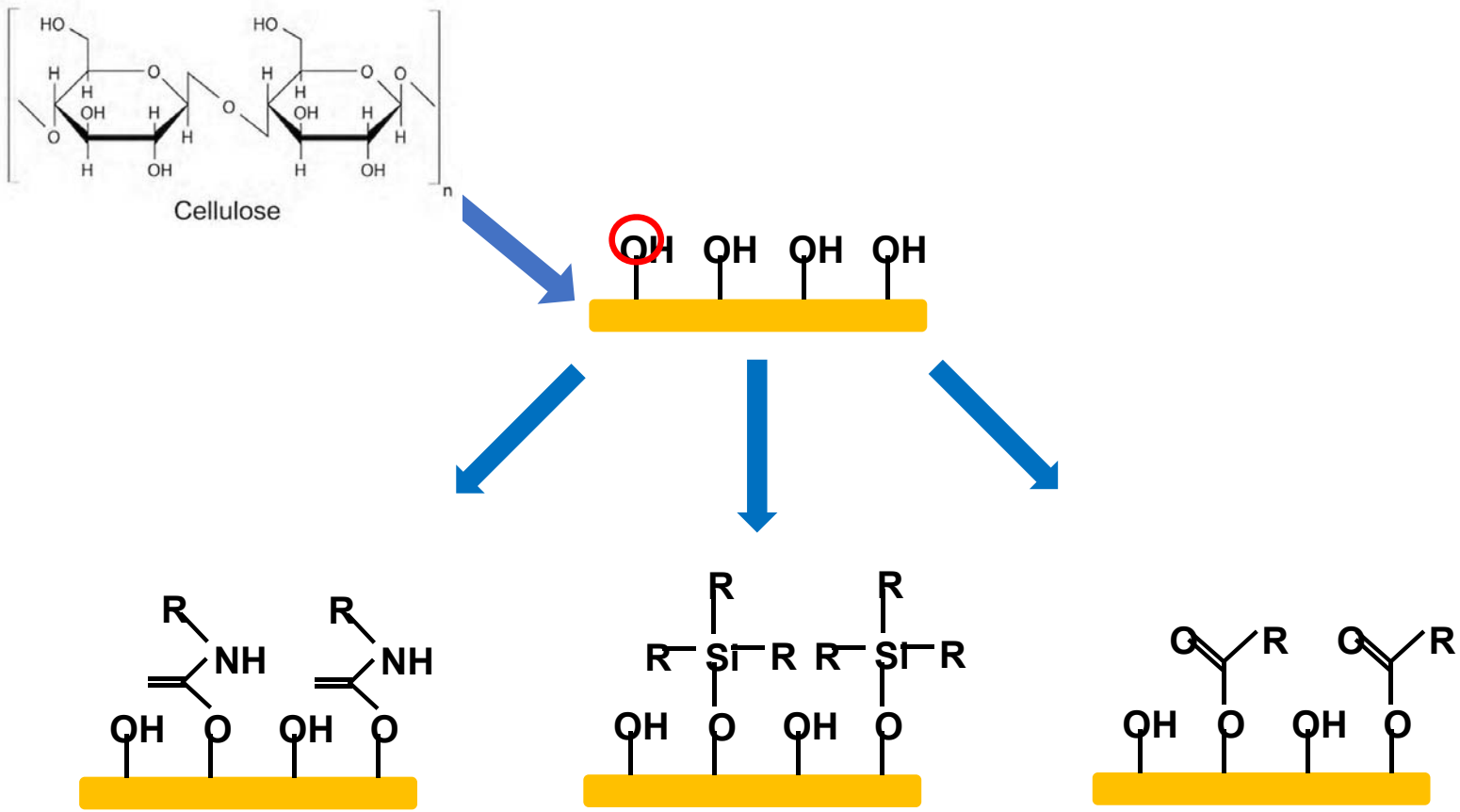
silane group addition with chloro silane

cellulose grafted with PLA.

cellulose grafted with PEG.



we do additive, chemical treatment, compound technique



biodegradable plastic is not largely used yet, why ?

compared to conventional plastic such as PP, PE, PVC, PMMA, Nylon, PS, ABS etc…

1. mechanically weak
2. thermally weak
3. deformation at molding (at heating)
4. low crystallinity
5. expensive

biodegradable Plastic

plastic that can be decomposed into H_2O and CO_2 by the work of microorganism in natural environment.

