M2794.007700 Smart Materials and Design

Nano Composite and Green Composite

June 01, 2017

Prof. Sung-Hoon Ahn (安成勳)

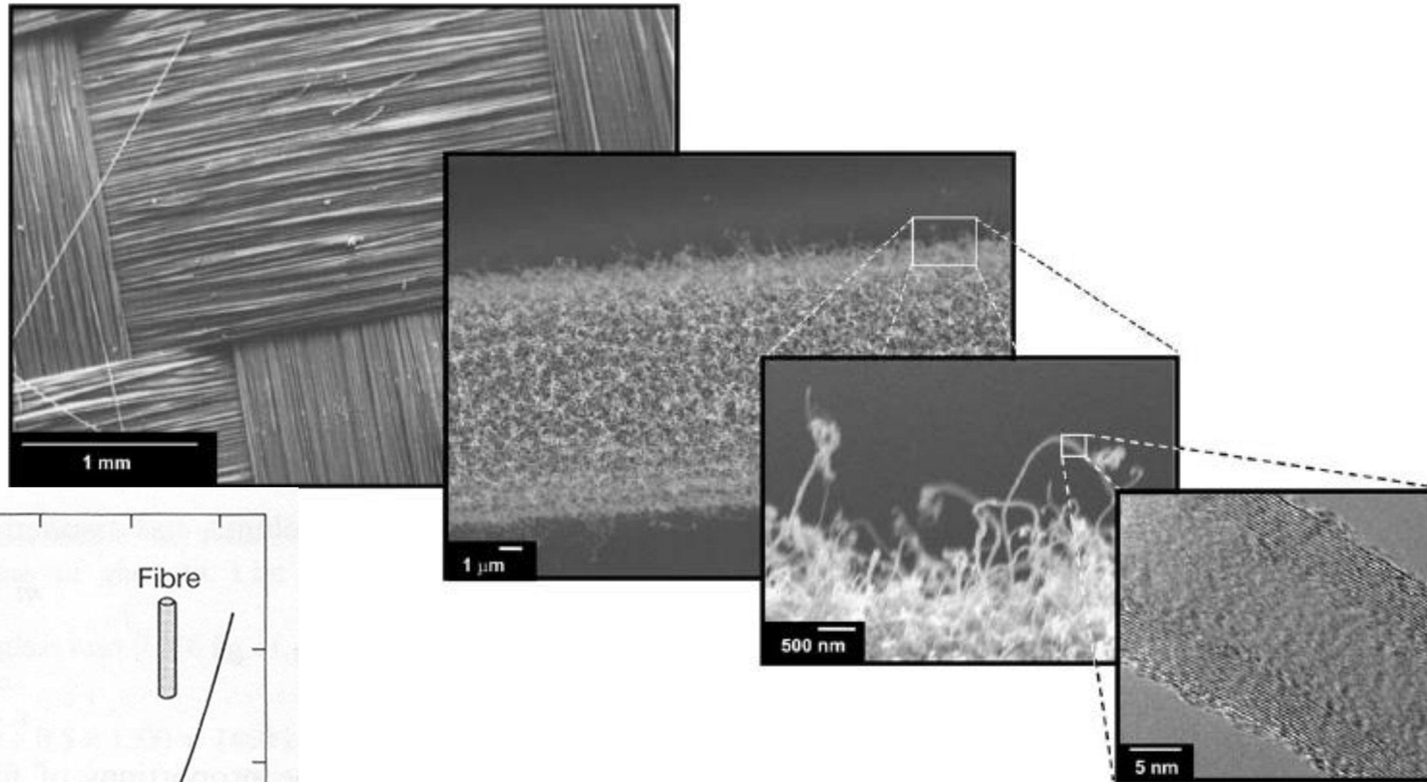
School of Mechanical and Aerospace Engineering
Seoul National University
http://fab.snu.ac.kr
ahnsh@snu.ac.kr

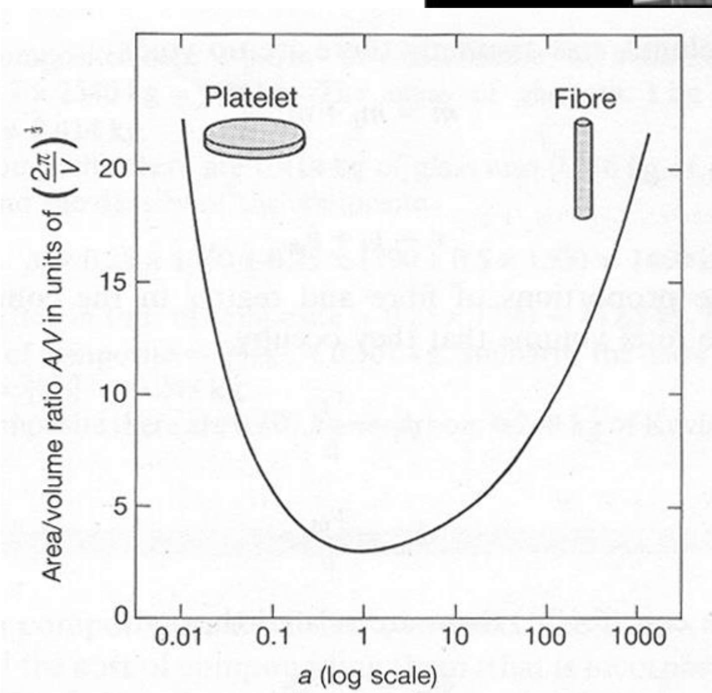
Nano composite and green composite

- **Nano Composite**
- **Green Composite**
- **Bio Composite**

"There's plenty of room at the bottom"
Richard Feynman

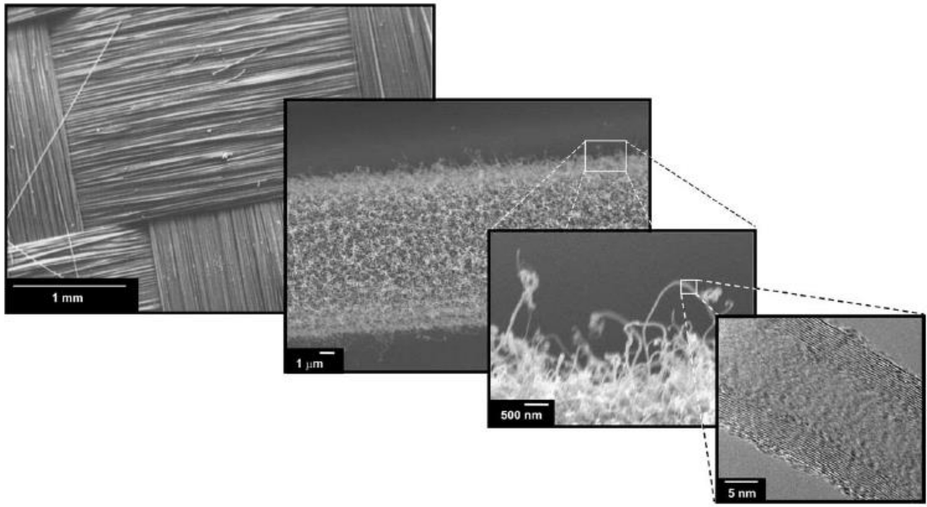
Introduction





Introduction

- **Matrix material**
  - Metal matrix composite
  - Ceramic matrix composite
  - **Polymer matrix composite**



- **Reinforcement material**
  - Fibrous-reinforced composite
  - **particulate-reinforced composite**

- **Nano particulate-reinforced composite**
  - Nanoparticle-reinforced composite
  - Nanofiber-reinforced composite
  - **Nanoplatelet-reinforced composite**

What are Nano composites

- A nanocomposite is a composite material, in which one of the components has at least one dimension that is around 10^{-9} m

Or

- A nanocomposite is as a multiphase solid material where one of the phases has one, two or three dimensions of less than 100 nm, or Structures having nano-scale repeat distances between the different phases that make up the material.

Kamigaito (1994)

Classification of nanocomposites

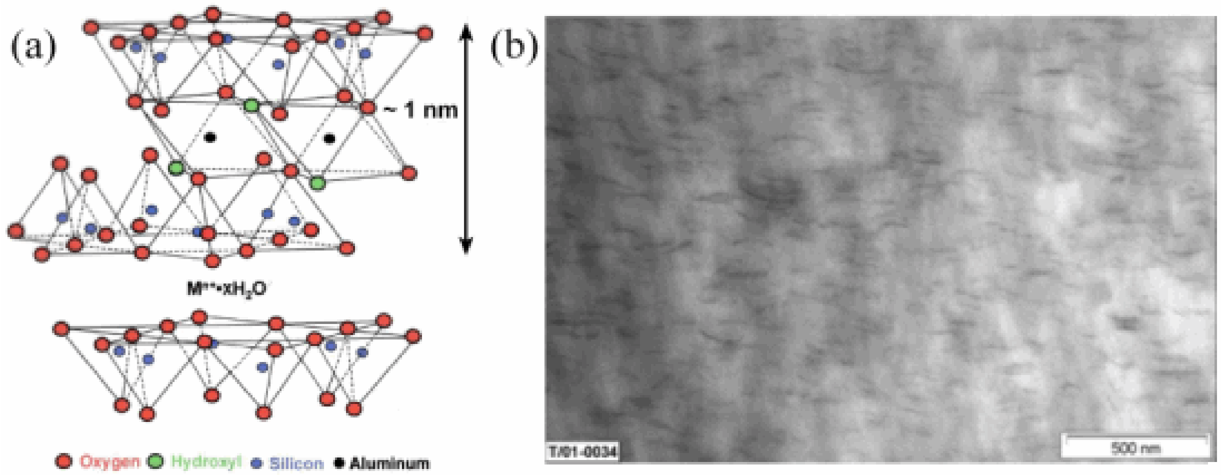
- **Polymer based**
  - Polymer/ceramic nanocomposites
  - Inorganic/organic polymer nanocomposites
  - Inorganic/organic hybrid nanocomposites
  - Polymer/layered silicate nanocomposites
  - Polymer/polymer nanocomposites
  - Biocomposites, Eg. Elastin-collagen

- **Non-polymer based**
  - Metal/Metal nanocomposites, Eg. Pt-Ru
  - Metal/ceramic nanocomposites, Eg. Polysilazane/polysiloxane
  - Ceramic/ceramic nanocomposites, Eg. Zirconia-toughened alumina

Kamigaito (1994)

Nanoclay properties

- Nanoclays are a broad class of naturally occurring inorganic minerals, of which plate-like montmorillonite is the most commonly used
- Potential benefits include increased mechanical strength, decreased gas permeability, superior flame-resistance, and even enhanced transparency when dispersed nanoclay plates suppress polymer crystallization

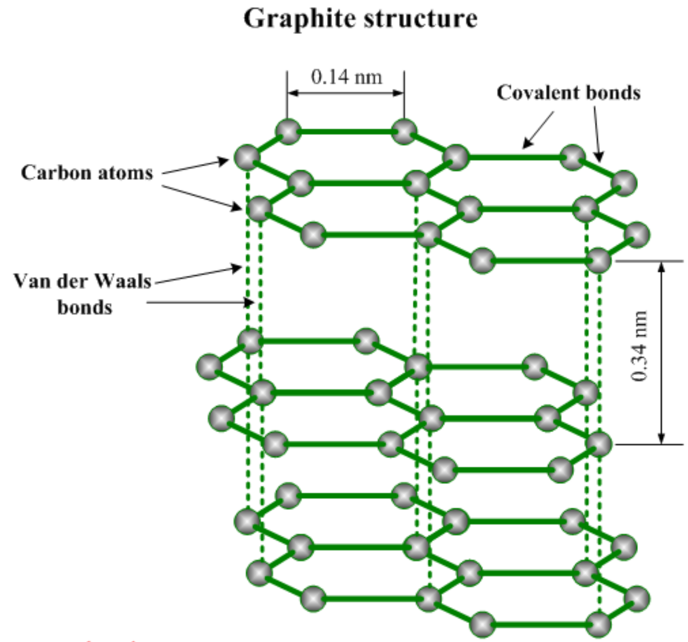


(a) Schematic of nm-thick montmorillonite clay aluminosilicate layers. (b) TEM micrograph of 2% Nanoclay

Giannelis, E. P. Advanced Materials 1996, 8, 29.

Graphite properties

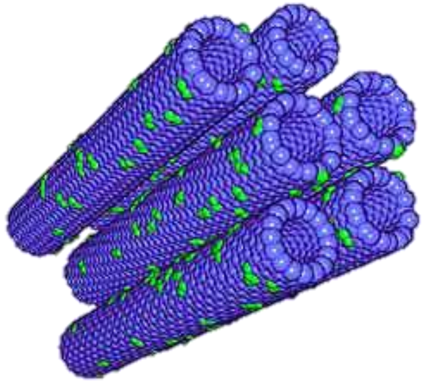
- Layered, planar structure
- High melting point above 1650℃, similar to that of diamond
- Be insoluble in water as well as other organic solvents
- Be a good conductor of electricity

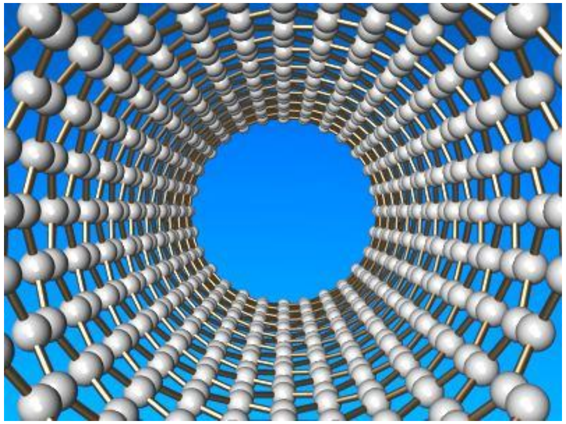


http://chemistrycarbons.blogspot.kr/2012/11/explanation-on-structure-of-graphite.html

Nanotube properties

- Superior **stiffness and strength** to all other materials
- Extraordinary **electric** properties
- Reported to be **thermally stable** in a vacuum up to 2800℃ (and we fret over CPU temps over 50℃)
- Capacity to carry an **electric current** 1000 times better than copper wires
- Twice the thermal conductivity of diamonds
- Pressing or stretching nanotubes can change their electrical properties by changing the quantum states of the electrons in the carbon bonds
- They are either conducting or semi-conducting depending on the their structure



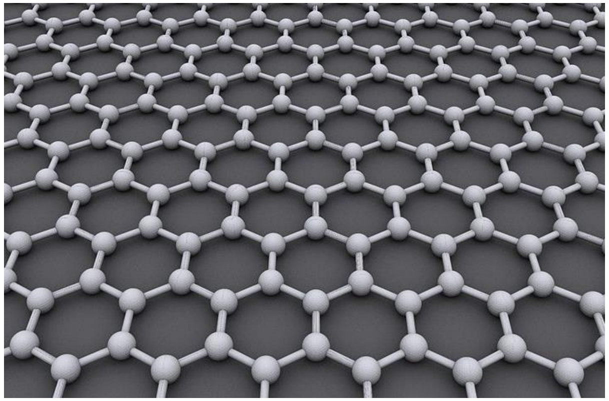


Carbon based nanotubes

http://www.pa.msu.edu/cmp/csc/simindex.html

Graphene properties

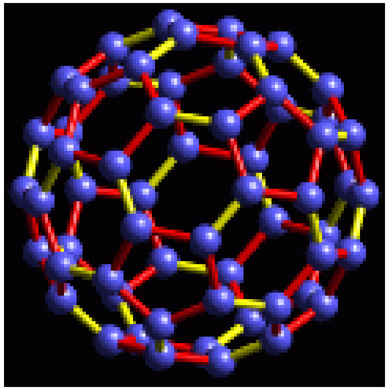
- **Mechanical Strengths**
  - Bond length is .142 nm long = very strong bond
  - High Young's modulus (~1,100 Gpa) ; high fracture strength (125 Gpa)
  - Strongest material ever measured, some 200 times stronger than structural steel
  - Very light at 0.77 milligrams per square meter, paper is 1000 times heavier
  - Single sheet of graphene can cover a whole football field while weighing under 1 gram
  - Also, graphene is very flexible, yet brittle (preventing structural use)



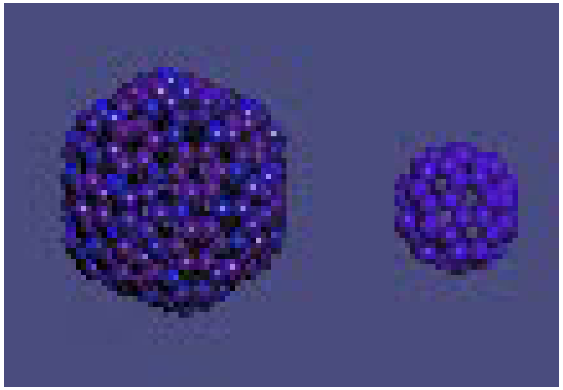
http://upload.wikimedia.org/wikipedia/commons/thumb/9/9e/Graphen.jpg/750px-Graphen.jpg

Bucky Ball properties

- Arranged in pentagons and hexagons
- A one atom thick separation of two spaces; inside the ball and outside
- **Highest** tensile strength of any known 2D structure or element, including cross-section of diamonds which have the highest tensile strength of all known 3D structures (which is also a formation of carbon atoms)
- Also has the **highest** packing density of all known structures (including diamonds)
- Impenetrable to all elements under normal circumstances, even a helium atom with an energy of 5eV (electron Volt)



Bucky Ball (C_{60})

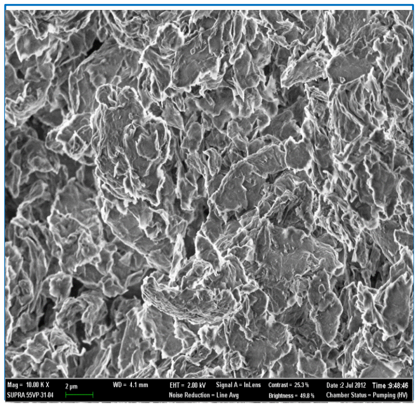


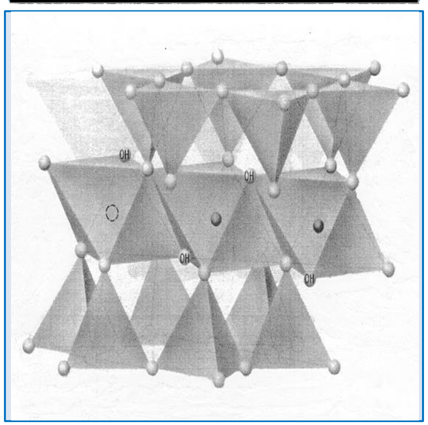
C240 colliding with C60 at 300 eV

http://www.pa.msu.edu/cmp/csc/simindex.html

Nano-fillers used in this study

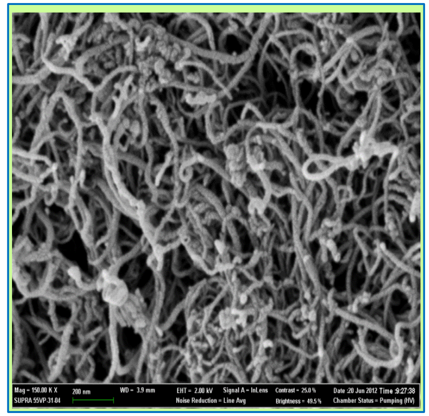
Nano-clay

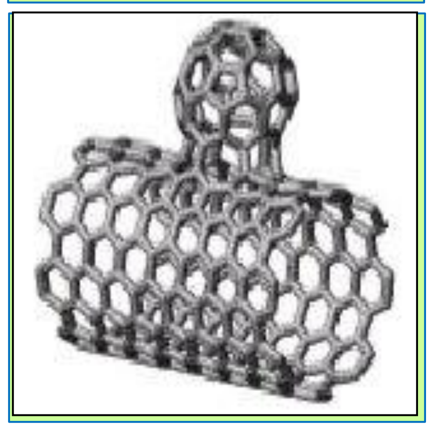




- 2 dimensional structure
- Layered structure
- Good mechanical property

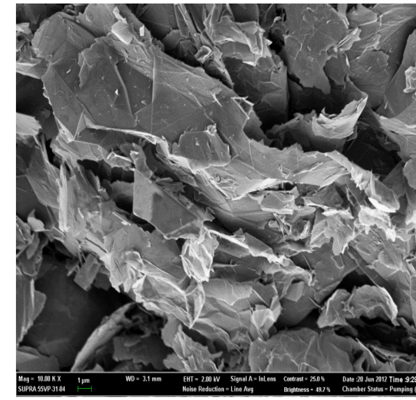
Carbon nanotube

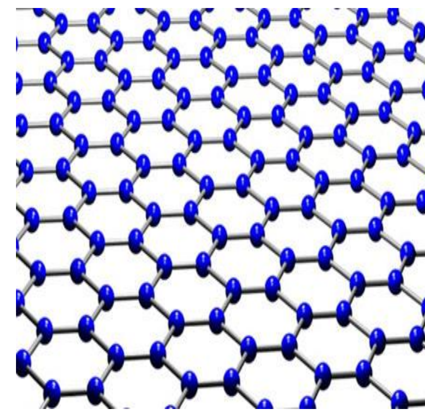




- 1 dimensional structure
- High mechanical strength
- High electrical
- Expensive

Exfoliated graphene nanoplates



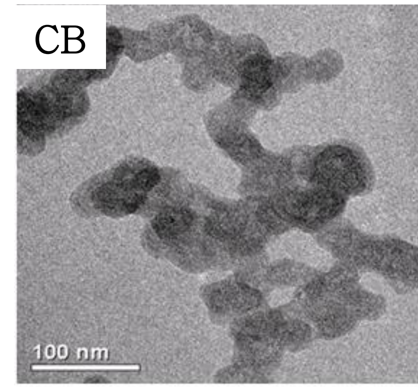


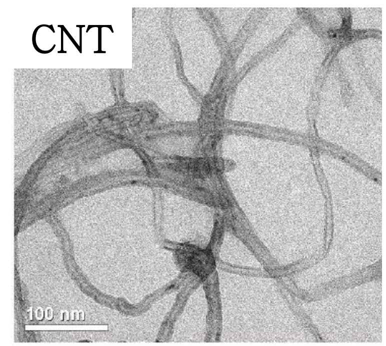
- 2 dimensional structure
- Layered structure
- Good electrical conductivity
- High EMI shielding ability

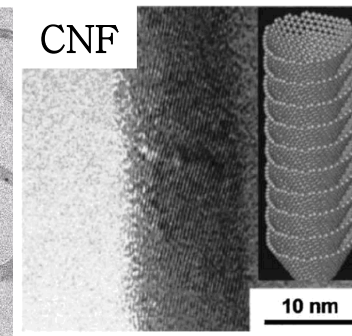
Kim, M.S., Yan, J., Joo, K. H., Pandey, J.K., Kang, Y. J., and Ahn, S.H., 2013, "Synergistic Effects of Carbon Nanotubes and Exfoliated Graphite Nanoplatelets for Electromagnetic Interference Shielding and Soundproofing," Journal of Applied Polymer Science, Vol 130, No. 6

