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
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.
Graphite properties

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

- Superior **stiffness and strength** to all other materials
- Extraordinary **electric** properties
- Reported to be **thermally stable** in a vacuum up to 2800°C (and we fret over CPU temps over 50°C)
- 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
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)
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 \((\text{C}_60)\)  
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

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**
  
  ![Chemical structures and images](image)

- **Nitric acid oxidation**
  - Immerse GNPs in HNO₃ at 100°C for 30 minute

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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.

![Graphs showing modulus and strength vs. volume fraction for As-received and Nitric Acid treated samples.](image-url)
Soundproofing Effect
Noise & Electromagnetic pollution

Noise pollution

Stress

Unhealthy

Thinking: Let’s solve both problems simultaneously.

Soundproofing materials

Application

Automotive

Electronics

Electromagnetic materials

Application

Research

Source: ask.nate.com

Source: E-Song EMC Products Guide

© Su
Dispersion of Nano Clay
## Preparation of material

<table>
<thead>
<tr>
<th>Clay</th>
<th>Type</th>
<th>Density</th>
<th>Particle Size</th>
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<tbody>
<tr>
<td>Clay</td>
<td>Cloisite®15A</td>
<td>1.66 g/cm³</td>
<td>≤ 2 μm</td>
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<table>
<thead>
<tr>
<th>Talc</th>
<th>Type</th>
<th>Density</th>
<th>Diameter</th>
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<tbody>
<tr>
<td>Talc</td>
<td>KR-2000</td>
<td>2.5~2.8 g/cm³</td>
<td>11 μm</td>
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<table>
<thead>
<tr>
<th>CNT</th>
<th>Type</th>
<th>Density</th>
<th>Diameter</th>
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<tbody>
<tr>
<td>CNT</td>
<td>MWNT CM-95</td>
<td>1.8 g/cm³</td>
<td>10-15 nm</td>
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<table>
<thead>
<tr>
<th>xGnP</th>
<th>Type</th>
<th>Density</th>
<th>Diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>xGnP</td>
<td>xGNP – M – 15</td>
<td>2.2 g/cm³</td>
<td>15 μm</td>
</tr>
</tbody>
</table>

- **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
- **Maleic anhydride (0.1 gram)**
- **Xylene (400 ml)** Solvent to dissolve PP and nanofillers

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Mechanical property

- ASTM standard D638-03

Impedance tube test

Schematic of four-microphone measurement setup

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

Diagram of energies of sound waves

(Reflected sound) (Absorption) (Transmitted sound)

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

(1)

- 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

Result

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

Comparison of STL of PP/fillers composites

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).

\[ SE(\text{dB}) = 10 \log \frac{P_i}{P_t} \]

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

Synergistic effect of soundproofing effect

- Comparison of the STL values of composites

![Graph showing comparison of STL values of composites](image)

- 1st place: 25dB
- 2nd place: 16dB
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

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

CNT → reflect and absorb more sound wave!

Synergistic effect of EMI SE

- Comparison of the EMI SE of composites

![Graph showing comparison of EMI SE of composites](https://via.placeholder.com/150)

1st place: 32dB

Poor: 5dB
Synergistic effect as function of filler concentration

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

- 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.

Small fillers → few synergy

Big aggregation → Poor synergy

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

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

Small fillers → few conductive paths

Many conductive paths
Application

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

Main merit: weight saving

Main merit: weight saving

Need: EMI SE ability

Interior composite: Soundproofing materials
Green (Bio) Composite
How long does it take?

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

<table>
<thead>
<tr>
<th>Products</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cotton rags</td>
<td>1-5 months</td>
</tr>
<tr>
<td>Paper</td>
<td>2-5 months</td>
</tr>
<tr>
<td>Rope</td>
<td>14 months</td>
</tr>
<tr>
<td>Orange peels</td>
<td>6 months</td>
</tr>
<tr>
<td>Wool socks</td>
<td>1-5 years</td>
</tr>
<tr>
<td>Plastic coated paper milk cartons</td>
<td>5 years</td>
</tr>
<tr>
<td>Plastic bags</td>
<td>10-20 years</td>
</tr>
<tr>
<td>Nylon fabric</td>
<td>30-40 years</td>
</tr>
<tr>
<td>Plastic bottle</td>
<td>~450 years</td>
</tr>
</tbody>
</table>
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