nano Cellulose

nano cellulose is the next generation environmentally friendly material that can be taken from plant, woods.

biodegradable plastic
+
biodegradable nano cellulose

1. improve mechanical strength

2. increase temperature durability, heat resistance, increase glass transition temperature

3. lower the thermal expansion coefficient
(prevention of heat deformation for plastic molding)

4. increase crystallinity

It has a great meaning to improve these properties with biodegradable material because this is also possible with glass fiber, carbon fiber, but they are not biodegradable.

mechanical strength of nano cellulose + general plastic composite

type of plastic	CNF (%)	Tensile Strength (MPa)	type of plastic	CNF (%)	Tensile Strength (MPa)
PE	0	10	ABS	0	43
PE+ CNF	33	24 - 25	ABS + CNF	23	50 - 51
PP	0	32	PC	0	44
PP+ CNF	40	48 - 49	PC + CNF	23	55 - 56
PS	0	29	PVB	0	44
PS+ CNF	23	36 - 37	PVB + CNF	23	54 - 55
PMMA	0	42	TPU	0	17
PMMA+ CNF	23	56 - 57	TPU + CNF	25	30
PA	0	42	POM	0	51
PA + CNF	13	43	POM + CNF	23	61
PVC	0	12			
PVC + CNF	23	22 - 23			

tensile strength

bending strength

elasticity

enhanced by making nano cellulose composite

bending strength, elasticity Is now shown.

mechanical strength of nano cellulose + biodegradable plastic composite

type of biodegradable plastic	CNF Concentration (%)	Tensile Strength (MPa)	Tensile Stroke (mm)	Elasticity (MPa)	Bending Strength (MPa)	Bending Stroke (mm)
polycaprolactone (PCL)	0	2				
PCL composite with CNF	23	8.5				
starch based plastic	0	8				
starch based plastic composite with CNF	23	19.5				
starch + PBAT based plastic	0	11	198	258.7		
starch + PBAT based plastic composite with CNF	25	24	4.2	1640		
starch + PLA based plastic	0	29	2.4	1869	42.7	4.8
starch + PLA based plastic composite with CNF	23	34	1.3	3567	59	3
Poly buthylene succinate (PBS)	0	38				
PBS composite with CNF	26	48				
Poly Lactic Acid (PLA)	0	62	2.8	2831	119	7.4
PLA composite with CNF	15	69	3.4	3502	120	4.8
poly(butylene adipate-co-terephthalate) (PBAT)	0	12				
PBAT composite with CNF	23	18.5				
polyhydroxyalkanoate (PHA)	0	16				
PHA composite with CNF	30	24.5				

tensile strength

bending strength

elasticity

enhanced by making nano cellulose composite

mechanical strength of nano cellulose + plastic scrap composite

type of waste plastic (recycle plastic)	CNF Concentration (%)	Tensile Strength (MPa)	Tensile Stroke (mm)	Elasticity (MPa)	Bending Strength (MPa)	Bending Stroke (mm)
polypropylene (PP) from plastic pallet (Black color)	0	21.8	6.4	1304	31.6	8.4
PP composite with CNF	40	32.4	4.1	2851	51.7	7
polyethylene (PE) from diaper (from factory, white color)	0	11.7	5.2	1239	14.3	16.4
PE composite with CNF	30	33.8	4.3	2958	46.3	9.4

tensile strength
bending strength
elasticity

enhanced by making
nano cellulose composite

By making nano cellulose composite with plastic scrap, it was possible to improve mechanical strength. This fact can promote reuse of plastic scrap in the world, and could be one of the strategy to reduce the plastic garbage.

influence of biodegradability of PLA by mixing with nano cellulose

	RT 1day	60℃ 1week			
	TOC	TOC	av	分解率（PLA換算）	分解率（CNF考慮）
PLA	6.342	17.47	17.46	2.22%	-
		17.45			
5%CNF PLA	7.159	18.52	18.505	2.39%	2.28%
		18.49			
10%CNF PLA	6.932	18.87	18.795	2.64%	2.40%
		18.72			
23%CNF PLA	7.532	21.13	21.125	3.53%	2.79%
		21.12			

Decomposition Rate (based on PLA weight)

Decomposition Rate (based on CNF weight)

TOC : Total Organic Carbon

By making PLA + Nano Cellulose Composite, mechanical strength has increased. On top of that, It was found that biodegradability also accelerated.