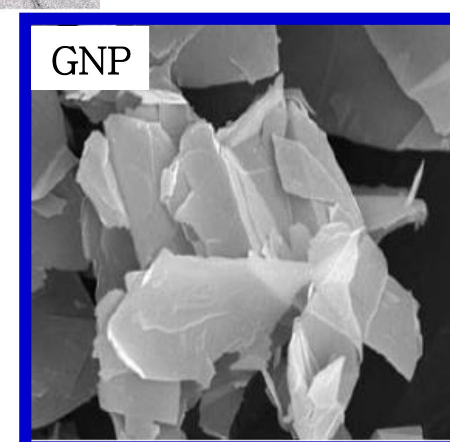
Nano-carbon particulate

- **Nanoparticle-reinforced composites**
  - Carbon black (CB)
- **Nanofiber-reinforced composites**
  - Carbon-nanofiber (CNF)
  - Carbon-nanotube (CNT)
- **Nanoplatelet-reinforced composites**
  - **Graphite nanoplatelet (GNP)**



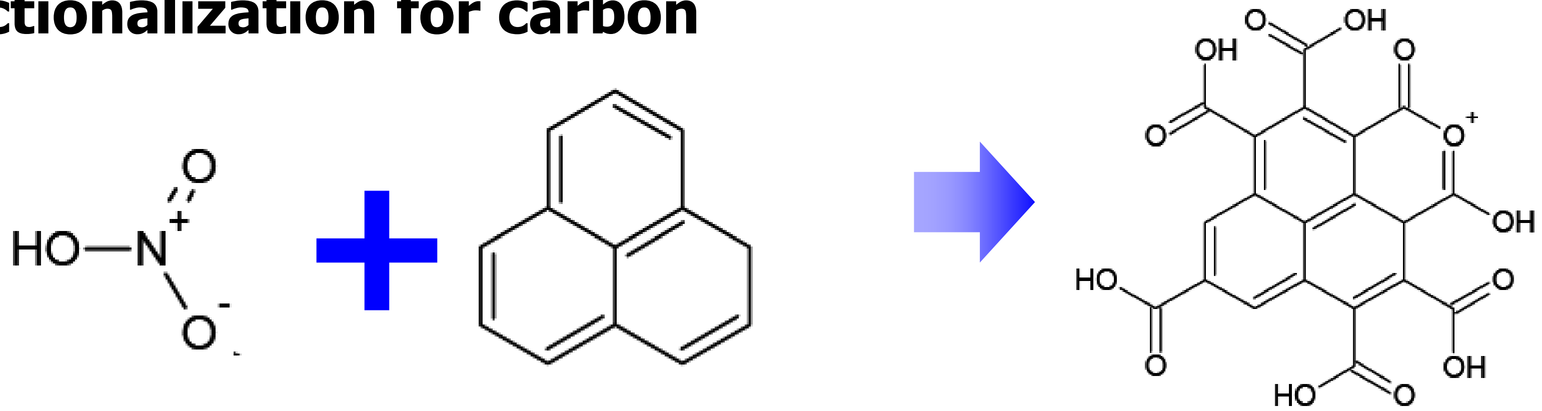




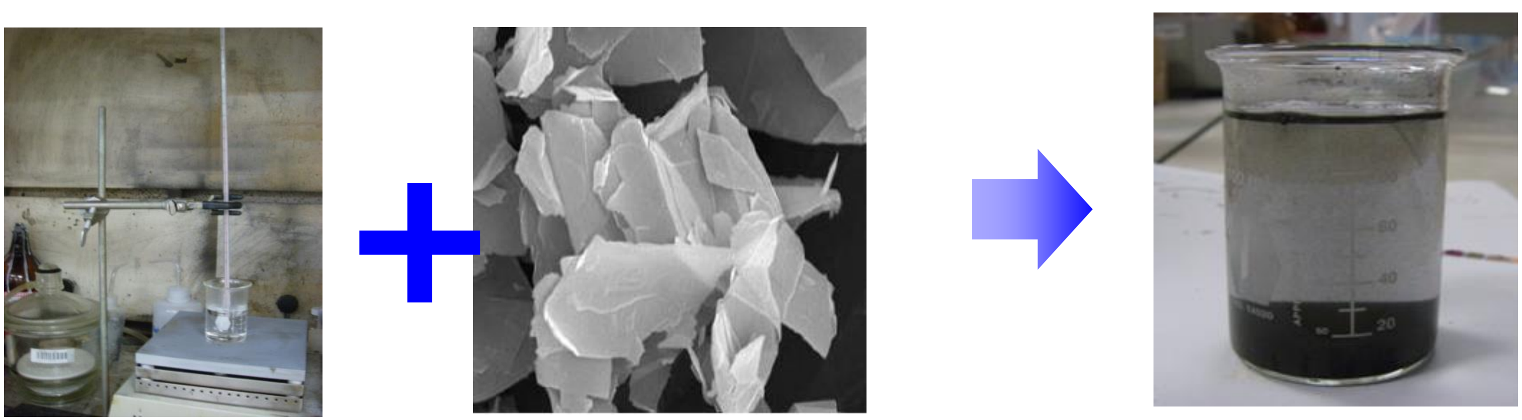


GNP Functionalization

- **Functionalization for carbon**

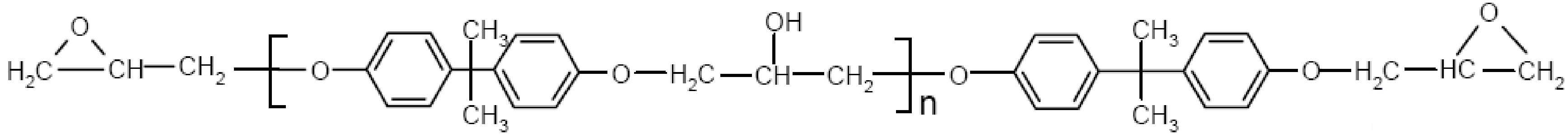


- **Nitric acid oxidation**
  - Immerse GNPs in HNO_3 at 100°C for 30 minute

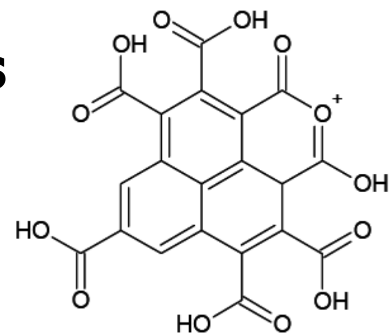


GNP/epoxy composite manufacture

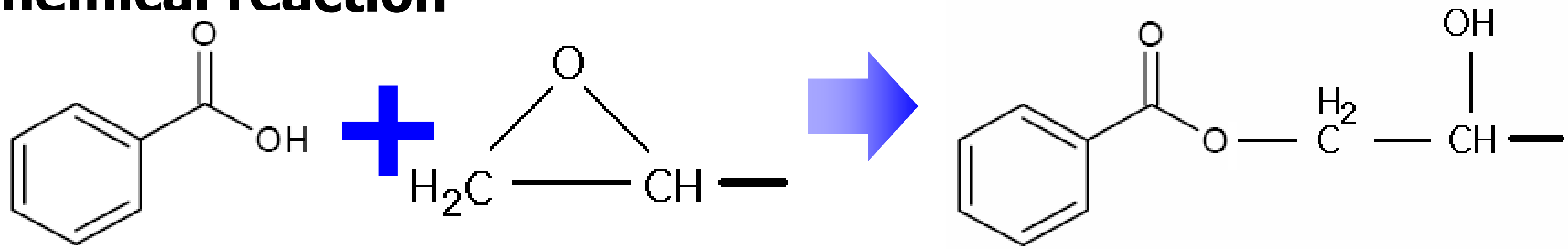
- **Epoxy DGEBA type**



- **Functionalized GNPs**

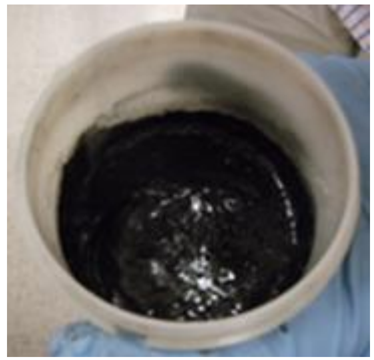


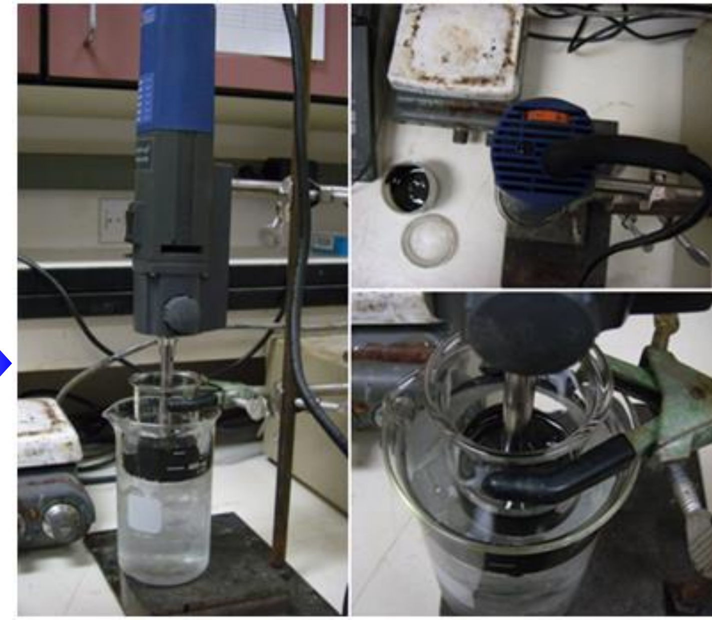
- **Chemical reaction**

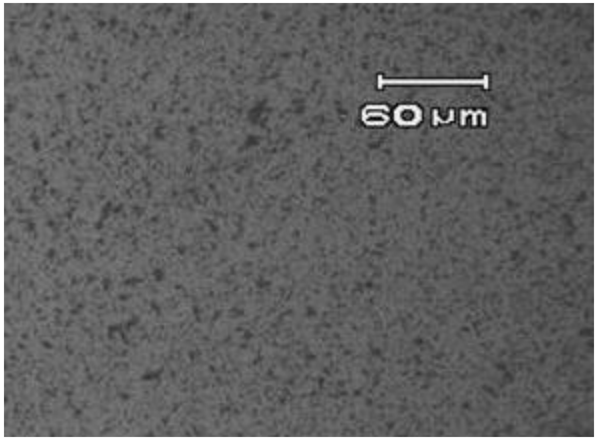


GNP/epoxy composite manufacture

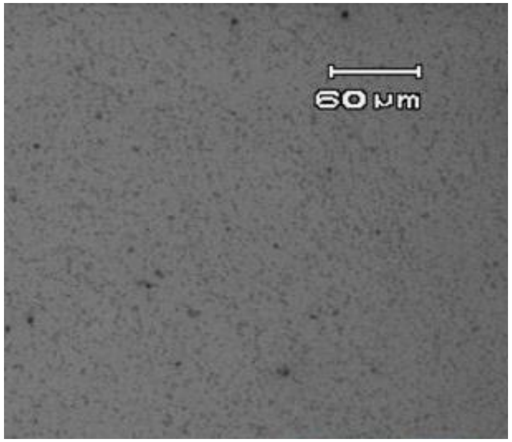
- **Mixing method**
  - Thinky mixer
  - Shear mixer
  - Ultra-sonicater



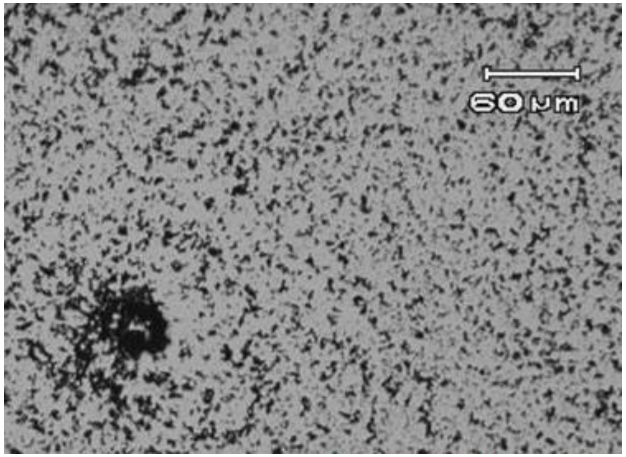




w/o sonication after 24 day.



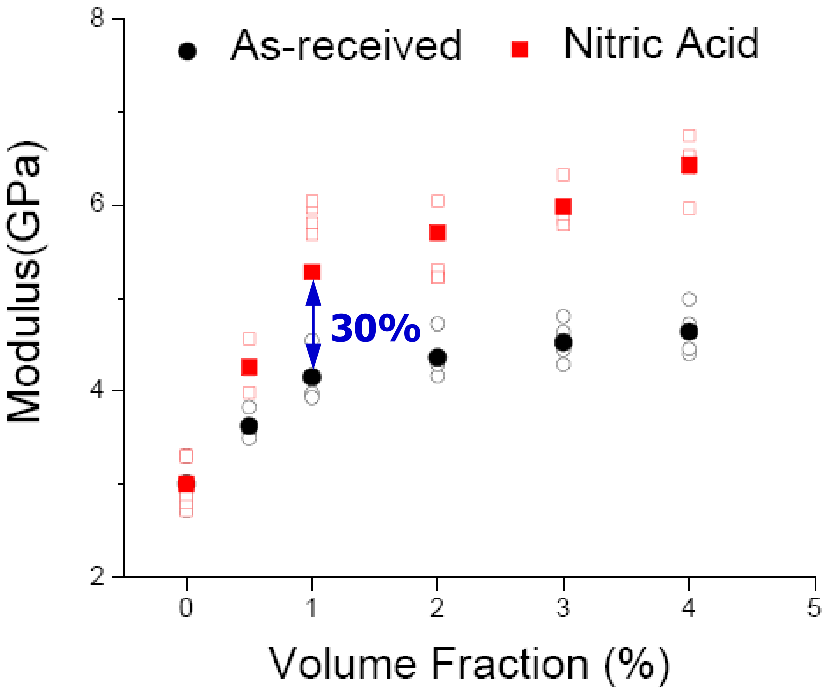
Sonication for 30 min.

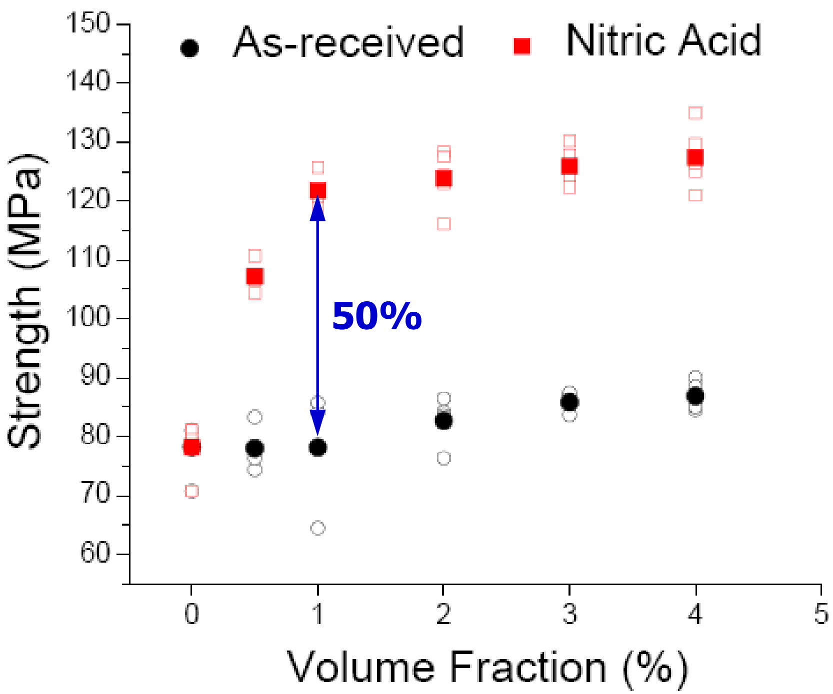


w/o sonication

Mechanical property

- **Tensile property**
  - Functionalized GNP composite’s properties are better than GNP composite’s properties.





Soundproofing Effect

Noise & Electromagnetic pollution

Noise pollution

Stress

WE

Unhealthy

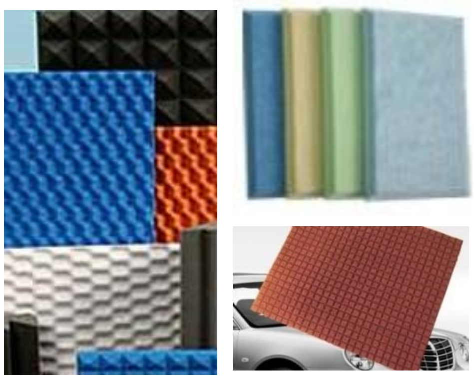
Electromagnetic pollution

Source : ask.nate.com

Thinking : Let's solve both problems simultaneously.

Research

Research



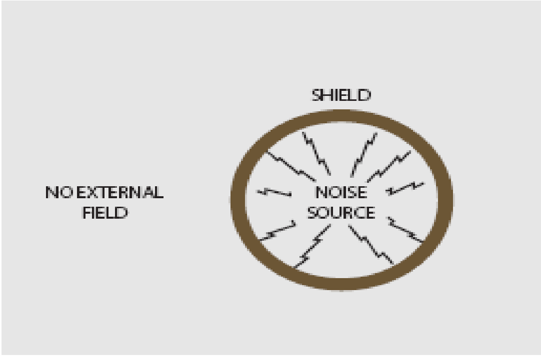
Soundproofing materials

Application

Automotive

Electronics

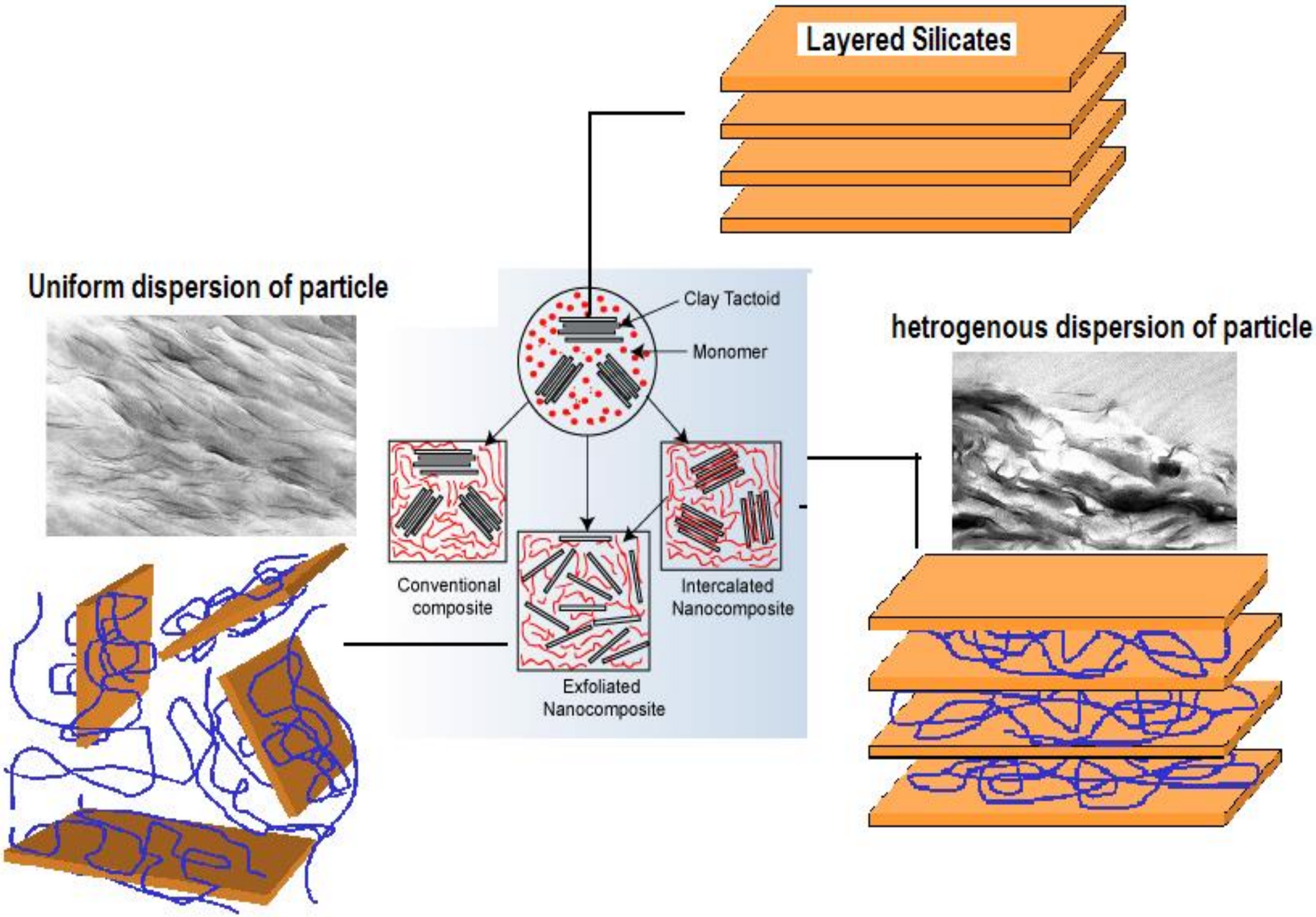
Application



Source : E-Song EMC Products Guide

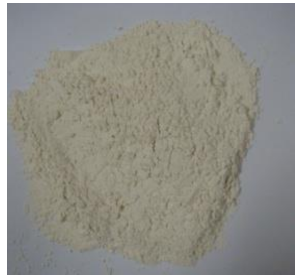
Electromagnetic materials

Dispersion of Nano Clay



Preparation of material

Polypropylene
HJ400 Samsung Company



Clay
(0.9wt%, 4.8wt%, 6.5wt%)
Southern Clay Products

Talc
(5wt%, 10wt%, 15wt%, 20wt%)
Kyoungki Chemical

CNT
(0.1wt%, 0.5wt%, 0.7wt%)
Hanwha Nanotech

xGnP
(0.1wt%, 0.5wt%, 0.7wt%)
Hanwha Nanotech

Clay	
Type	Cloisite®15A
Density	1.66 g/cm^3
Particle Size	≤ 2μm
Talc	
Type	KR-2000
Density	2.5~2.8 g/cm^3
Diameter	11μm
CNT	
Type	MWNT CM-95
Density	1.8g/cm3
Diameter	10-15nm
xGnP	
Type	xGNP – M – 15
Density	2.2 g/cm3
Diameter	15μm

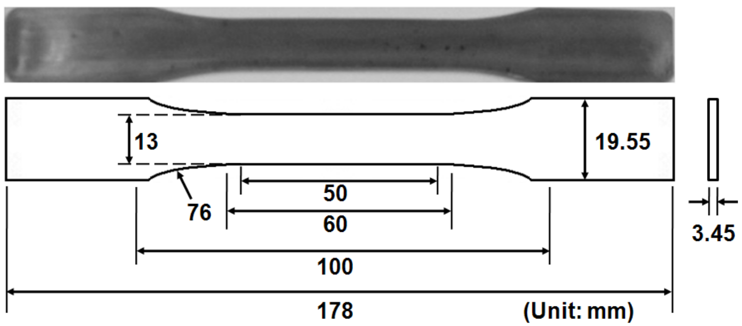
Maleic anhydride
(0.1 gram)

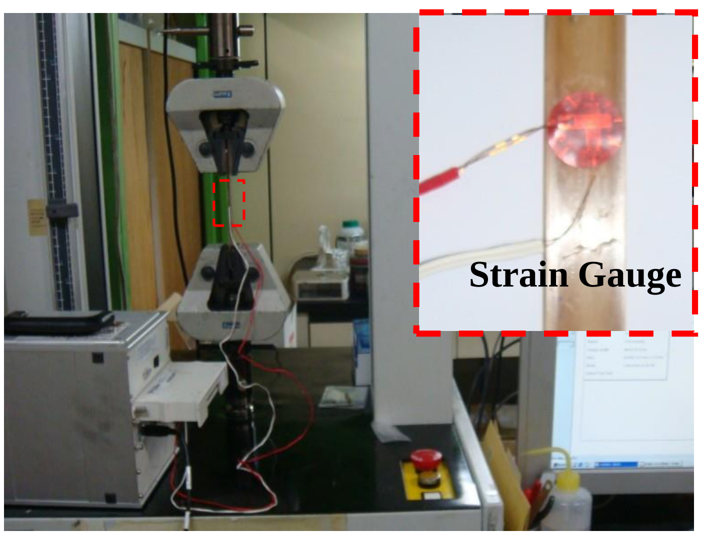
Xylene (400 ml)
Solvent to dissolve
PP and nanofillers

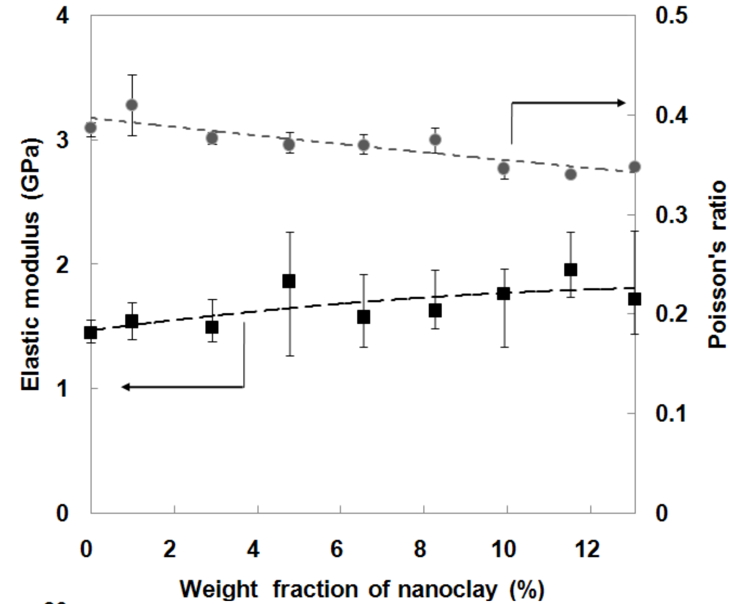
Lee J C, Hong Y S, Nan R G, et al. Soundproofing effect of nano particle reinforced polymer composites. Journal of Mechanical science and Technology, 2008, 22(8): 1468-1474.

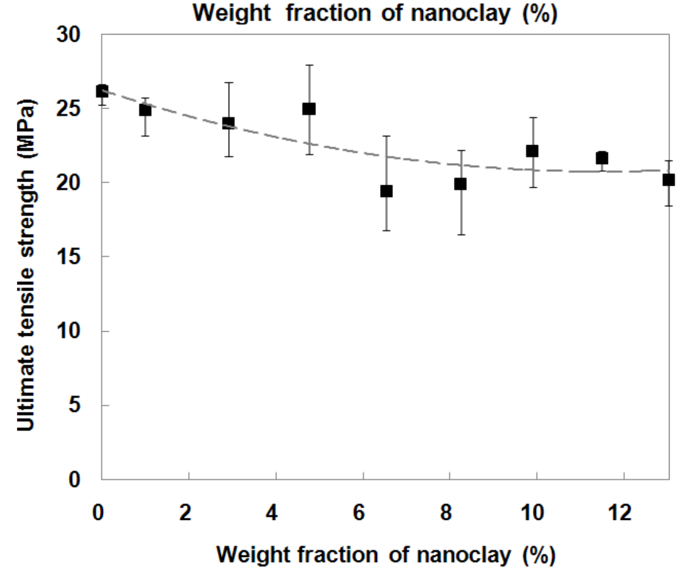
Mechanical property

- ASTM standard D638-03



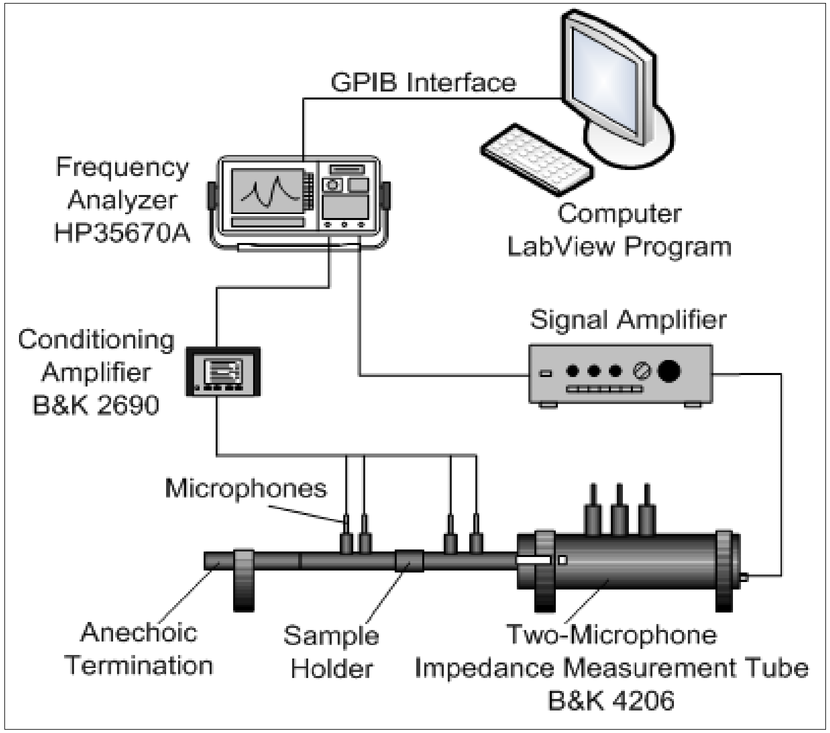






Yan J, Kim M S, Kang K M, et al. Evaluation of PP/Clay composites as soundproofing material. Polymers & Polymer Composites, 2014, 22(1): 65.

Impedance tube test



Schematic of four-microphone measurement setup

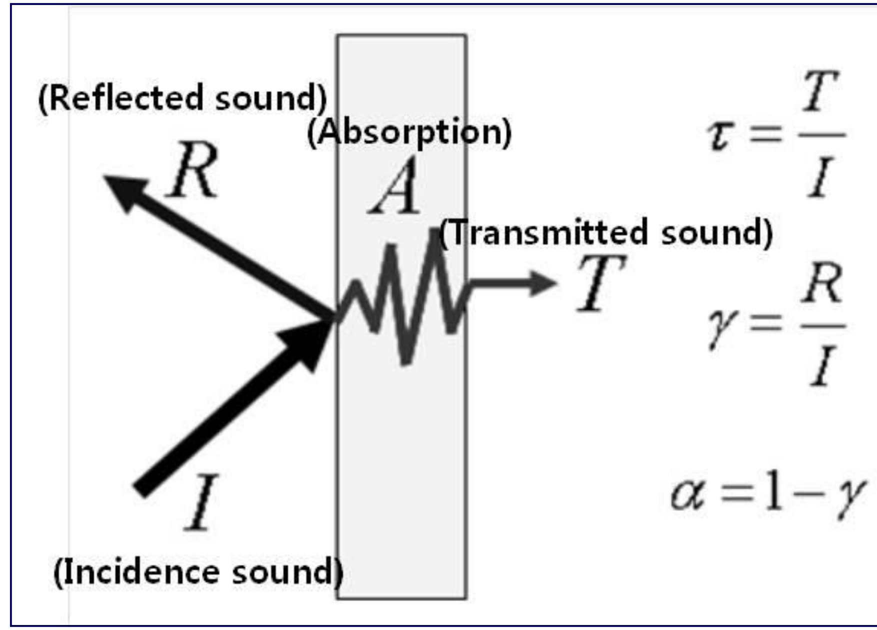


Diagram of energies of sound waves

$$STL(dB) = 10\log\frac{I_i}{I_t}$$ ------- (1)

Test set-up:

- Four 0.25-inch Brüel & Kjær (B&K) 4196 microphones,

- A B&K Type 4206 impedance tube,

- A B&K Type 2690 Nexus conditioning amplifier,

- An HP 35670A frequency analyzer,

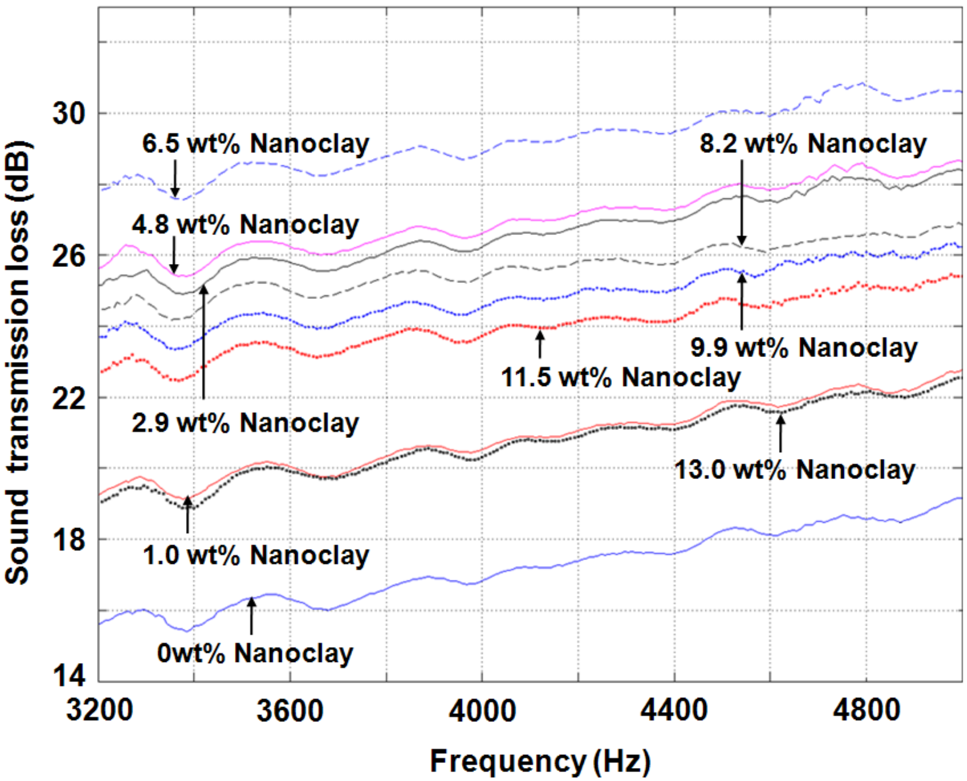
- Lab View Version 7.0 software

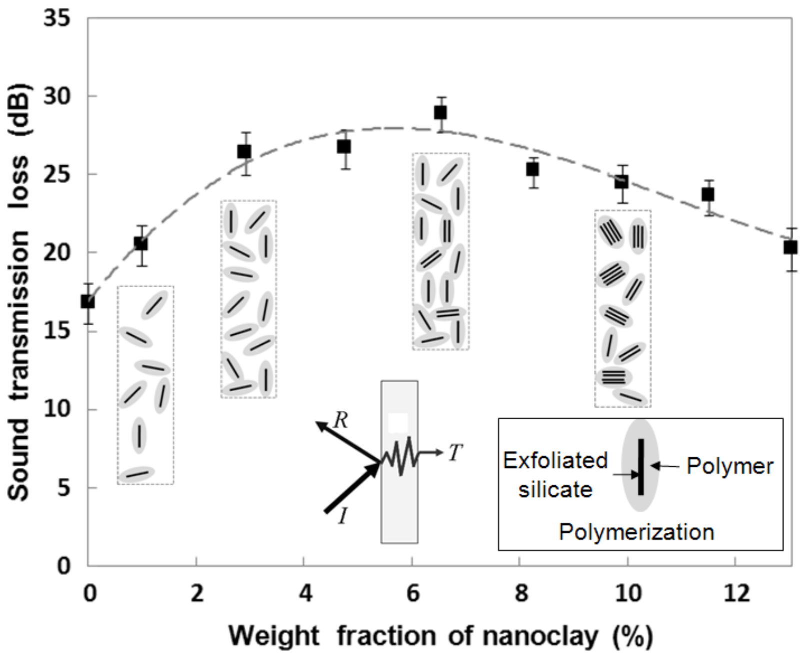
- **STL(Sound Transmission Loss): difference between the sound power levels of the incident sound and the transmitted sound**

- STL intensity is described by decibels (dB) according to Equation (1), where I_i is the incident acoustic power and I_t is the transmitted acoustic power

Kim M S, Yan J, Kang K M, et al. Soundproofing properties of polypropylene/clay/carbon nanotube nanocomposites. Journal of Applied Polymer Science, 2013, 130(1): 504-509.

Result

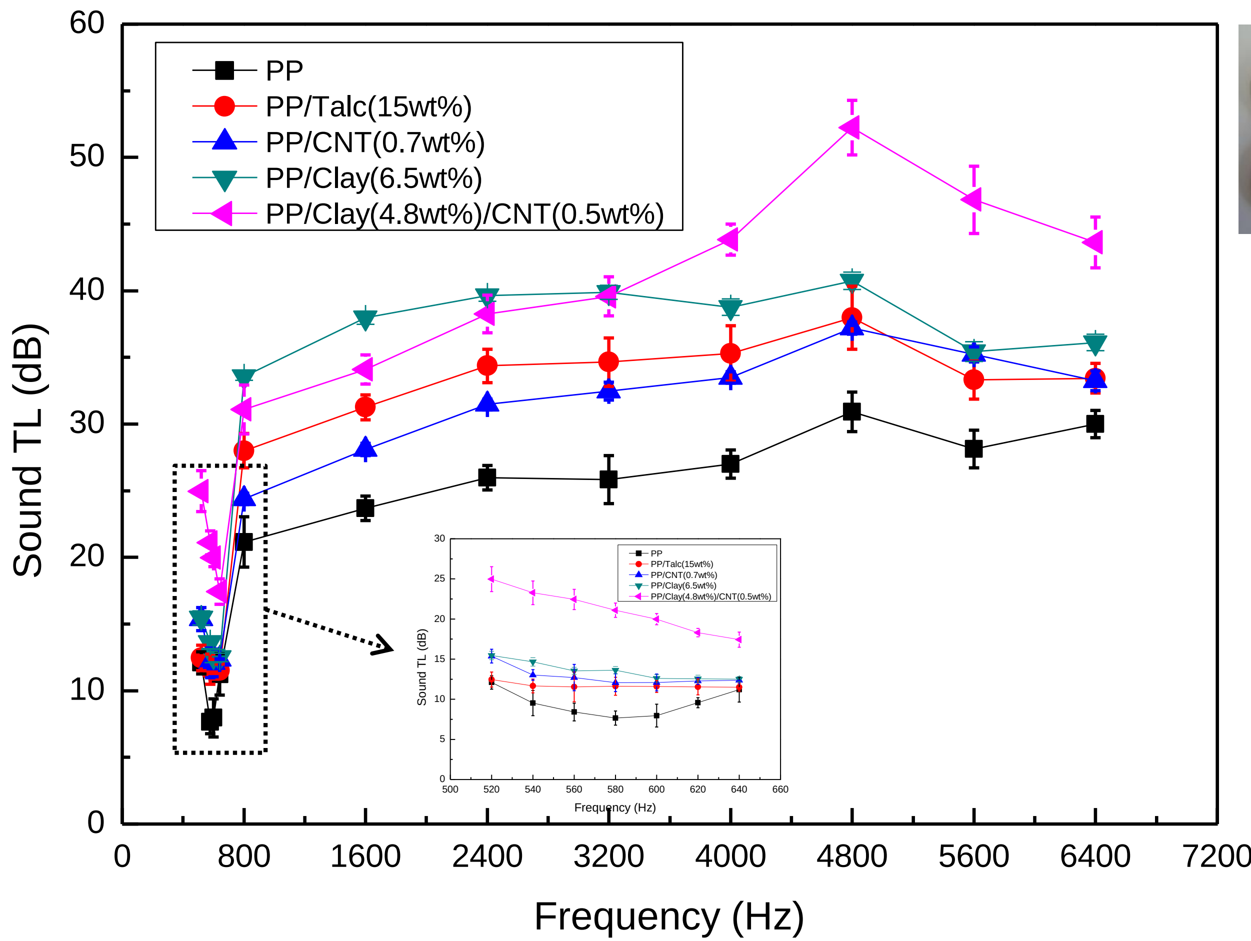




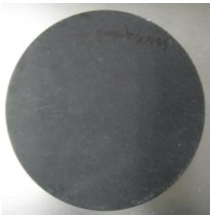
Average STL of nanoclay-reinforced PP composites between 3400 and 4600 Hz.

Kim M S, Yan J, Kang K M, et al. Soundproofing properties of polypropylene/clay/carbon nanotube nanocomposites. Journal of Applied Polymer Science, 2013, 130(1): 504-509.

Comparison of STL of PP/fillers composites



Diameter: 29mm
Thickness: 3mm

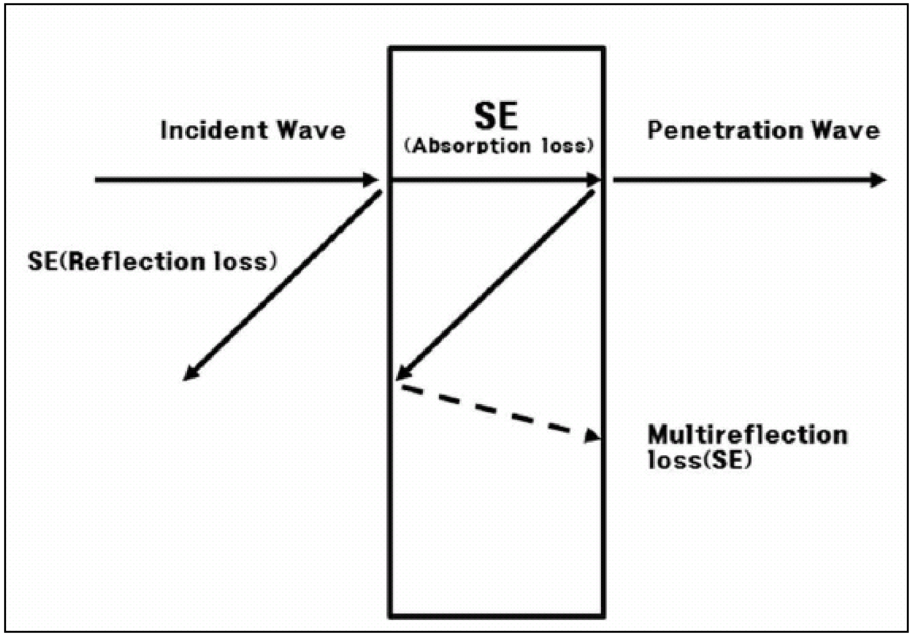


Diameter: 100mm
Thickness: 3mm

Kim M S, Yan J, Kang K M, et al. Soundproofing properties of polypropylene/clay/carbon nanotube nanocomposites. Journal of Applied Polymer Science, 2013, 130(1): 504-509.

EMI Shielding Effectiveness

EMI shielding effectiveness mechanism



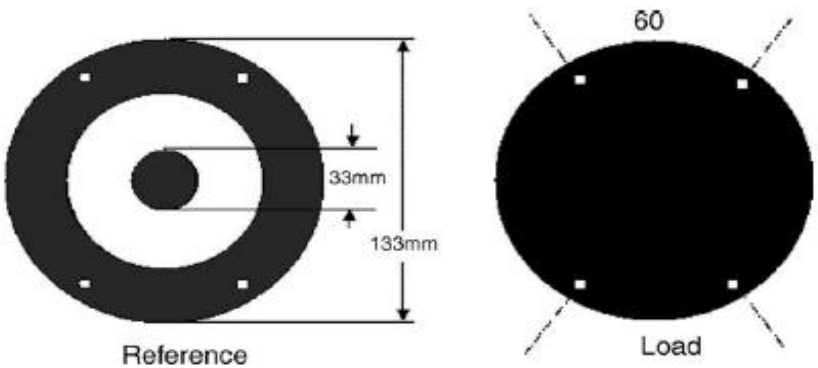
When an EM field is passed through an object, there are three phenomena : absorption attenuation, attenuation due to reflection, and attenuation due to successive internal reflections (usually neglected).

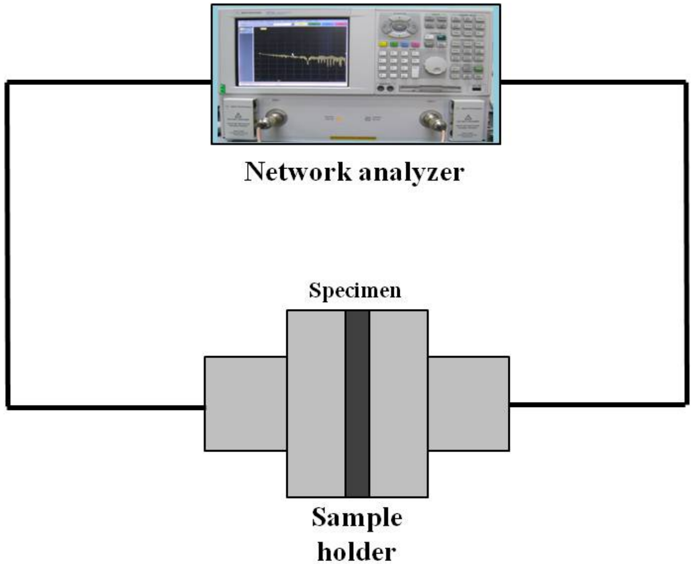
$$SE(dB) = 10\log\frac{P_i}{P_t}$$

The ratio of power received with the load specimen in place (Pt) and with the reference specimen in place (Pi).