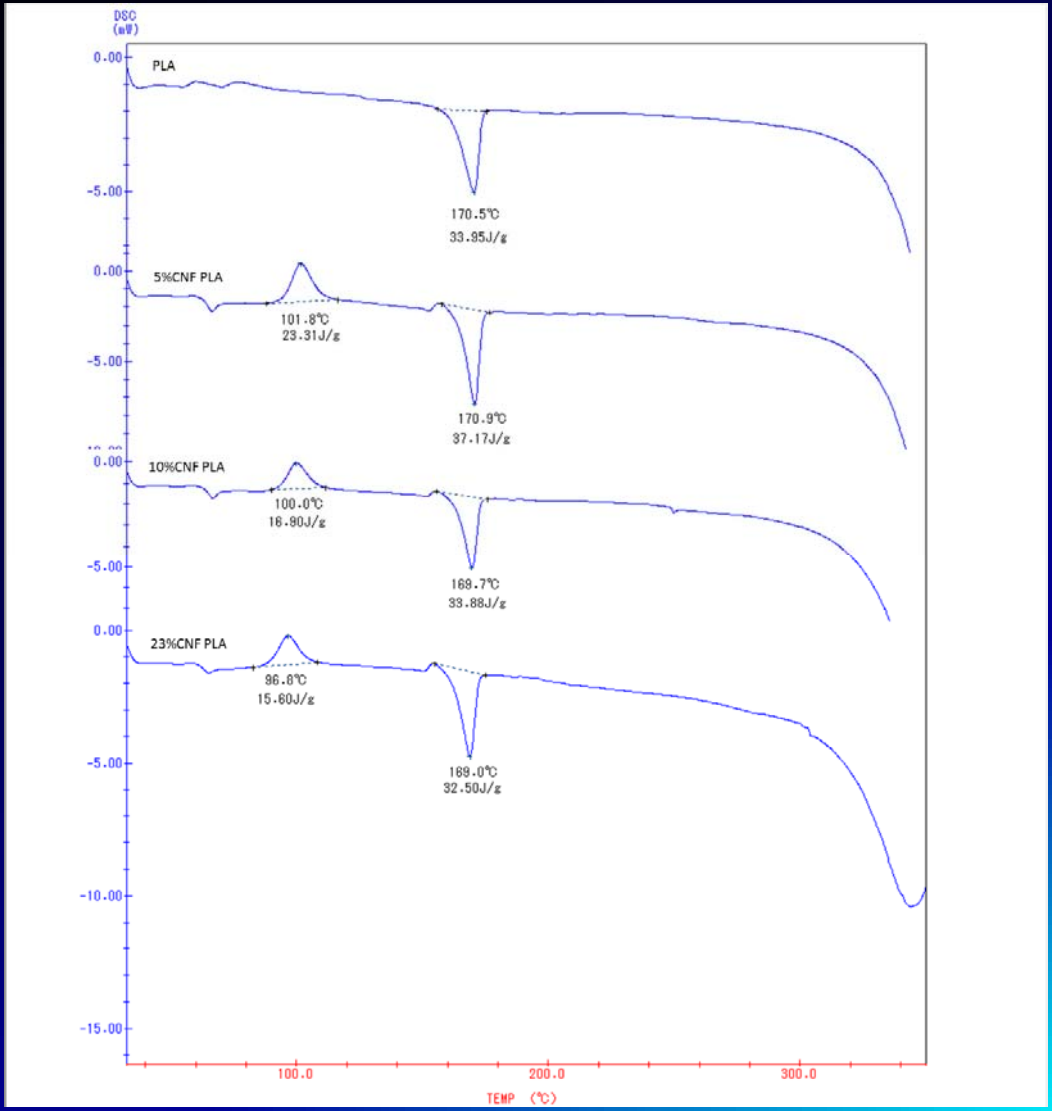
We are planning to measure biodegradability with other plastics as well.

thermal property of PLA + Nano Cellulose Composite

All of sample have peaks almost at the same position.

The new peaks were observed with PLA mixed with nano cellulose approximately at 100°C. This is suggested to be due to crystallization.

This means nano cellulose is effective as nucleating agent.