Measurement setup of EMI SE

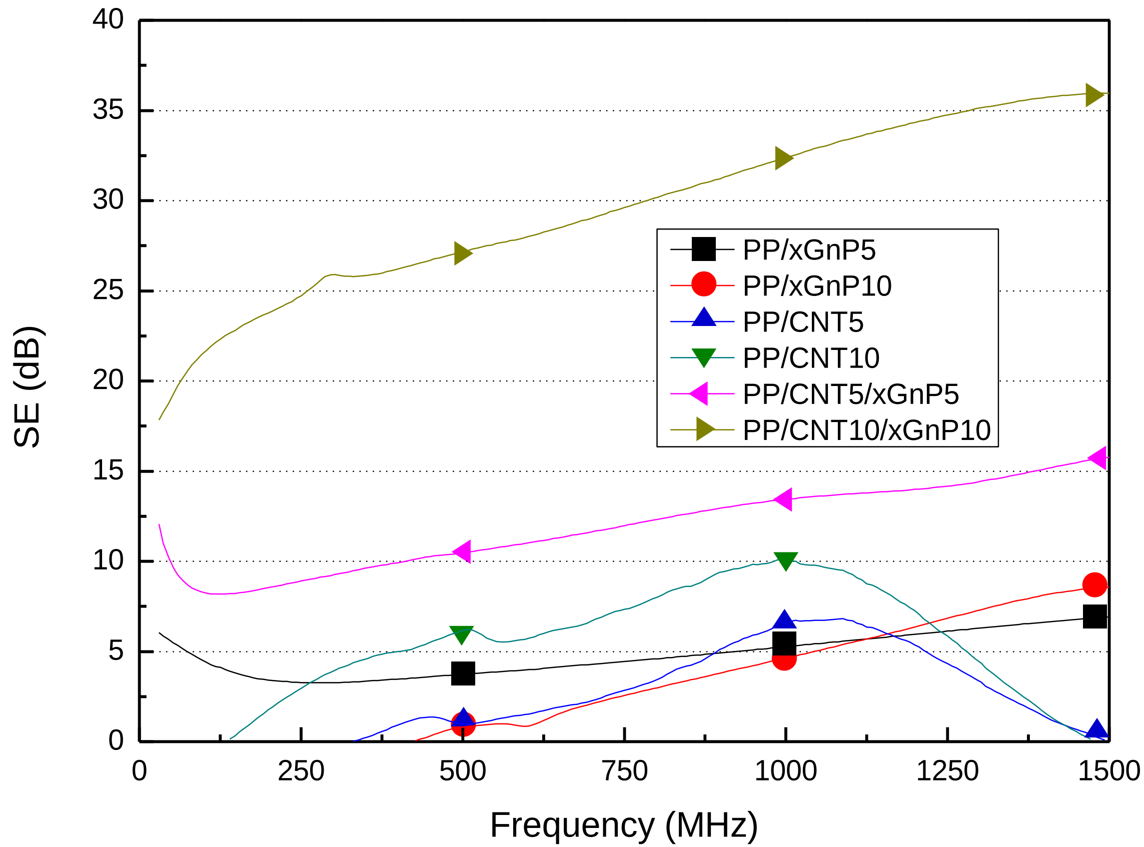
ASTM D 4935-99 (Diameter : 133mm, Thickness : under 1.5mm)





- Coaxial Transmission Line Method
- Agilent Technologies, N5230A PNA-L Network Analyzer
- Frequency : 30MHz -1.5GHz

Comparison of EMI SE of composites tested in this study as a function of CNT and xGnP content

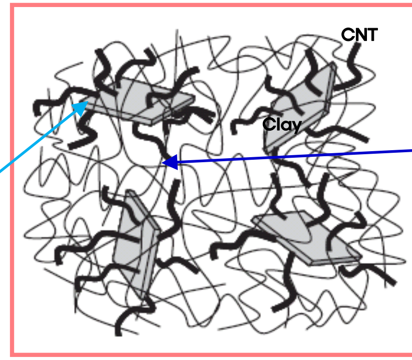


- As the amount of nanofiller loading increased, EMI SE also increased
- At the same nanofiller loading, PP/CNT/xGnP nanocomposites have considerably higher
- EMI SE than other nanocomposites

Synergistic Effect of Nanocomposites

Synergistic effect of nanocomposites

Strong combination



Homogeneous dispersion

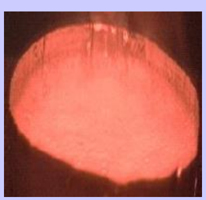
Synergistic effect

(polymer + nanofiller)

Efficient property enhancement

Mechanical

Electrical



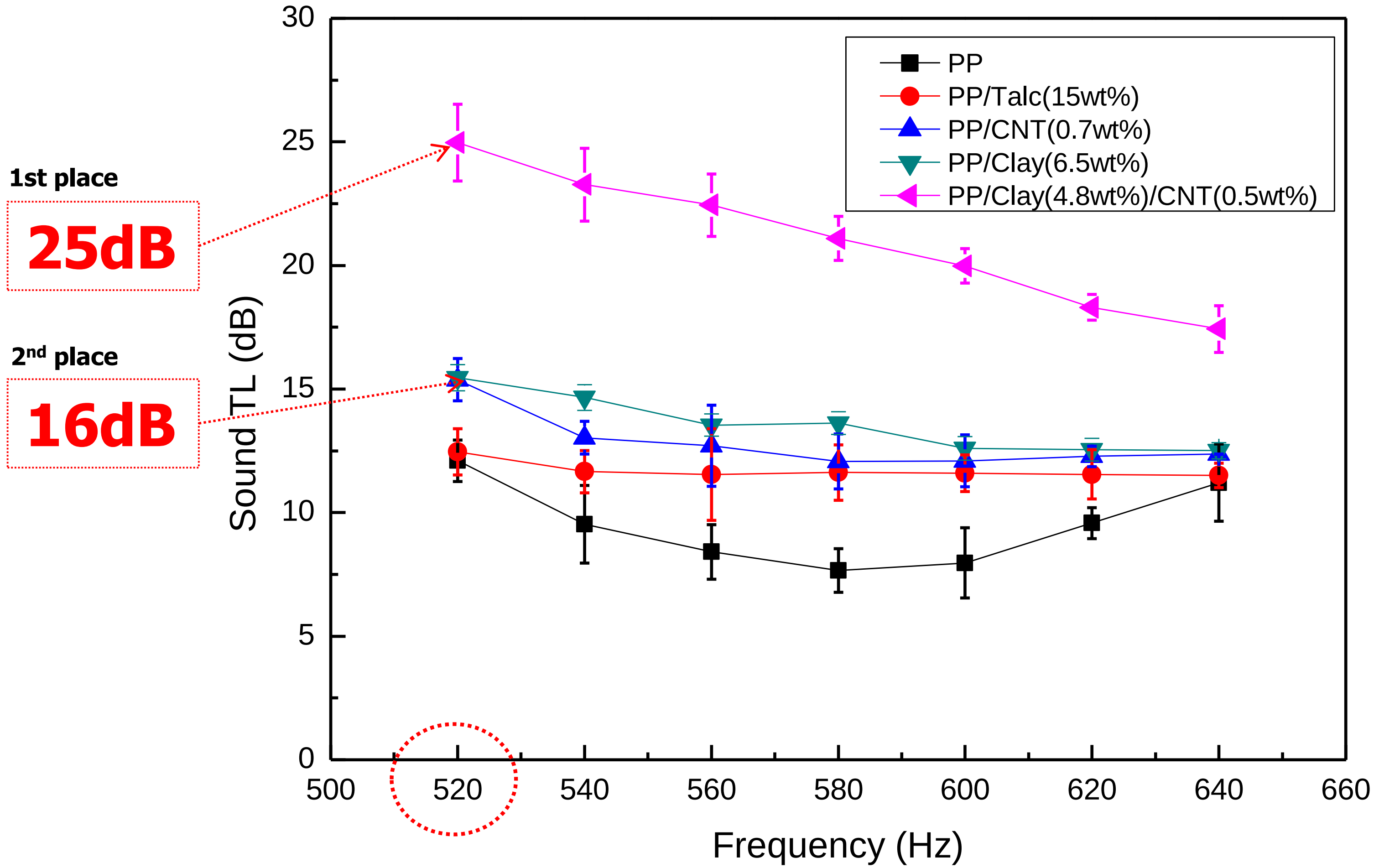
Thermal

EMI SE

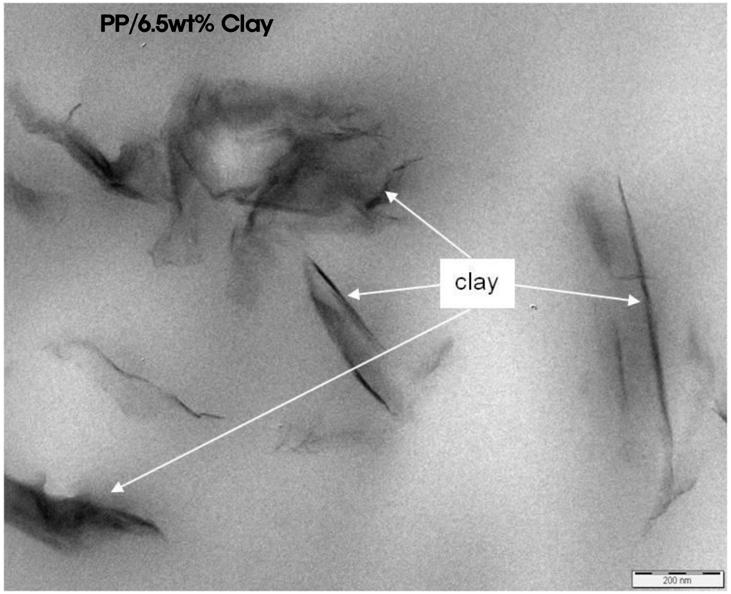
Growth of Carbon Nanotubes on Clay: Unique Nanostructured Filler for High-Performance Polymer Nanocomposites, *Adv. Mater. 2006, 18, 73–77*

Synergistic effect of soundproofing effect

- **Comparison of the STL values of composites**



TEM micrographs of PP/Clay & PP/Clay/CNT composite



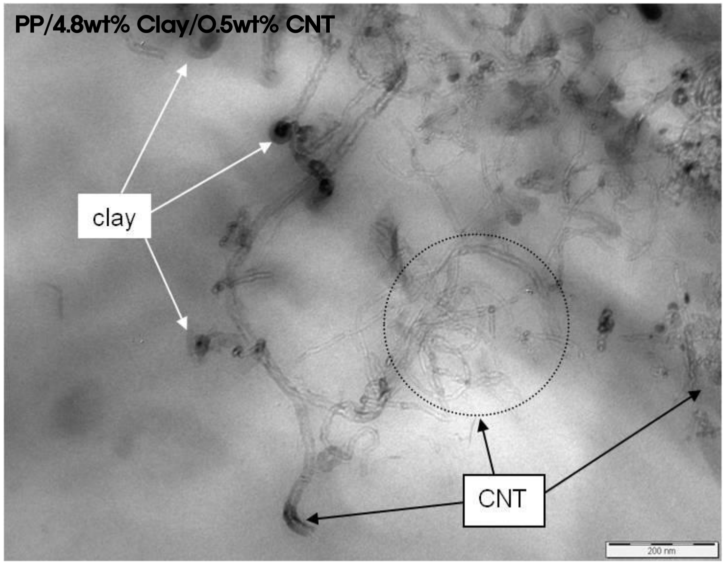
Why good soundproofing(2nd place)?

① Clay → dispersed homogeneously

② Good dispersion → affects property

→ **Synergistic effect**

What mechanism?



Why best soundproofing(1st place)?

① Clay → dispersed homogeneously

② CNT → connected to the clay

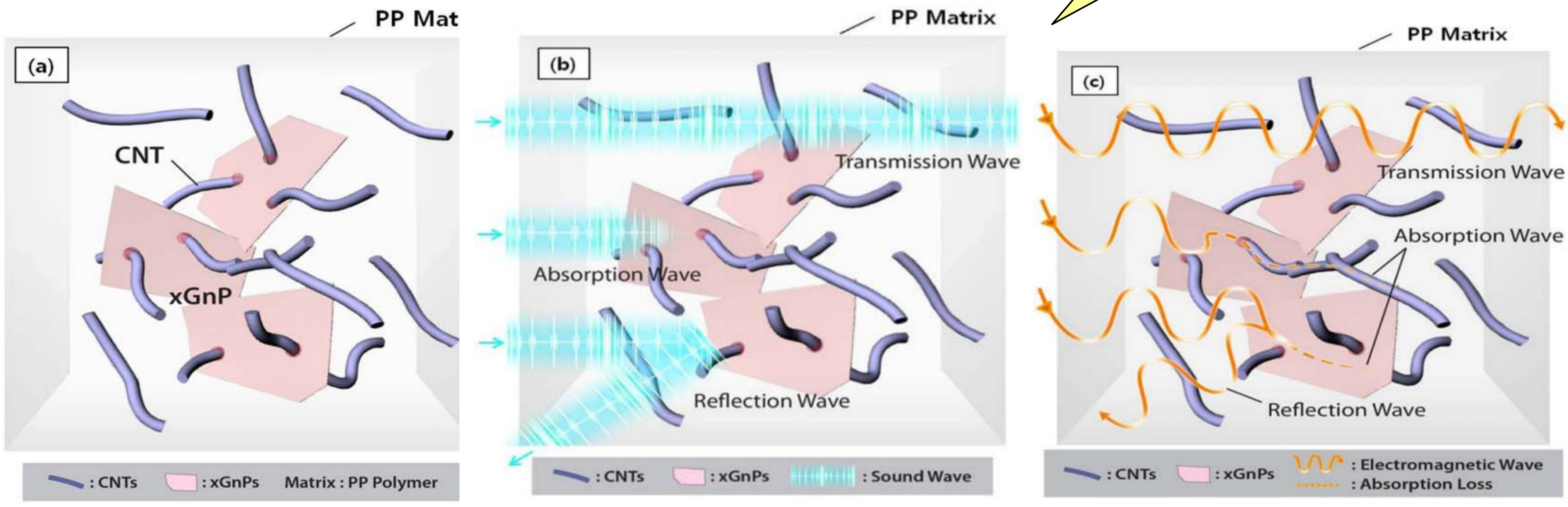
(+ entangled and wrapped around the clay)

③ Co-network structures → affects property

→ **Best synergistic effect**

Schematics diagram of EMI SE of nanocomposites (PP/xGnP & PP/xGnP/CNT composite)

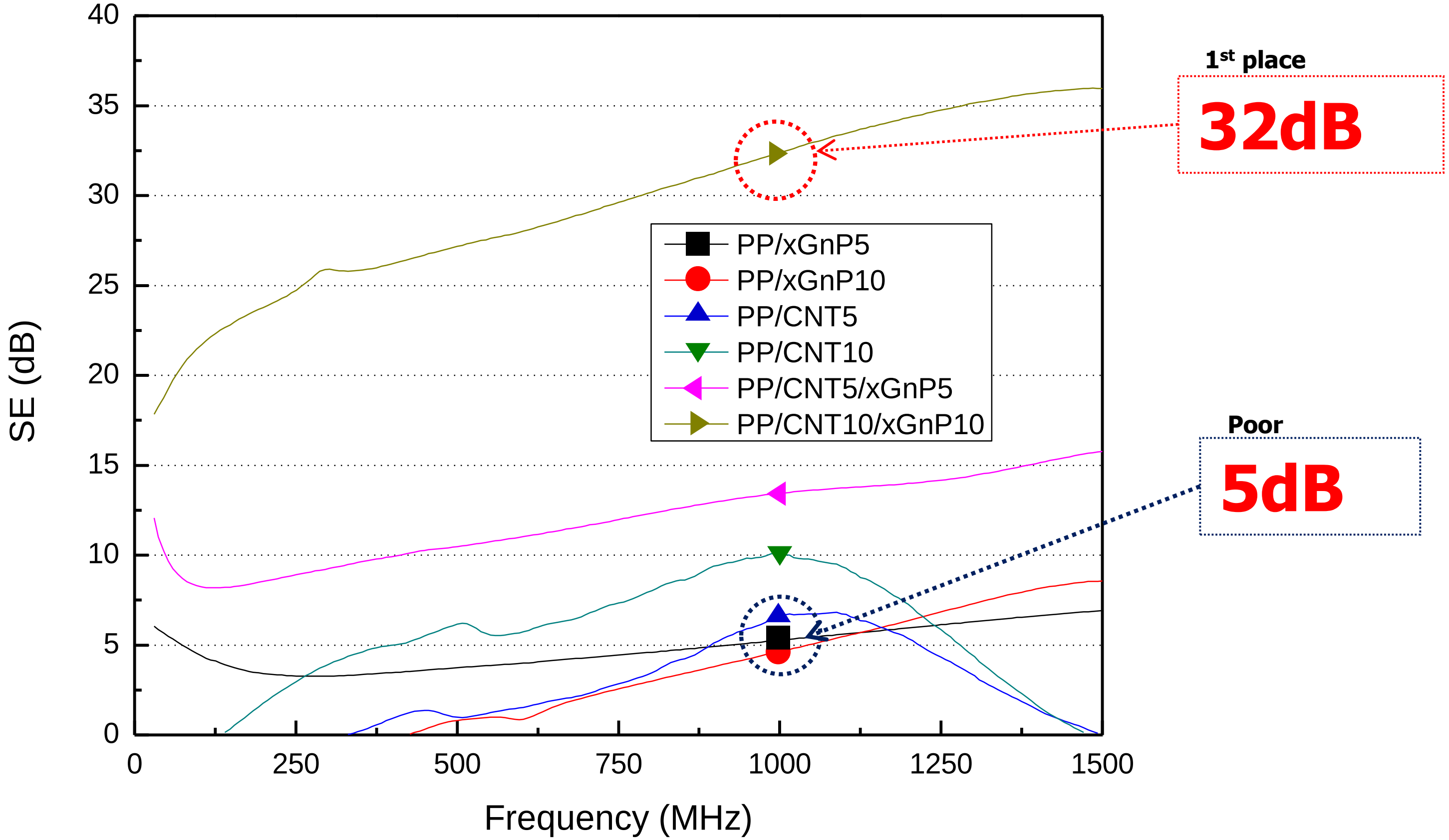
CNT → reflect and absorb more sound wave!



Kim, M.S., Yan, J., Joo, K. H., Pandey, J.K., Kang, Y. J., and Ahn, S.H., 2013, "Synergistic Effects of Carbon Nanotubes and Exfoliated Graphite Nanoplatelets for Electromagnetic Interference Shielding and Soundproofing," Journal of Applied Polymer Science, Vol 130, No. 6

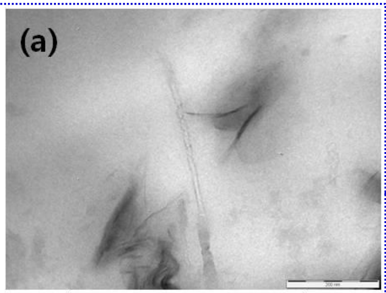
Synergistic effect of EMI SE

- **Comparison of the EMI SE of composites**



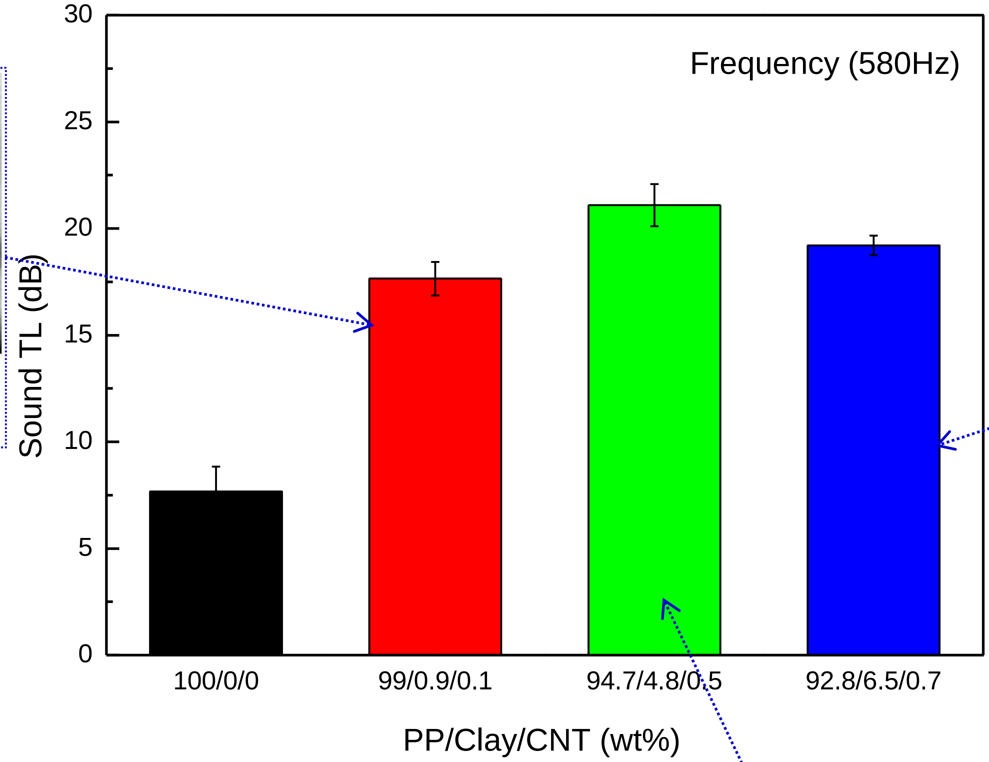
Synergistic effect as function of filler concentration

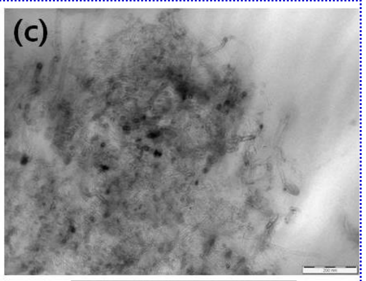
- **STL of PP/Clay/CNT as function of filler concentration**



PP/Clay/CNT
(99/0.9/0.1)

Small fillers
→ few synergy





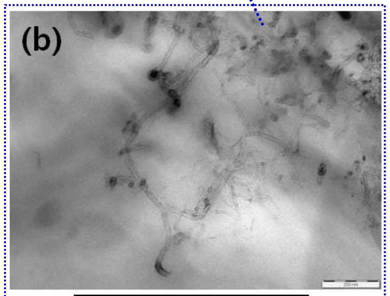
PP/Clay/CNT
(92.8/6.5/0.7)

Big aggregation
→ Poor synergy

- STL value of PP/Clay/CNT increases consistently until 4.8wt% clay and 0.5wt% CNT content.

- And, then STL value decreases.

As the amount of filler loading increased, aggregation of the nanofillers also increased.

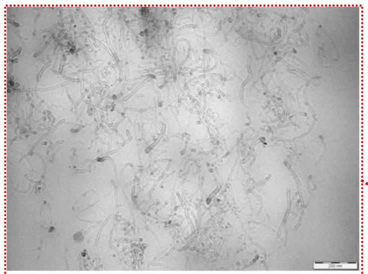


PP/Clay/CNT
(94.7/4.8/0.5)

Good dispersion
→ strong interfacial adhesion
→ Good synergy

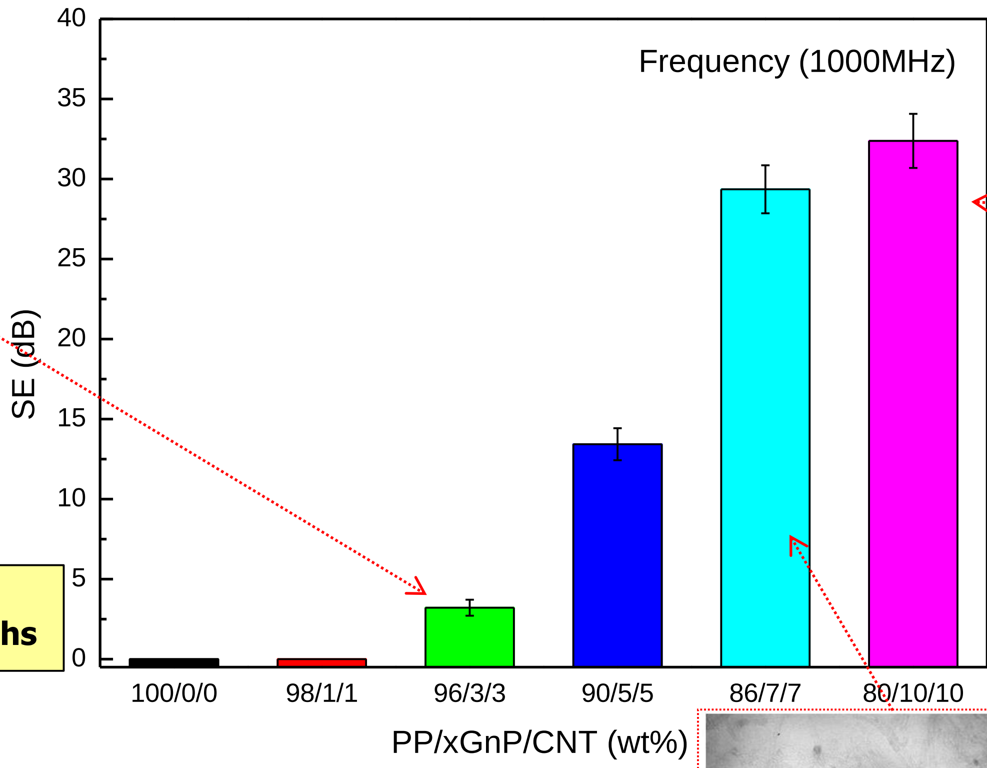
Synergistic effect as function of filler concentration

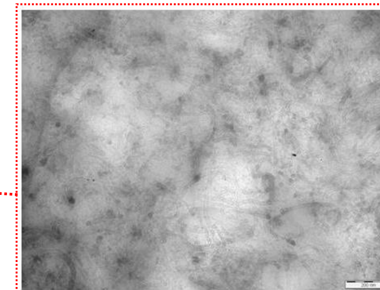
- **EMI SE of PP/xGnP/CNT as function of filler concentration**



PP/CNT/xGnP
(96/3/3)

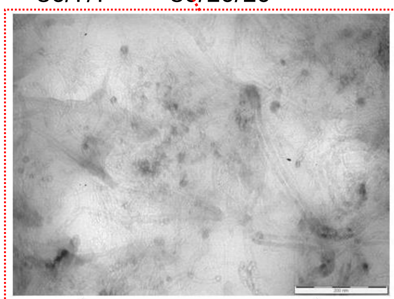
Small fillers
→ few conductive paths





PP/CNT/xGnP
(80/10/10)

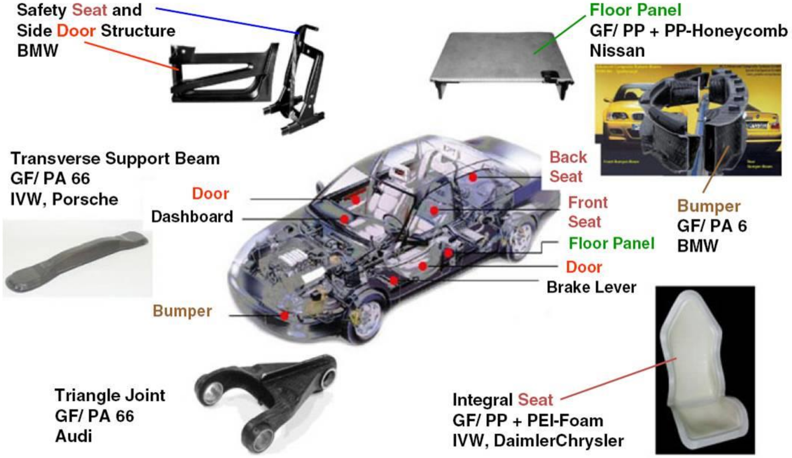
Many conductive paths

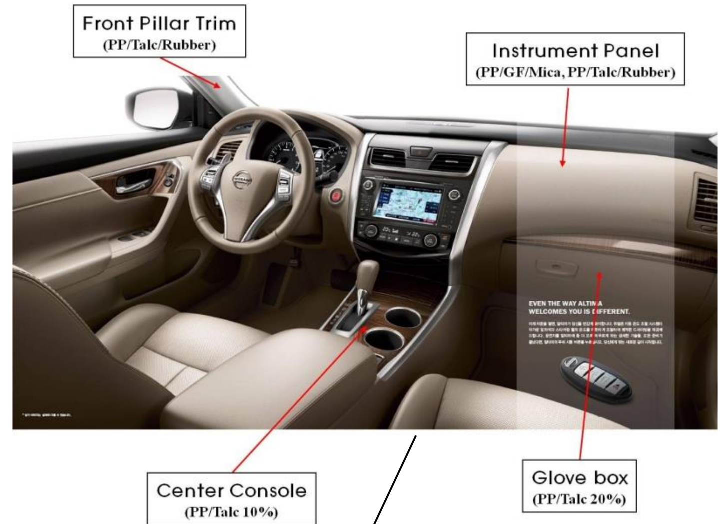


PP/CNT/xGnP
(86/7/7)

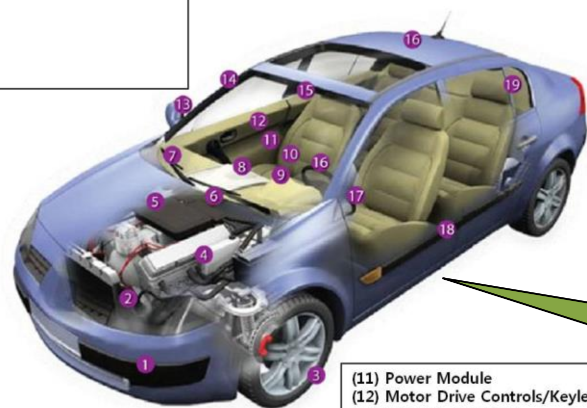
EMI SE of PP/xGnP/CNT increases consistently with the nanofillers content.

Application





(1) Active Cruise Control / Collision Avoidance
(2) Power Modules: BLS, High Current Chokes
(3) Tire Pressure Monitoring
(4) Vehicle Stability Control
(5) Electrical Clutch Actuation/Engine Control Unit
(6) Night Vision System
(7) Motor Drive Control
(8) In-Car Entertainment
(9) Head Up Display
(10) Climate Control



(11) Power Module
(12) Motor Drive Controls/Keyless Entry
(13) Lighting /Exterior
(14) Motor Drive Controls
(15) Embedded Functions in Rearview Mirror
(16) Satellite Radio/Navigation
(17) Driver Safety/Communication
(18) Power Modules
(19) Motor Drive Control

10-15% of total weight of the car are polymer composites.

Main merit: weight saving

Interior composite :
Soundproofing materials

Need: EMI SE ability

Green (Bio) Composite

How long does it take?

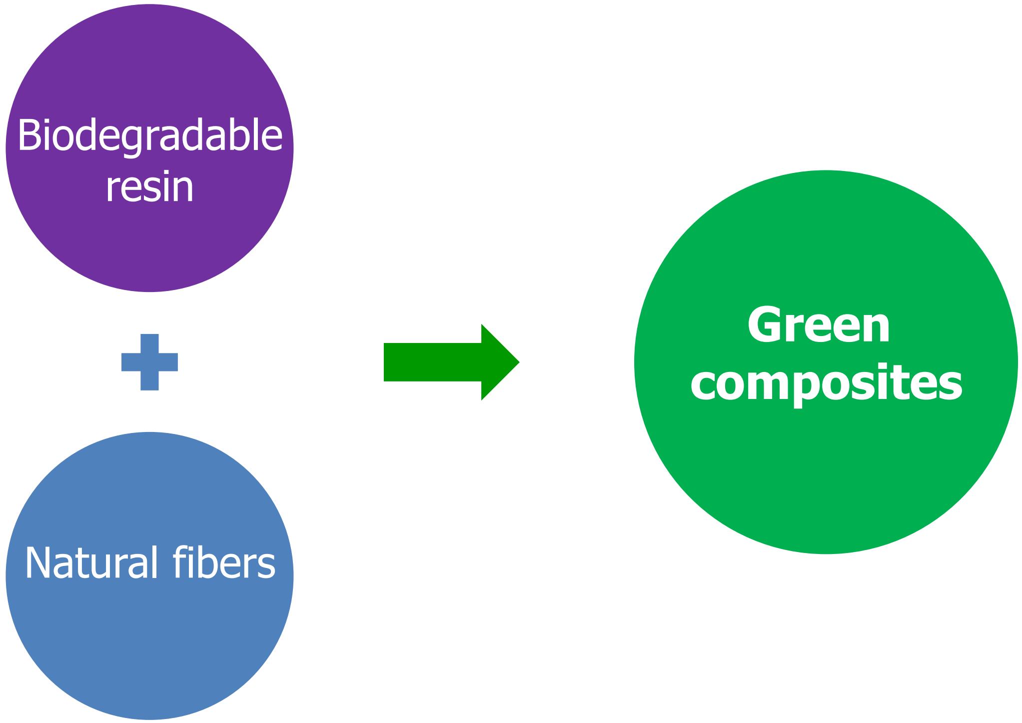
- **Complete mineralization and degradation time for products**

Products	Time
Cotton rags	**1-5 months**
Paper	**2-5 months**
Rope	**14 months**
Orange peels	**6 months**
Wool socks	**1-5 years**
Plastic coated paper milk cartons	**5 years**
Plastic bags	**10-20 years**
Nylon fabric	**30-40 years**
Plastic bottle	**~450 years**

http://www.friendlybags.com/some-facts.html

Green Composites

- **Green composite** combines plant fibers with natural resins to create natural composite materials



Green Composites

- **Polymer matrices**
  - Biodegradable polymers
    - Natural –
      - Polysaccharides – Starch, Cellulose, Chitin, Pullulan…
      - Proteins – Collagen/Gelatin Casein, Albumin, Fibrogen, Silks, Elastin
      - Polyesters – Polyhydroxyalkanoates
      - Other polymers – Lignin Natural Rubber
    - Synthetic
      - Poly – amides /anhydrides /amide-enamines /vinyl alcohol…

- **Fibers**
    - Natural /biofibers may be classified in two broad categories: Non-wood fibers and wood fibers
    - Natural fibers such as kenaf, flax, jute, hemp and sisal have attracted interest, especially as E glass fiber substitute in the automotive industry
    - Other fibers: Coir, Bamboo, Pineapple, Ramie

Green Composites

- **Potato car makes debut at Sexy Green Car Show**

A group of students at Warwick University in England have built a 125mph car called Eco One using mostly biodegradable materials.

- Tires come from potatoes

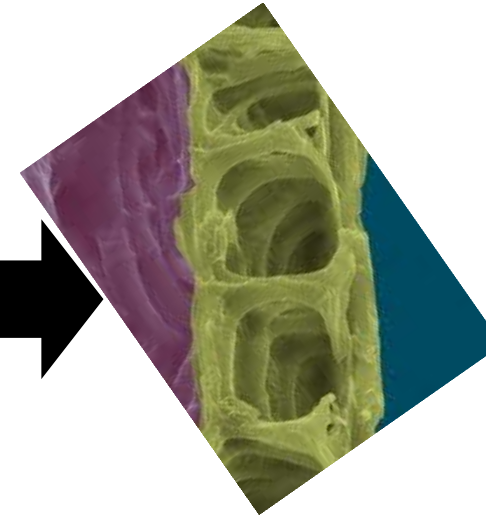
- Brakes pads are made from cashew nut shells

- Body is hemp

- It runs on biofuels

The goal is to build a vehicle that is 95 percent bio-degradable or recyclable. The chassis is made from steel for strength but plant products can substitute for plastic in many areas.

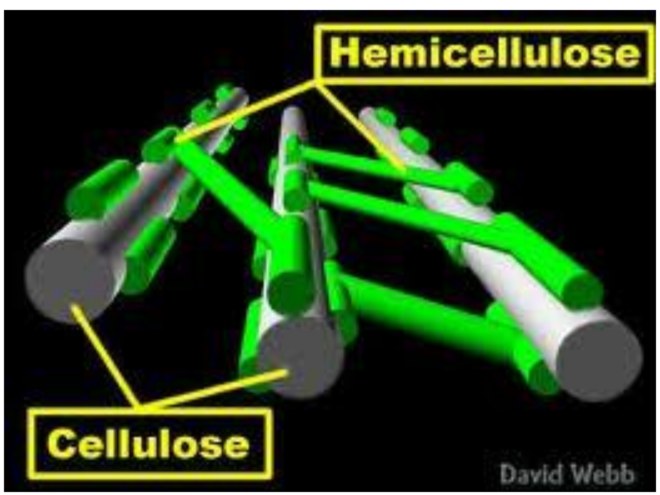
Nanocomposites from natural material



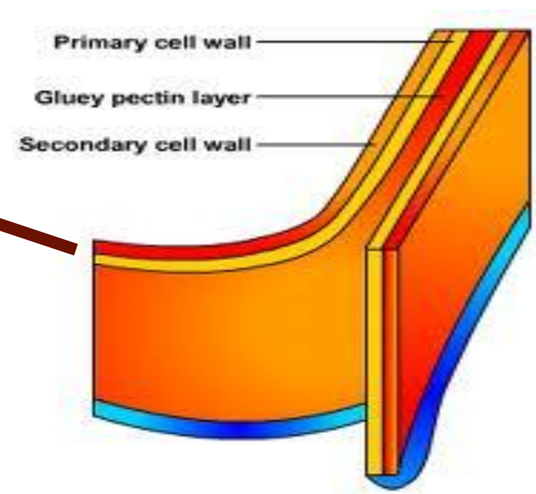
Biomass

Trees

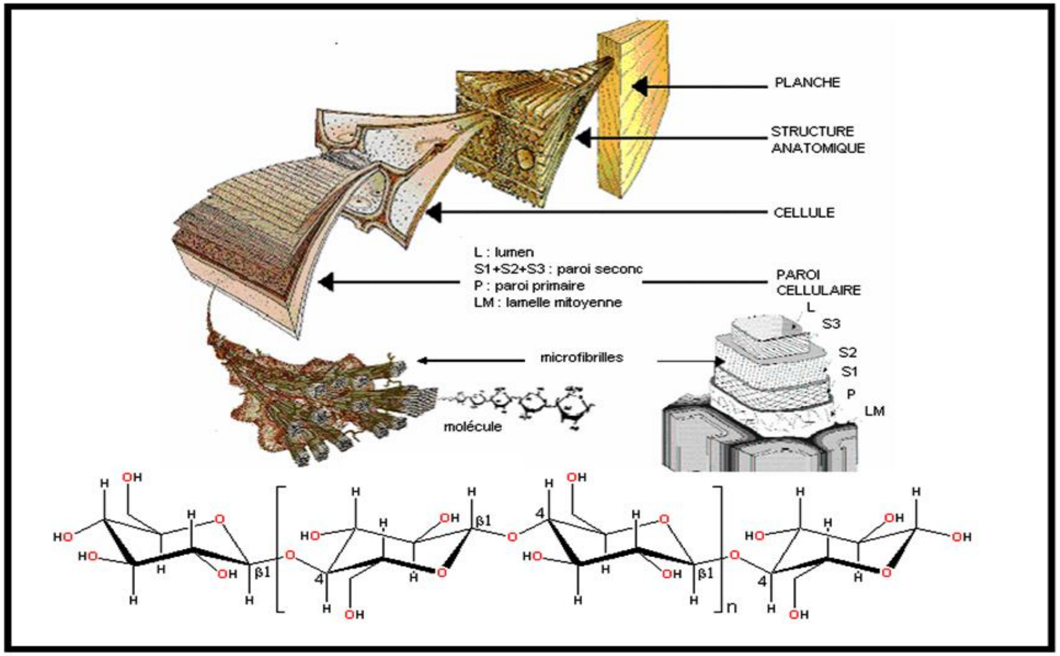
Plant Cell wall



Primary wall



Cellulose



Essential component of all plant fiber

- Form a microcrystalline structure with region of low and high chain order
- Hemicellulose, lignin pectin and wax etc are comprise of matrix, in which cellulose embedded
- Nano size crystallite may be extracted and applied as filler

Native cellulose → (Chemical and mechanical treatments) → **Microfibrils** → (Acid hydrolysis) → **Rod like crystals, nano whiskers, 3-10 nm width, several nm length**

Why Nano-Cellulose

Crystalline VS Natural Vs Synthetic Fibers

	Density (g/cm^3)	Diameter	Mean Length of Fiber (mm)	Tensile Strength (MPa)	Young's Modulus (GPa)
Flax Fiber Bundle	1.5	20 µm	30	345-1100	100
Hemp Fiber Bundle	1.3-1.4	22 µm	20	690	69
Cellulose Nanofibers	-	**10-70 nm**	**36-40 molecular chains**	**7500**	**130**
Elementary fibril (Micelle)	-	35 A°	100 glucan units	-	-
Monoclinic unit cell	-	10.3 A°	-	-	**260**
E-glass	2.5	9 µm	-	1700	70
Carbon fiber	1.7	70-500 nm	-	3445	230-240

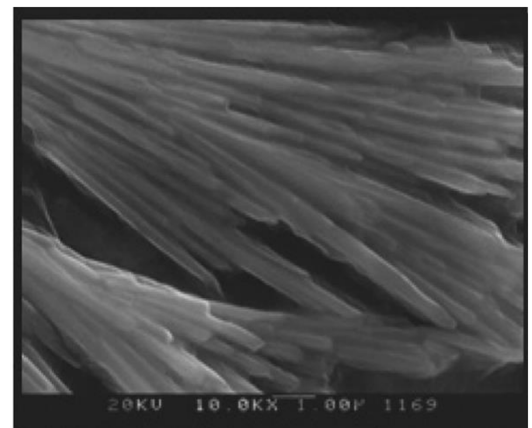
Dufresne etal. J. Phys. Chem. B, 108 (2004) 10845.