Other property

Sample	PP	PP + Nano Cellulose 40%
MFR (g / 10min.)	20.4	2.53

sample	PP		PP + Nano Cellulose 40%	
Coefficient of Linear Expansion	MD	TD	MD	TD
23 - 60°C (x 10^{-5} / K)	7.66	11.2	3.34	9.54
23 - 160°C (x 10^{-5} / K)	5.78	16.5	6.49	15.1

Sample	PP	PP + Nano Cellulose 40%
Deflection temperature under load (°C)	62	106.2

MFR becomes low and deflection temperature under load, will become higher, by making nano cellulose composite material.

combination of nano cellulose composite and foaming technology

Foaming is useful technology because plastic can be lighter and can be used as insulating material.

The most known and famous foaming product is foamed poly styrene.

Two major technology for foaming (chemical foaming, physical foaming)

foamed poly styrene

So far, chemical foaming have been often used as industrial use, Although it is said that chemical foaming is not environmentally friendly technology.

As physical foaming technology, chlorofluorocarbon or hydrocarbon gases have been often used. However, these gas is said to be toxic, and furthermore, they can destroy ozone layer. On top of that, these gases can be flammable and one of the reason for global warming.

supercritical CO_2 foaming technology

We have been successfully making foamed plastic by supercritical CO_2, N_2 gas foaming technology.

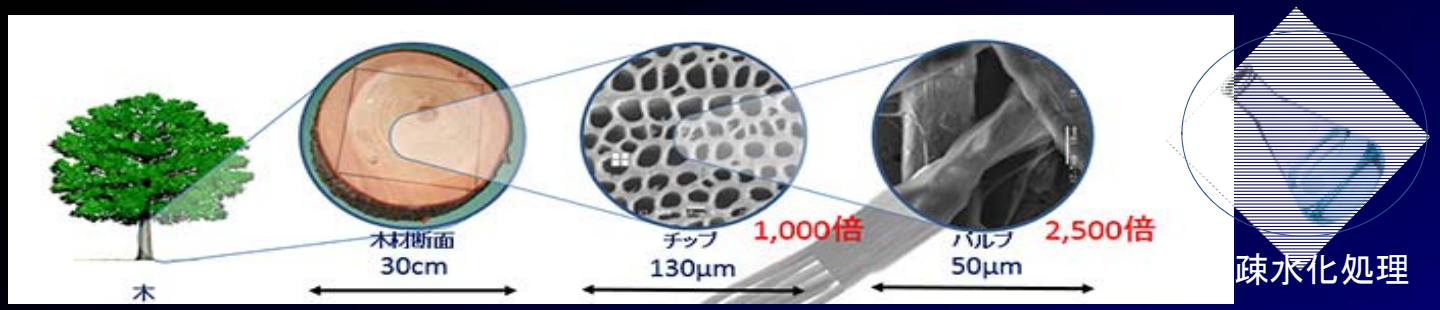
With our new foaming technology, foamed plastic such as foam PP, PMMA, PLA, PS, ABS and other various types of foam plastics can be made, because this technology can make pores smaller than conventional method.

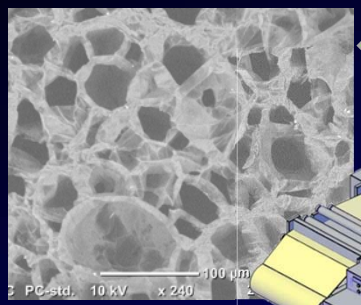
With this technology, plastic is expected to be even stronger and lighter.

At the moment, even with 40% of CNF, mechanical strength increase is 1.5 - 2.5 times, compared to the one without CNF.

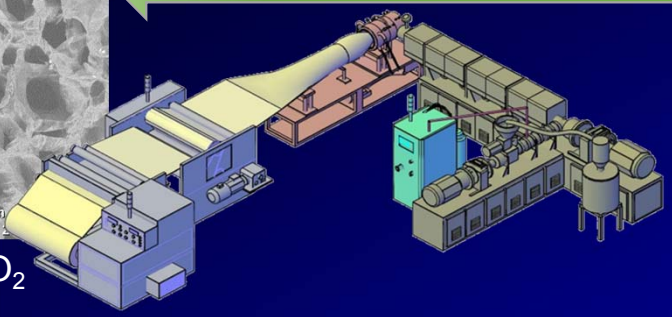
With Supercritical CO_2 Foaming Technology, could mechanical strength be stronger even with lower CNF concentration??