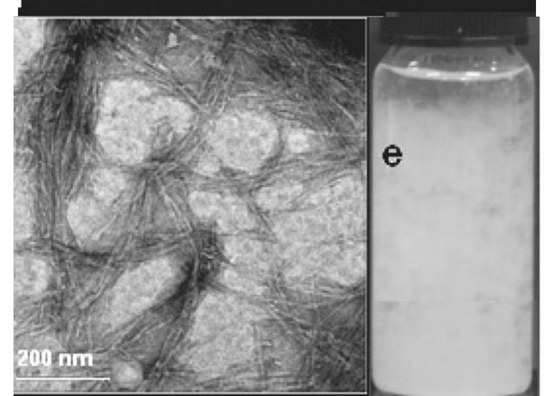
Sources of Nano-Cellulose

Potato, Flax, Rice Husk, Sugar cane, wheat straw, Banana, Coconut, Bamboo

Sources of Nano-Cellulose

Korean Grass- SNU campus

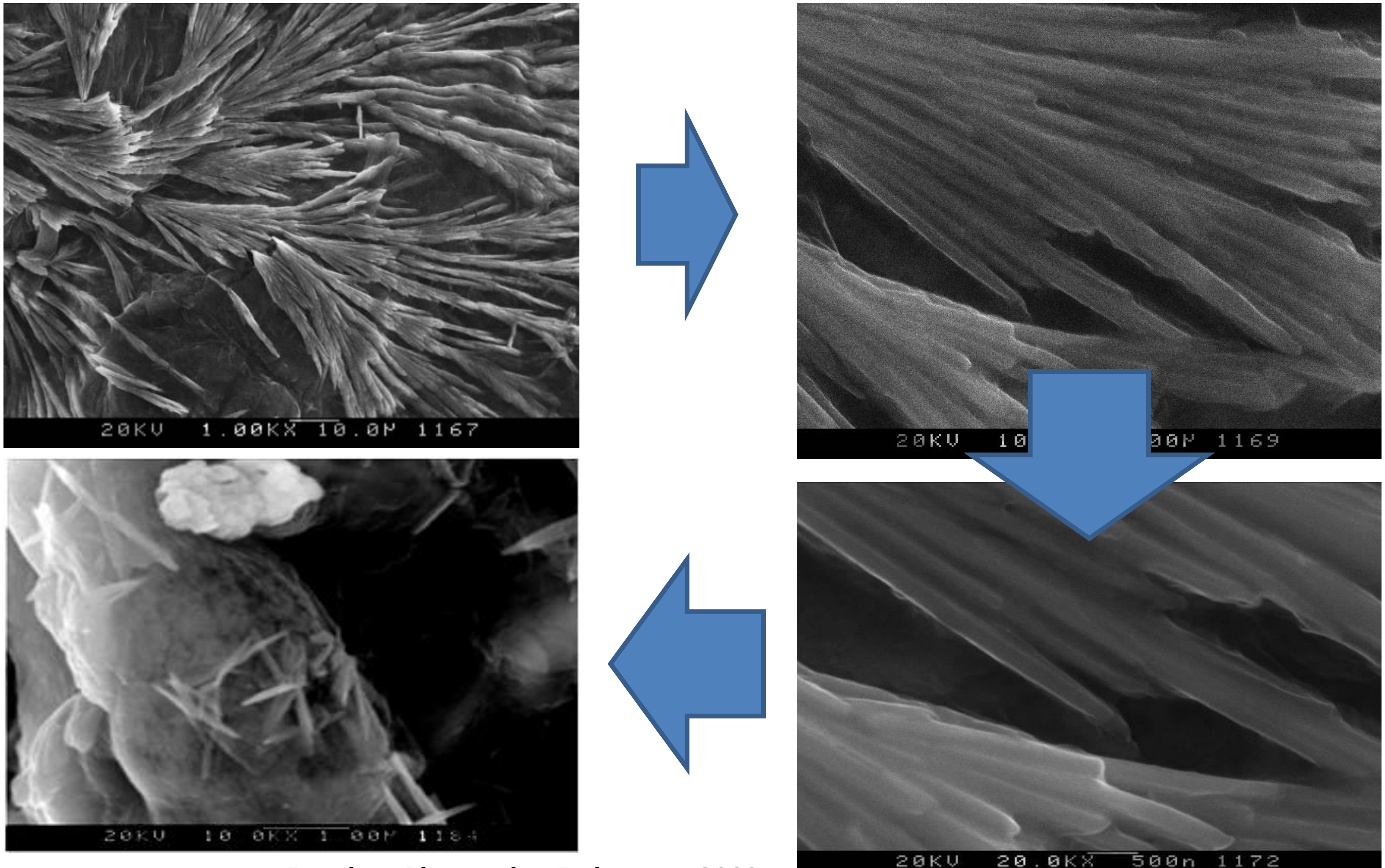




Unlimited, Almost Free, No Fertilizer, Seed requirement, deep penetrated roots

Pandey, Ahn et.al. Macromolecular Research . 2008

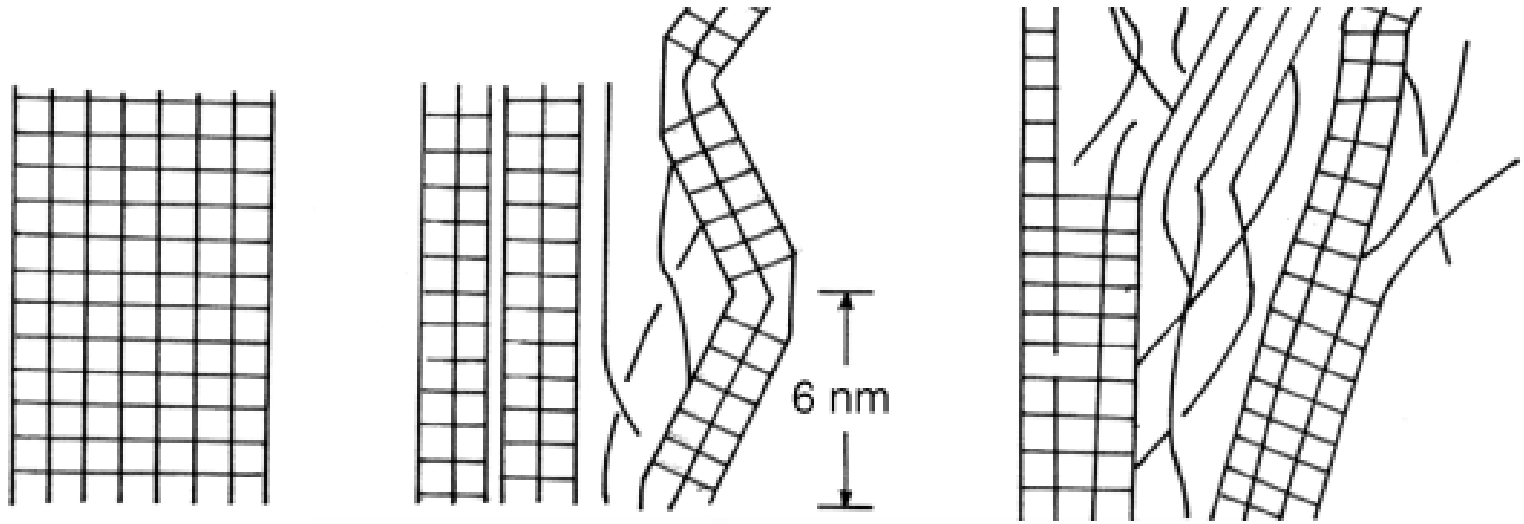
Morphology of Nano-Cellulose

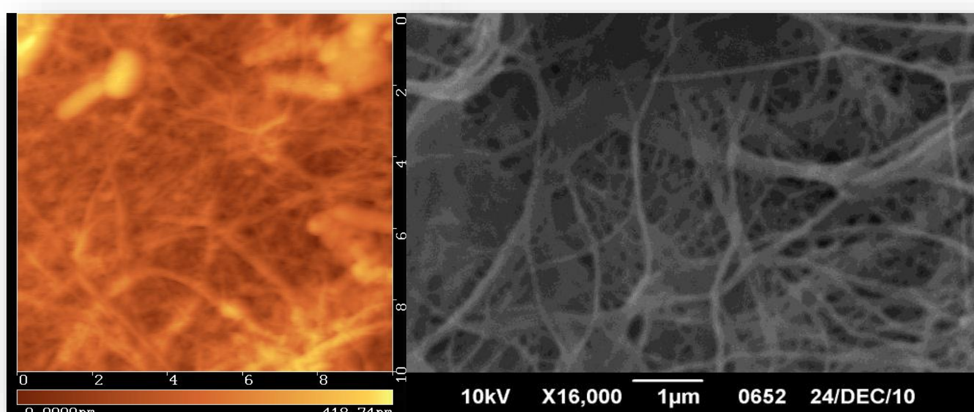


Pandey, Ahn et.al. e-Polymers. 2009

Extraction: Mechanical treatments

Cellulose bundle | **Mechanical defibrillation** | **Nano-cellulose fibers**



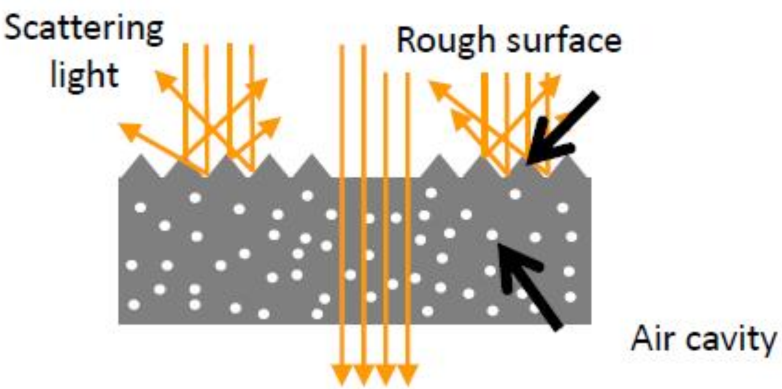


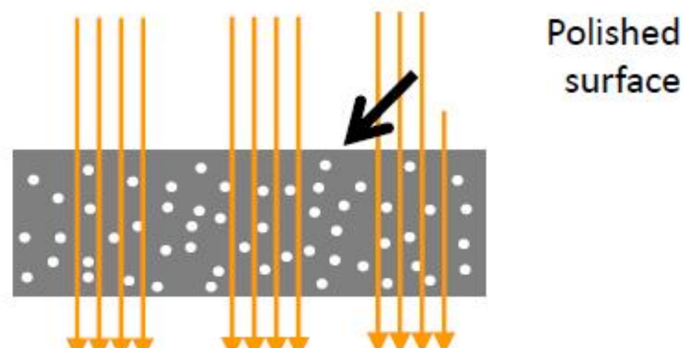
Nanocomposites of cellulose

Optically Transparent Composites

Translucent nanofiber sheet

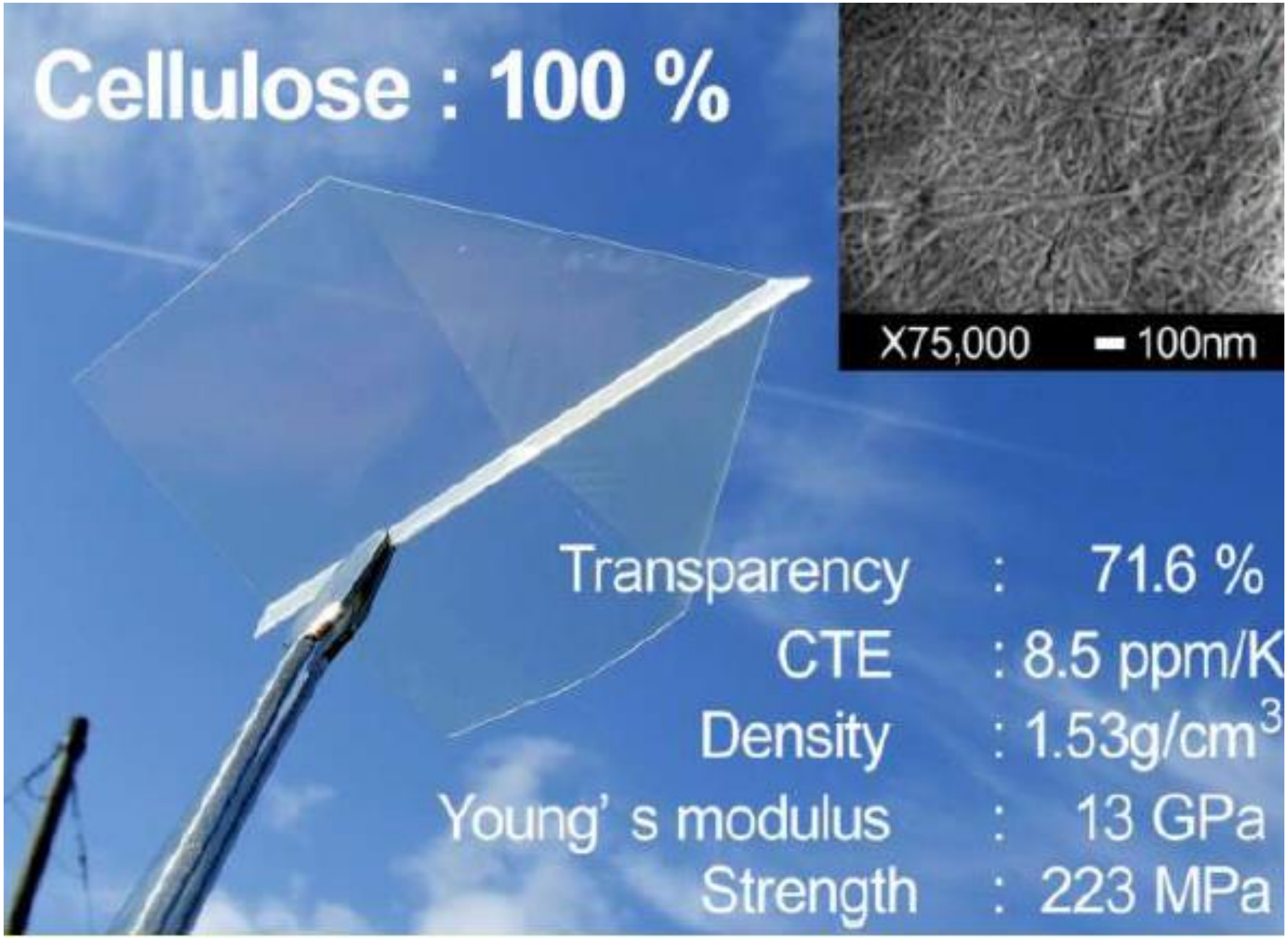
Transparent nanofiber sheet





Cavities are small enough to avoid light scattering

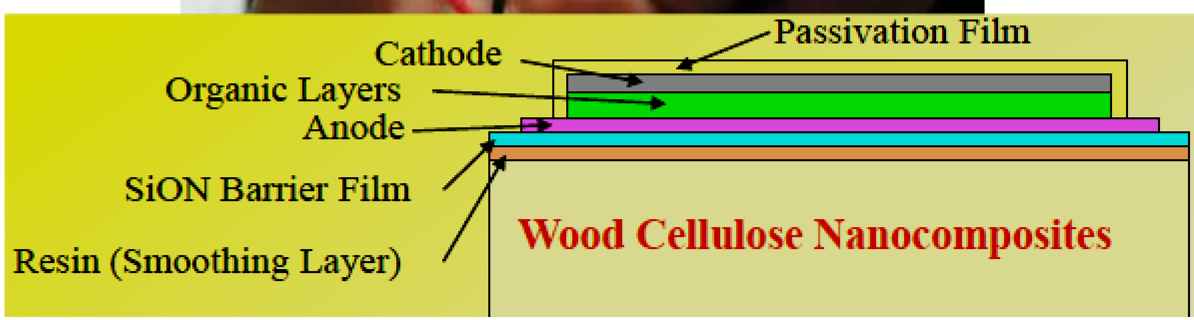
Nanocomposites of cellulose



M.Nogi et.al. , Adv. Mater. 2009

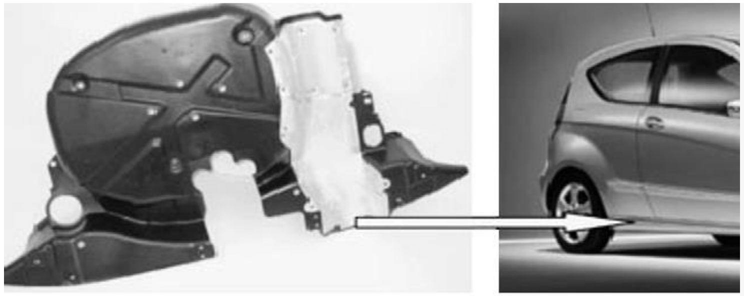
Nanocomposites of cellulose

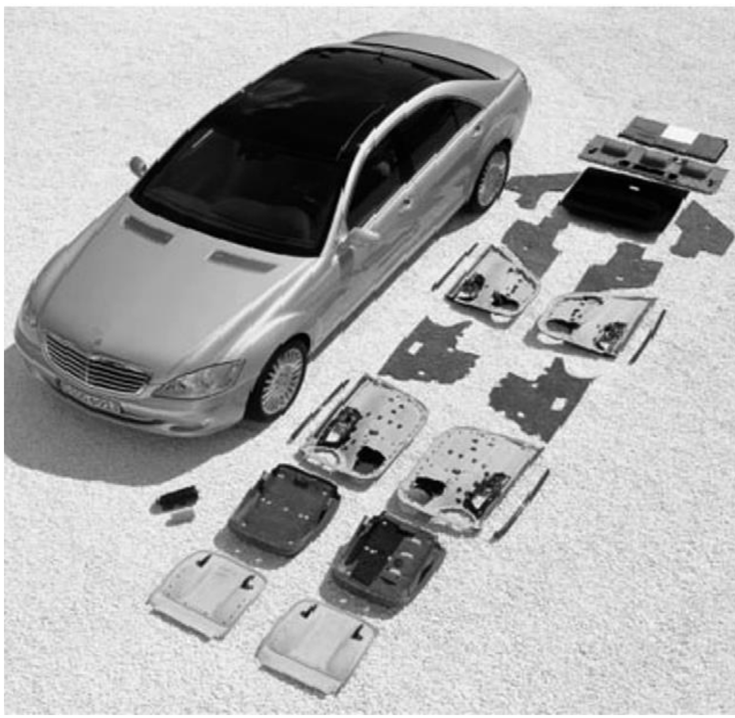
Luminescence of an OLED deposited on the wood nanofiber-composite



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

Green Nanocomposites for Automotive Parts





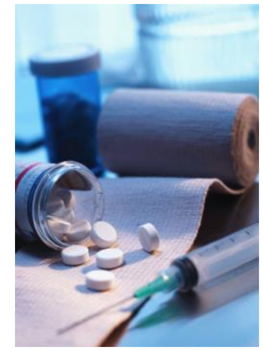
Automotive component	Typical weight of fibre kg
Front door liners	1.2–1.8
Rear door liners	0.8–1.5
Boot liners	1.5–2.5
Parcel shelves up to	2.0
Seat backs	1.6–2.0
Sunroof sliders up to	0.4
NVH material min	0.5
Headliners average	2.5

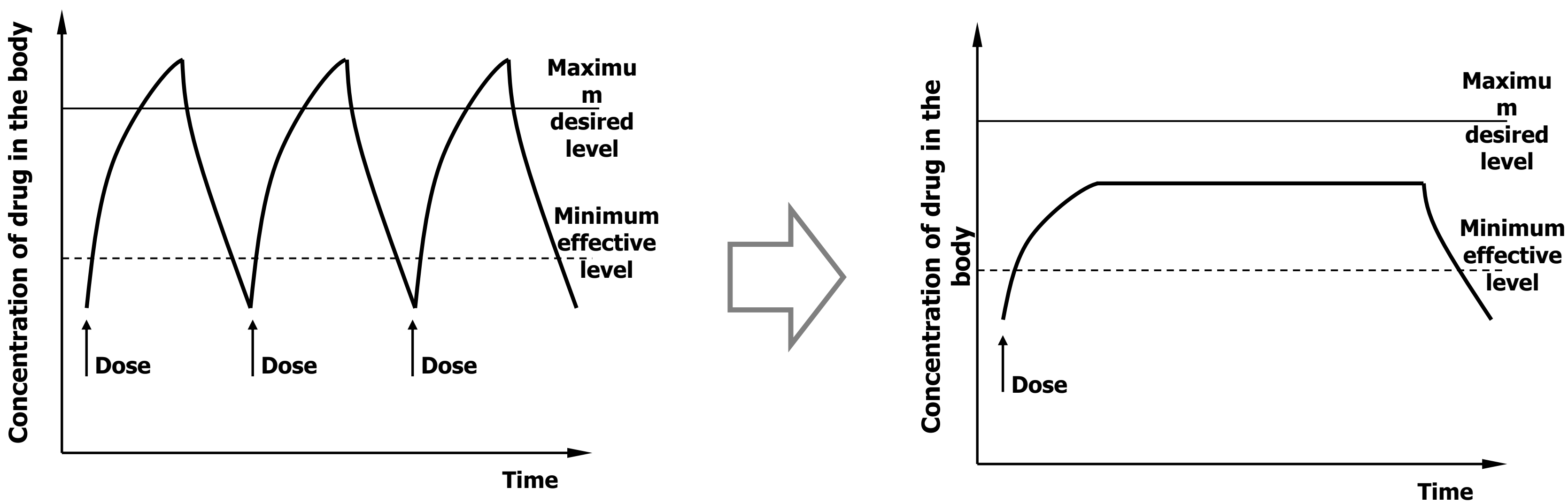
Primary importance to the automotive industry is the weight reduction of the components, which is possible up to 30% when using bio-fibres. ~ 20 % fuel efficiency

M. Kaup, M. Karus, ''Naturfasern fu¨r die Europa¨ische Automobilindustrie'', Nova Institute 2002, http://www.nova-institut.de

Introduction to DDS

- **Advantages of controlled drug delivery**
  - Delivered at intended sites
  - Less side effects
  - Replacing multiple injection or oral DDS
  - Improvement of patients' quality of life

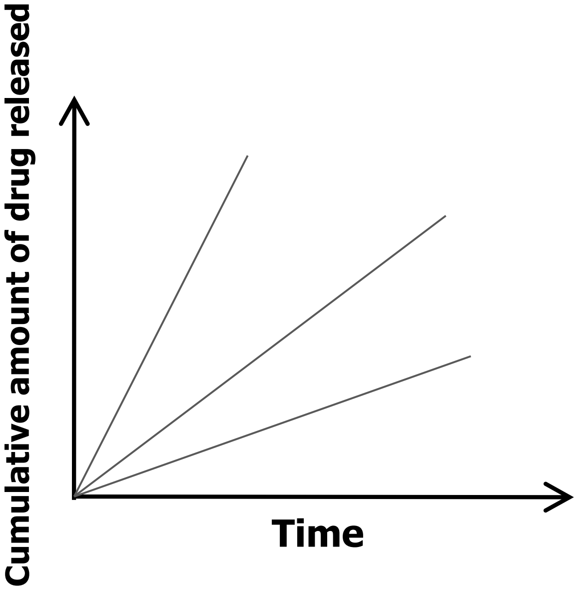




Comparison of conventional drug delivery (left) and controlled drug delivery (right)

Objectives

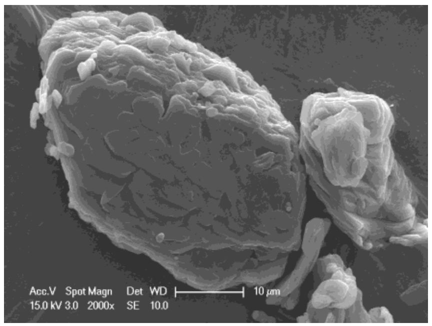
- **Development of implantable drug delivery system**
  - Controlled drug release *in vitro/in vivo* environment
  - Shape stability *in vivo* environment
    - Amount of released drug: about 60%
    - Long term release (weeks ~ months)
    - Linear release profile



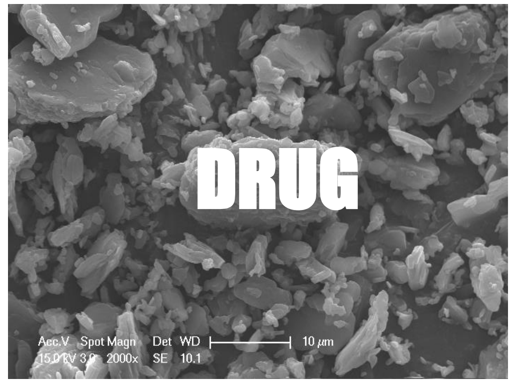
- **Methods**
  - Fabrication method: micro-fabrication methods
  - Material: biodegradable polymers, drugs, and additives
  - Shape: scaffold

Drug-Polymer Composite

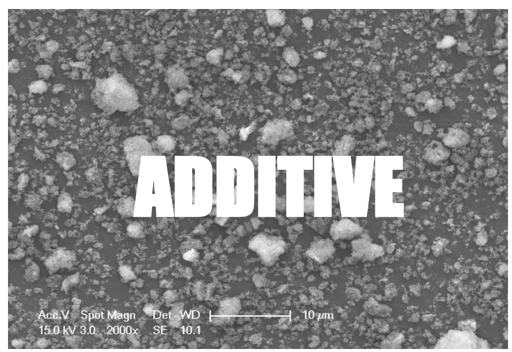
- **Process**



5-FU particle (about 100㎛ width)



Ground 5-FU (about 10㎛ width)



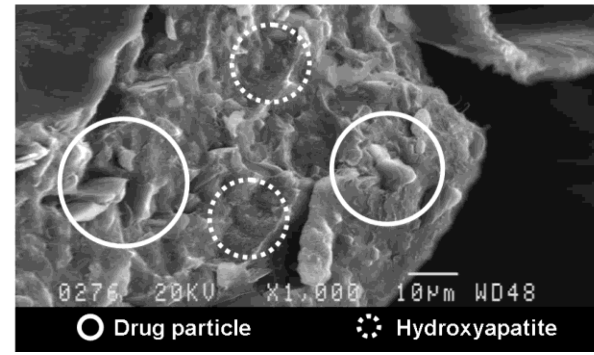
HA particles

$[\text{-OCH(CH}_3\text{)CO-}]_x[\text{-OCH}_2\text{CO-}]_y$

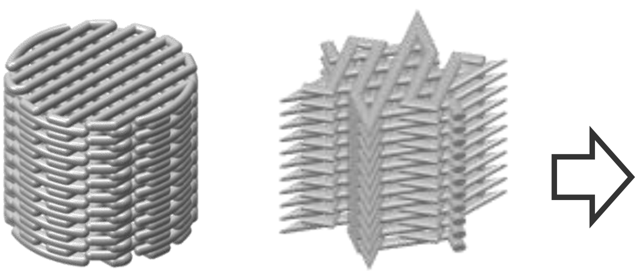
POLYMER

High Shear Mixing Method in 120 ℃

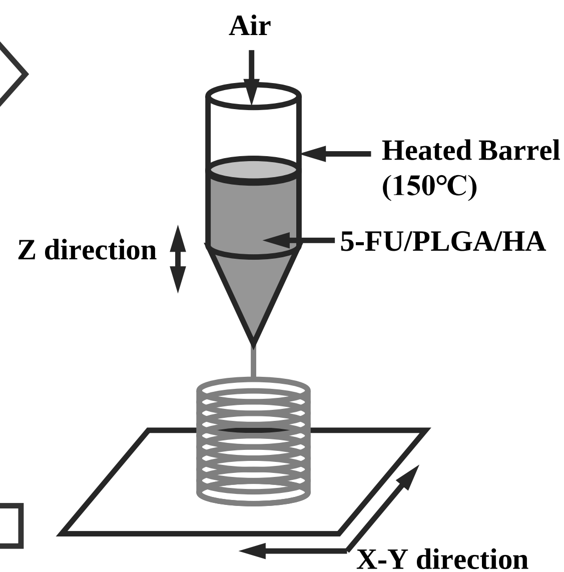
Matrix: PLGA
DL-poly(lactide-co-glycolide)



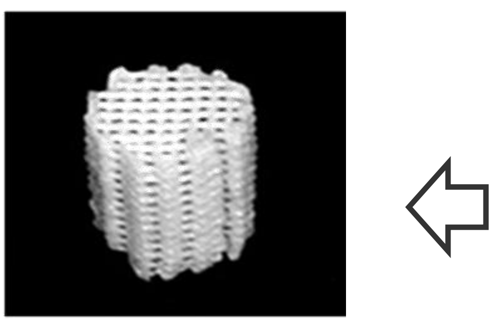
Direct Technique



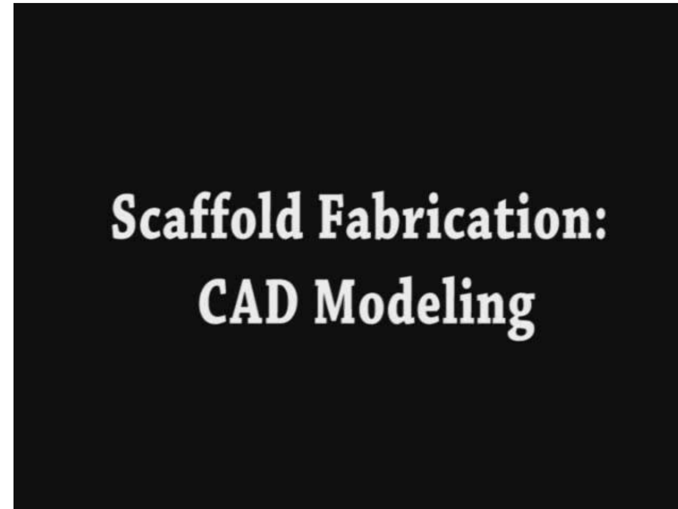
Design of drug delivery system

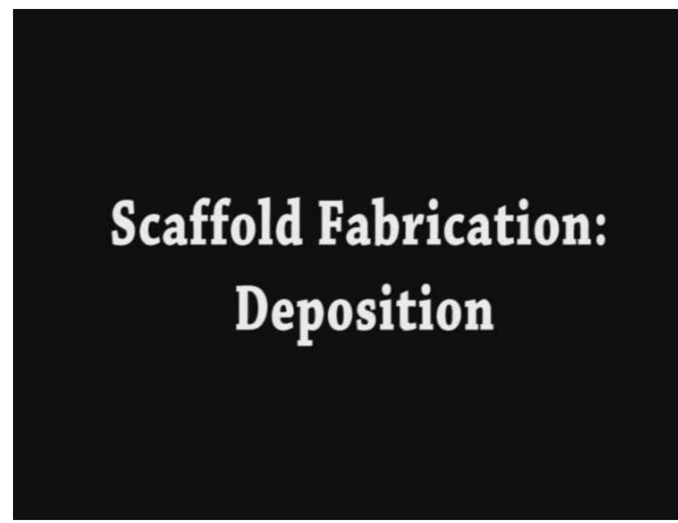


Material deposition



Fabricated drug delivery system

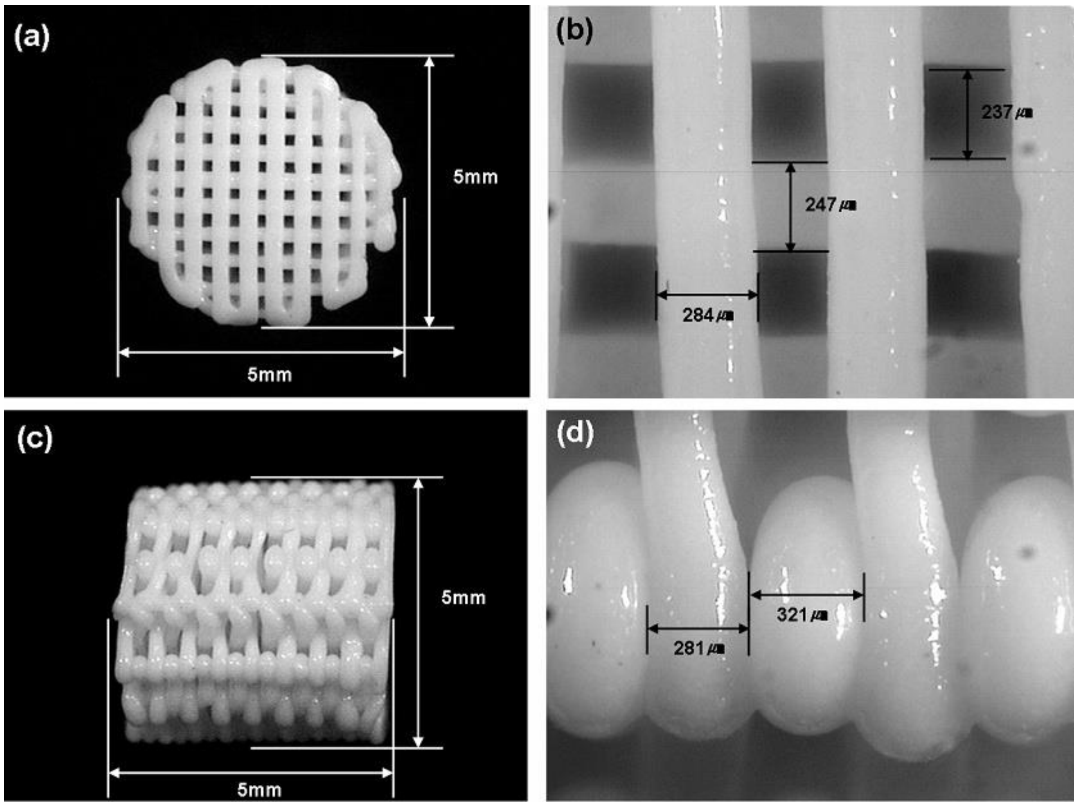




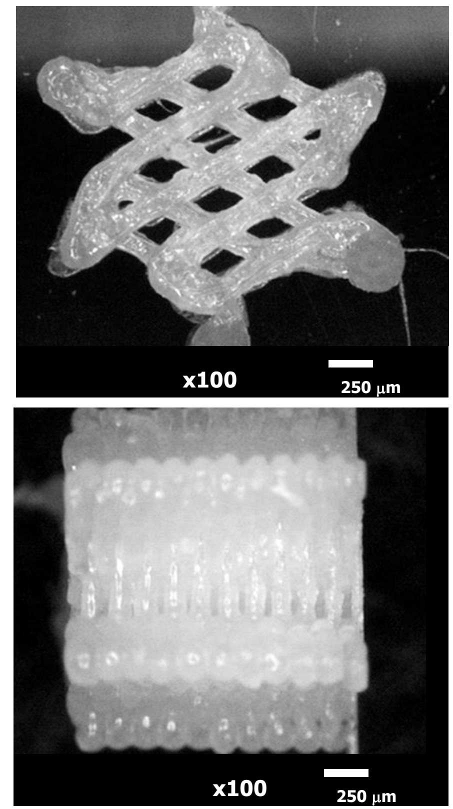
Chu, W.S., Jeong, S.Y., Kim, S.G., Ha, Won-Shik, Chi, Sang-Chul, and Ahn, S.H.*, 2008, "**Fabrication of Biodegradable Drug Delivery System with Controlled Release Made of PLGA/5-FU/Hydroxyapatite**," Rapid Prototyping Journal, Vol. 14, No. 5, pp. 293-299

Direct Technique

- **Fabricated scaffolds**



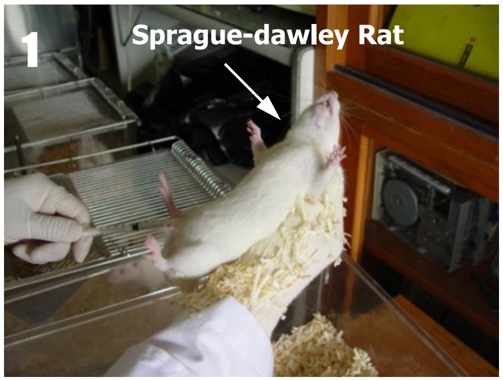
Fabricated PLGA (50:50)/5-FU (10 wt%) DDS of scaffold type specimens (17 layers, $[0°_9/90°_8]$, ϕ5 mm × 5 mm)



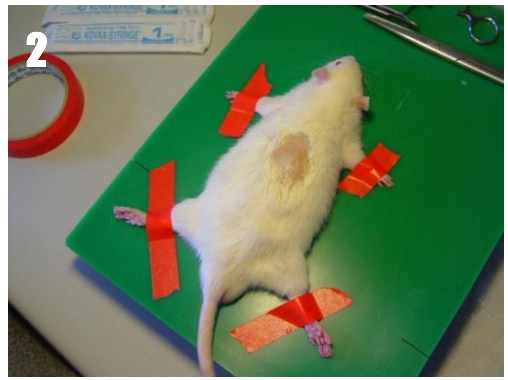
Fabricated star drug delivery system (22 layers, $[\pm 60°]_{11}$, ϕ2 mm × 2 mm)

IN VIVO EXPERIMENT

- **Implantation of drug delivery system**



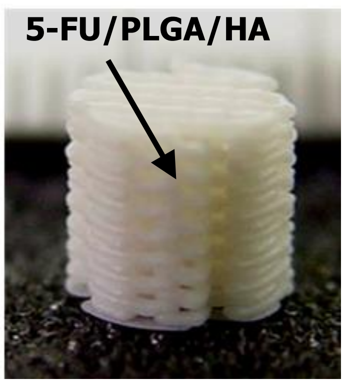
Anesthetize mouse



Remove hairs

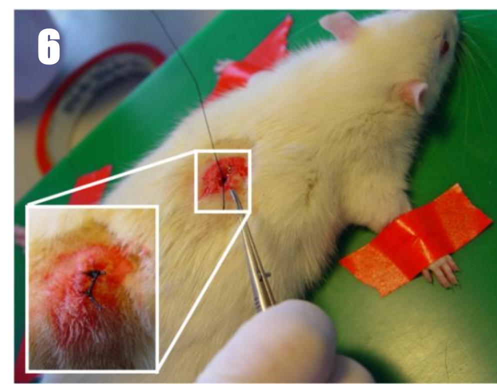
Incise back skin

4



Prepare scaffold DDS

Insert the scaffold



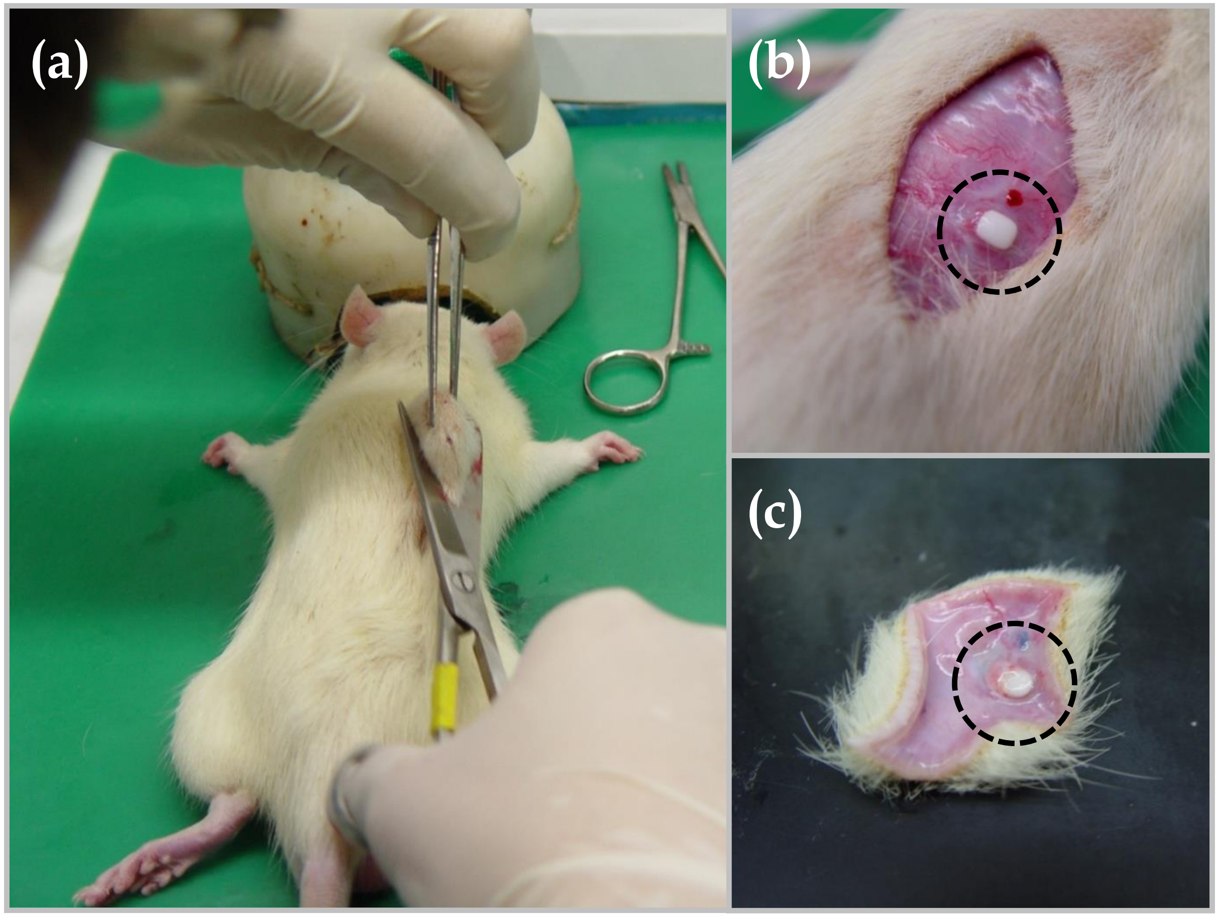
Suture the skin

Anesthesia

(100㎎/kg for Sprague-dawley Rat), 25㎎ of Ketamine(90vol%)+Xylazine(10vol%), 1 ㎖ needle

In Vivo Experiment

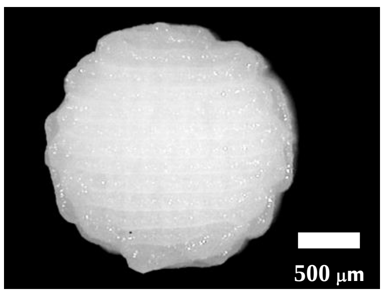
- **Extraction of drug delivery system**

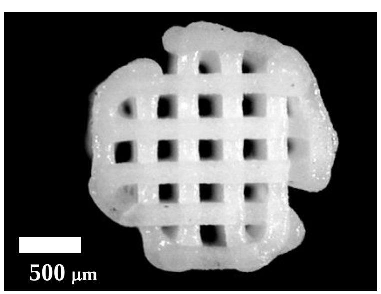


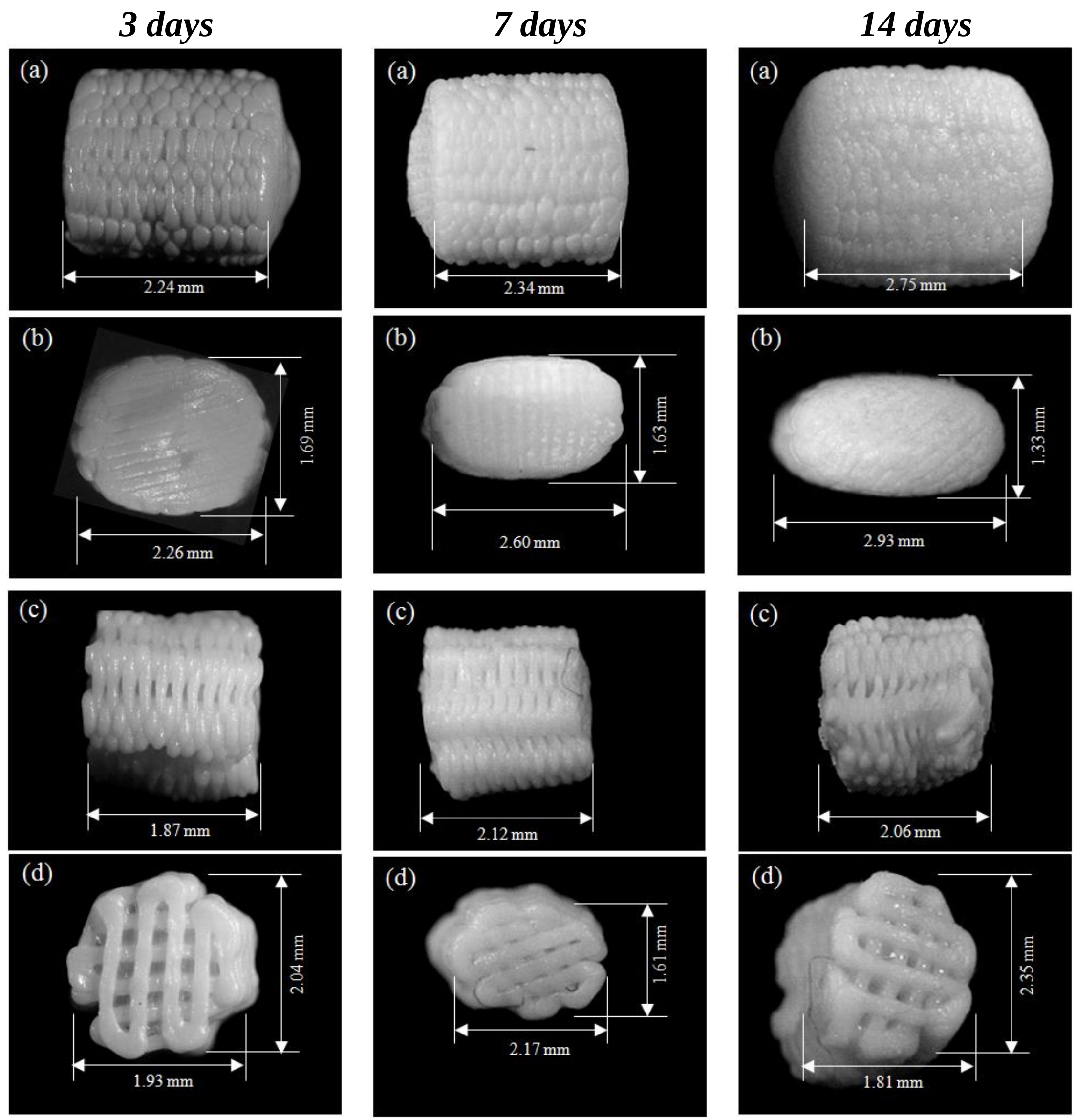
Extraction of drug delivery system (a) excise back skin of the rat, (b) drug delivery system on the back of rat after remove the back skin, (c) drug delivery system with excised back skin

In Vivo Experiment

- **Stability of cylinder shape scaffold**
  - 5-FU/PLGA(85:15)/HA

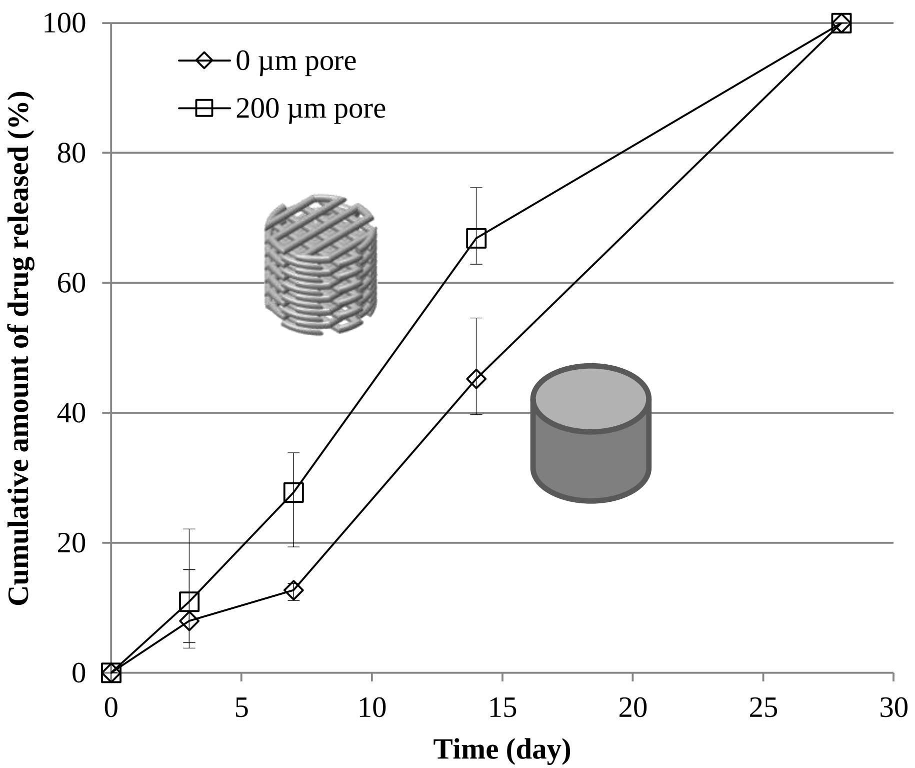






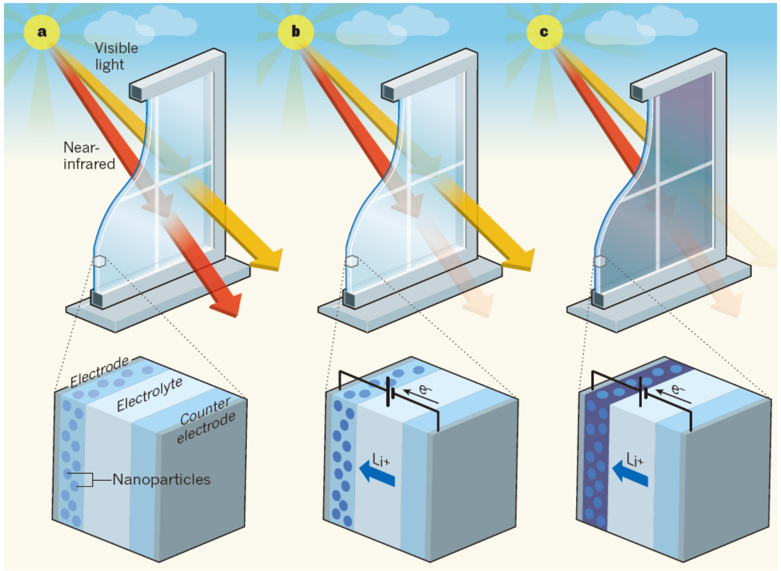
Drug Release

- **Drug release *in vivo* environment**
  - 5-FU/PLGA(85:15)/HA
  - Non-porous and 200 μm pore



Introduction to Electrochromic Window

- **Electrochromic Window (ECW)**



$$Li^{+} + e^{-} + WO_3 \leftrightarrow LiWO_3$$

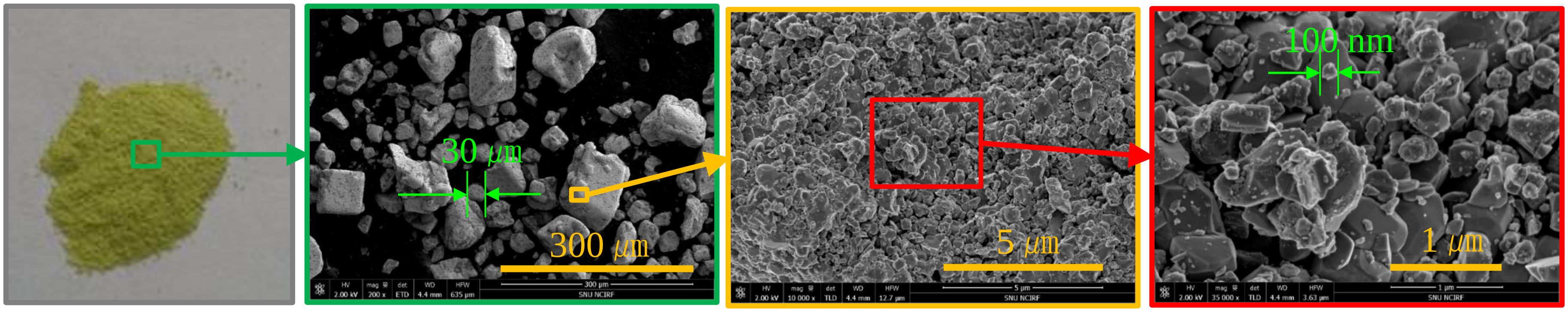
(Transparent) **(Blue)**

Ref) BRIAN A. KORGEL, "Composite for smarter windows", MATERIALS SCIENCE, NATURE, VOL 500, 15 AUGUST 2013.