combination of nano cellulose composite and foaming technology





CNF reinforced supercritical CO_2



molding with supercritical CO_2
foaming extrusion machine

Combining nano cellulose composite and supercritical CO_2 foaming technology. Would plastic be even stronger and lighter??

combining nano cellulose composite technology and supercritical CO_2 foaming technology

supercritical CO_2 supplying machine

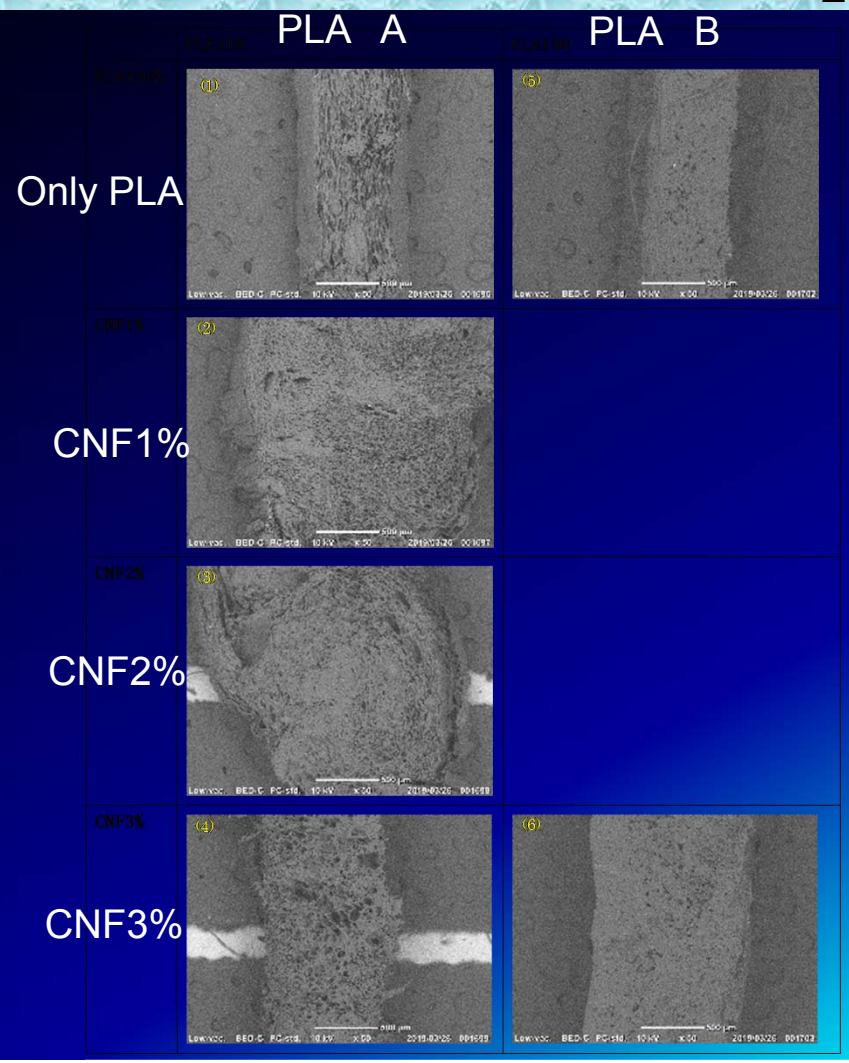
twin extruder under supercritical CO_2 condition

There has been some report that mechanical strength increased when carbon fiber composite was made with supercritical gas foaming condition. Therefore, we will apply this idea to our nano cellulose composite with supercritical CO_2 condition.