- Electrochromism : a reversible change in a material's optical properties (transmittance, absorbance and reflectance) under an applied voltage
- Electrochromic materials : many transition metal oxide materials, some organic molecules and polymers
- Electrochromic Window : a dynamic windows allowing us to control daylight, solar heat gain, and internal heat loss through windows of buildings and vehicles

Electrochromic material

▪ Electrochromic material (WO_3)

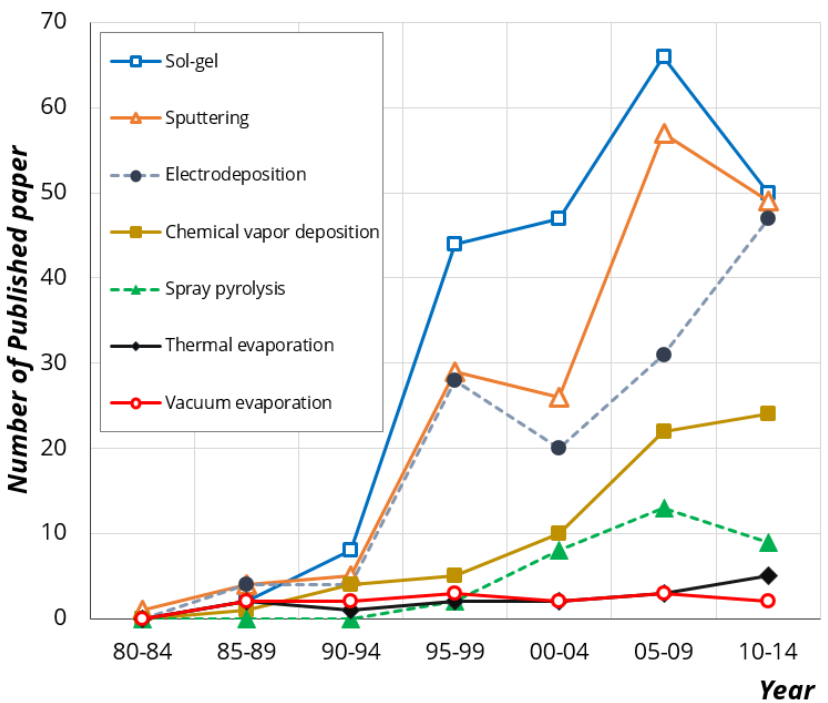


- Tungsten oxides (WO_3)
  - ➢ The most extensively studied inorganic EC material
  - ➢ Not toxic and have good electrochemical and optical properties

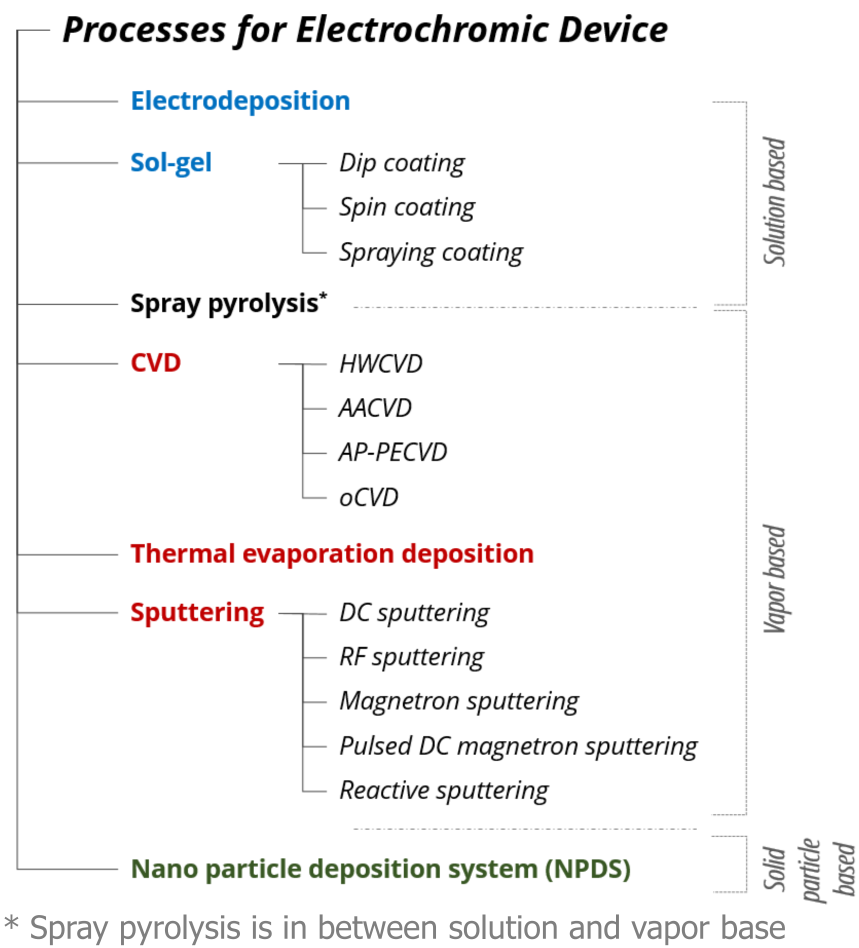
- WO_3 powders images observed by Scanning Electron Microscope (SEM)
  - ➢ A few tens of micrometers size originally (Bulk)
  - ➢ Each powder consists of a lot of particles which had a few tens to hundreds of nanometer size.

Fabrication methods of ECW

- **Major processes used to deposit materials**
- Sol-gel, Sputtering, Electrodeposition, CVD
- There is no dominant process for ECDs
- Each process has advantages and limitations.



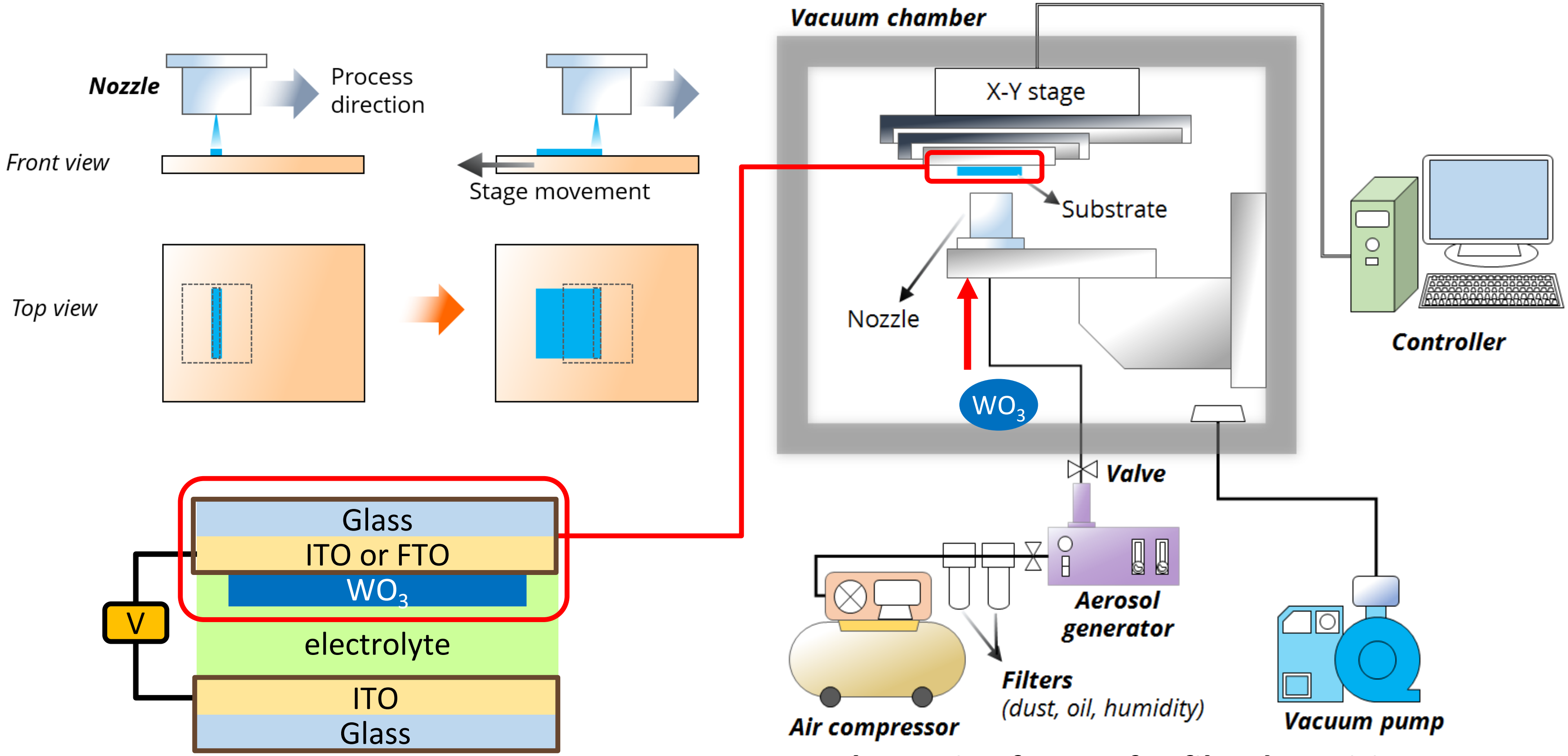
Fabrication methods trend of electrochromic devices



Fabrication methods for electrochromic devices

Fabrication method of ECW (NPDS)

- **Fabrication of Low-Cost ECW Using Nano Particle Deposition System (NPDS)**

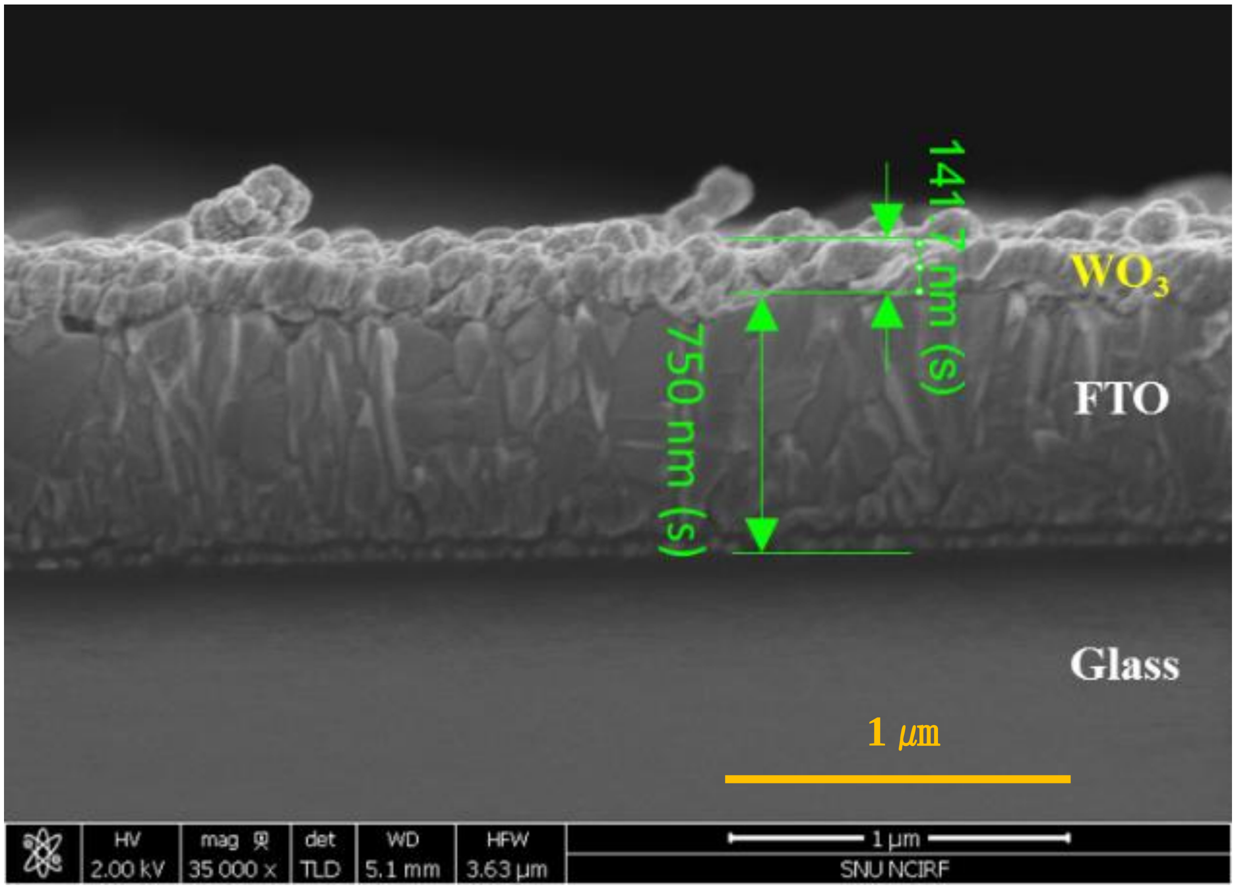


A schematic of NPDS for film deposition

- Nano Particle Deposition System (NPDS) : WO_3 particles deposition on a substrate without any precursors at room temperature and under a low vacuum condition.
- Easy and cost-effective process for mass production of thin films.

Deposition Results – Thickness

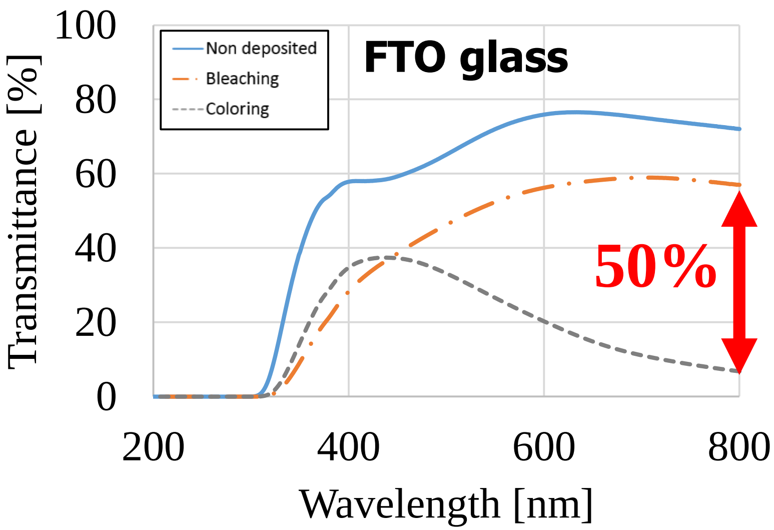
- **Cross-section image**



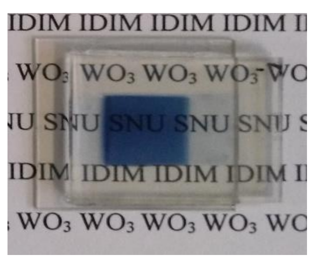
- The thickness of WO_3 films was also measured by a SEM
- A cross-section image of a specimen was used
- The thickness of an FTO coating and WO_3 film is 750 nm and 141.7 nm respectively

Coloring/Bleaching

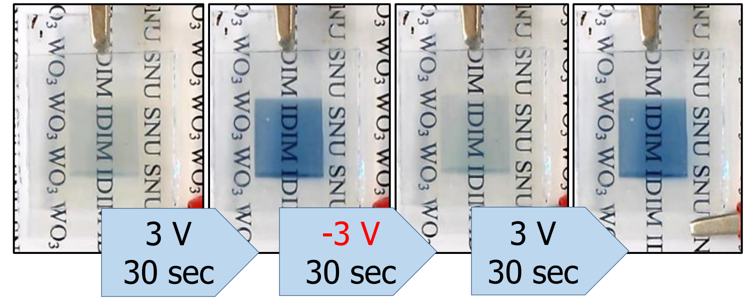
- **Transmittance**



Bleaching



Coloring

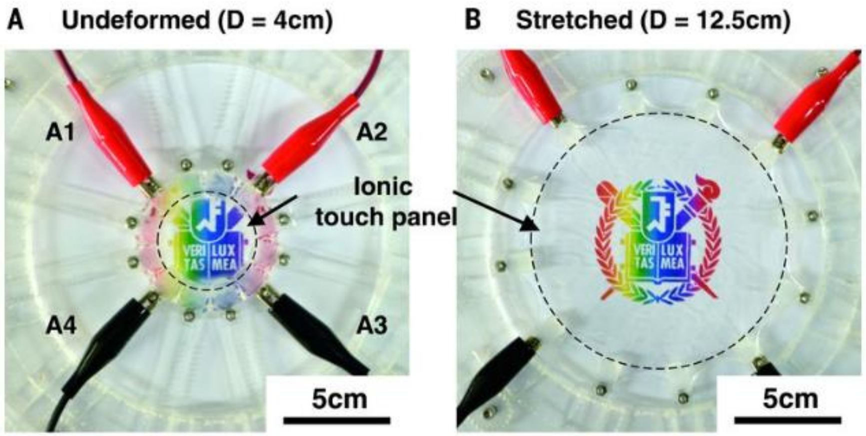


- Required voltage : 3V(coloring), -3V(bleaching)
- Coloring/Bleaching time : 30 seconds

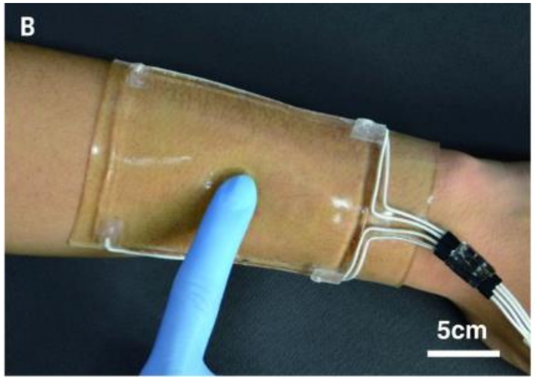
Park, S.I., Kim, S., Choi, J.O., Song, J.H., Ahn, S.H. and Taya, M., 2015, "Low-cost fabrication of WO3 films using a room temperature and low-vacuum air-spray based deposition system for electrochromic device applications," Thin Solid Films, Elsevier (Netherland), Vol. 589, pp. 412-418

Hydrogel Application

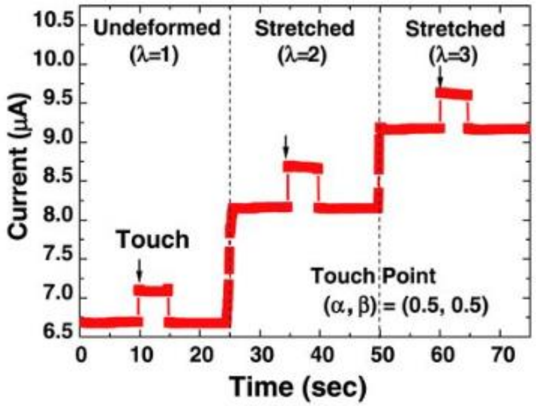
Highly stretchable, transparent ionic touch panel



Diameter of stretchable hydrogel ionic panel from D=4 cm to D = 12.5 cm



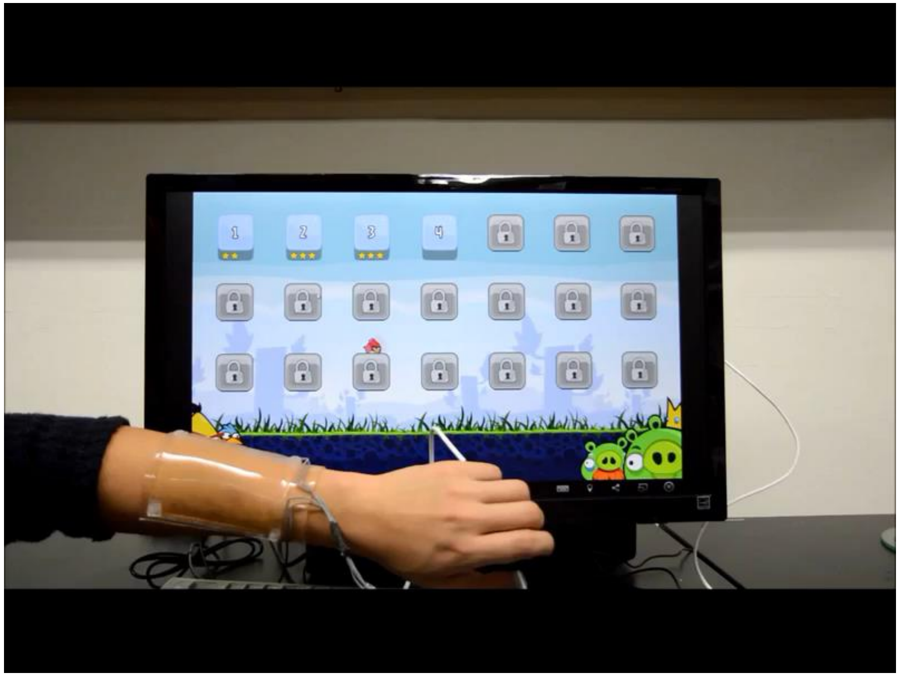
An epidermal touch panel was developed on a VHB substrate so as to insulate the panel from the skin and to mount the panel on a curved surface



The A1 current was measured before (λ = 1) and after stretching (λ = 2 and λ = 3). The baseline current increased according to the stretch of the panel. However, the touching currents were insensitive to the stretching.

Hydrogel Application

(Video) A tune was played using the epidermal touch panel
[Twinkle Twinkle Little Star]



(Video)Angry Birds was played by using the epidermal touch panel
[Tapping, Holding, Dragging and Swiping]