PLA + Nano Cellulose Composite under Supercritical CO_2

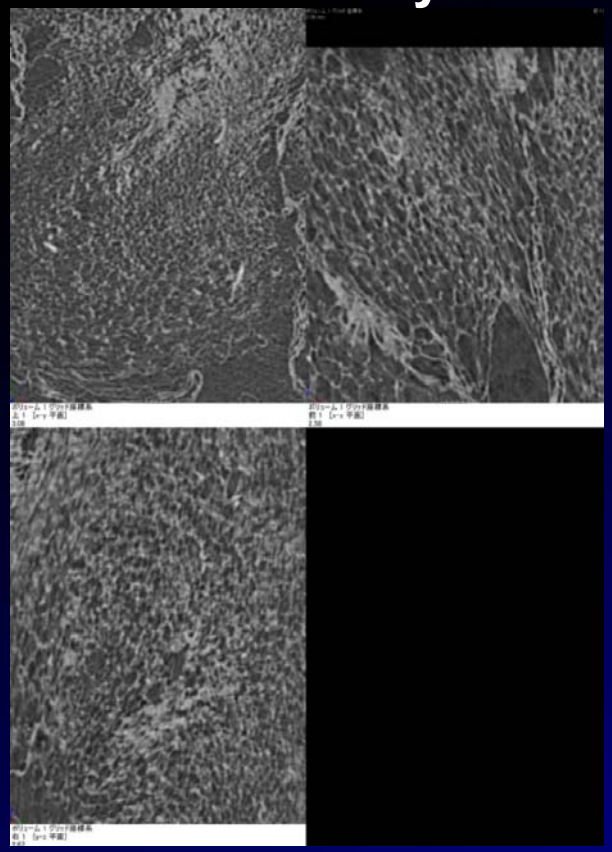
Foam (gas bubble) size of approximately 50μm were observed with only PLA A.
With CNF 1 %, foam size became a little less than 10μm. Not much obvious difference was observed with CNF 2 or 3%.

Foam (gas bubble) size of approximately 20 - 50μm were observed with only PLA B.
With CNF 3 %, foam size became a little smaller as much as 10 – 30μm.

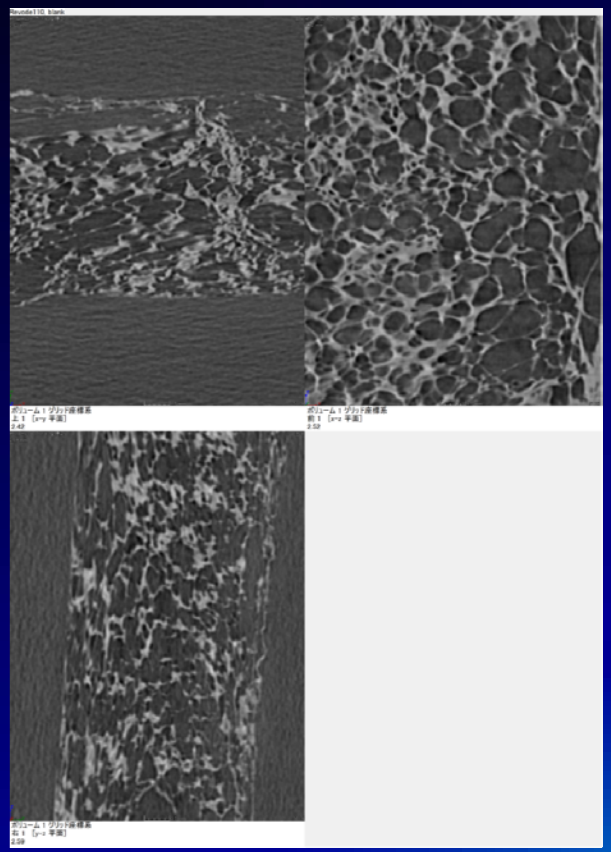


Micro X-ray CT image

PLA only



PLA CNF 1%



Foam (gas bubble) size of approximately 30 – 80 μm were observed with only PLA . With CNF 1 %, foam size became approximately 10μm. Bubble can be observed where CNF trace can be seen. This means CNF may have functioned as foam nucleating agent.

PLA + Nano Cellulose Composite under Supercritical CO_2

PLA A

CNF1%

CNF2% increased foaming ratio

PLA B

PLA only

CNF3% increased foaming ratio

PLA + Nano Cellulose Composite under Supercritical CO_2

PLA only	57 MPa
PLA + CNF 2 % (supercritical CO2)	64 MPa
PLA + CNF 15 % (normal pressure)	65 MPa

This is 1 time experiment result, need further experiment for confirmation.

Cutting edge technology to make Biodegradable plastic + Nano Cellulose + plastic foaming

with this technology, we made
foamed PLA + Nano Cellulose composite

PLA
+
Nano Cellulose composite material
+
supercritical foaming technology

All new triple technology : cutting edge highly advanced technology. We are the only one company in the world

Thank you

NANO SAKURA
FOR SUSTAINABLE DEVELOPMENT

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