Hemicellulose
Cellulose

Primary cell wall
Gluey pectin layer
Secondary cell 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

<table>
<thead>
<tr>
<th></th>
<th>Density (g/cm³)</th>
<th>Diameter</th>
<th>Mean Length of Fiber (mm)</th>
<th>Tensile Strength (MPa)</th>
<th>Young’s Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flax Fiber Bundle</td>
<td>1.5</td>
<td>20 μm</td>
<td>30</td>
<td>345-1100</td>
<td>100</td>
</tr>
<tr>
<td>Hemp Fiber Bundle</td>
<td>1.3-1.4</td>
<td>22 μm</td>
<td>20</td>
<td>690</td>
<td>69</td>
</tr>
<tr>
<td>Cellulose Nanofibers</td>
<td>-</td>
<td>10-70 nm</td>
<td>36-40 molecular chains</td>
<td>7500</td>
<td>130</td>
</tr>
<tr>
<td>Elementary fibril (Micelle)</td>
<td>-</td>
<td>35 Å°</td>
<td>100 glucan units</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Monoclinic unit cell</td>
<td>-</td>
<td>10.3 Å°</td>
<td>-</td>
<td>-</td>
<td>260</td>
</tr>
<tr>
<td>E-glass</td>
<td>2.5</td>
<td>9 μm</td>
<td>-</td>
<td>1700</td>
<td>70</td>
</tr>
<tr>
<td>Carbon fiber</td>
<td>1.7</td>
<td>70-500 nm</td>
<td>-</td>
<td>3445</td>
<td>230-240</td>
</tr>
</tbody>
</table>

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

Scattering light

Rough surface

Air cavity

Cavities are small enough to avoid light scattering
Nanocomposites of cellulose

Cellulose : 100 %

- Transparency: 71.6 %
- CTE: 8.5 ppm/K
- Density: 1.53 g/cm³
- Young’s modulus: 13 GPa
- Strength: 223 MPa

Nanocomposites of cellulose

Luminescence of an OLED deposited on the wood nanofiber-composite

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

<table>
<thead>
<tr>
<th>Automotive component</th>
<th>Typical weight of fibre (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Front door liners</td>
<td>1.2–1.8</td>
</tr>
<tr>
<td>Rear door liners</td>
<td>0.8–1.5</td>
</tr>
<tr>
<td>Boot liners</td>
<td>1.5–2.5</td>
</tr>
<tr>
<td>Parcel shelves up to</td>
<td>2.0</td>
</tr>
<tr>
<td>Seat backs</td>
<td>1.6–2.0</td>
</tr>
<tr>
<td>Sunroof sliders up to</td>
<td>0.4</td>
</tr>
<tr>
<td>NVH material min</td>
<td>0.5</td>
</tr>
<tr>
<td>Headliners average</td>
<td>2.5</td>
</tr>
</tbody>
</table>
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 μm width)
  - High Shear Mixing Method in 120 °C
  - Ground 5-FU (about 10 μm width)

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

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

- POLYMER

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Direct Technique

Design of drug delivery system

Fabricated drug delivery system

Z direction

Heated Barrel (150°C)

5-FU/PLGA/HA

X-Y direction

Material deposition

Scaffold Fabrication: CAD Modeling

Scaffold Fabrication: Deposition

Direct Technique

- Fabricated scaffolds

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

Fabricated star drug delivery system (22 layers, [±60°]11, φ2 mm × 2 mm)
Implantation of drug delivery system

1. Anesthetize mouse
2. Remove hairs
3. Incise back skin
4. Prepare scaffold DDS
5. Insert the scaffold
6. Suture the skin

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

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In Vivo Experiment

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

3 days

7 days

14 days
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)

- 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 window 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

Processes for Electrochromic Device

- Electrodeposition
- Sol-gel
  - Dip coating
  - Spin coating
  - Spraying coating
- Spray pyrolysis*
- CVD
  - HWCVD
  - AACVD
  - AP-PECVD
  - oCVD
- Thermal evaporation deposition
- Sputtering
  - DC sputtering
  - RF sputtering
  - Magnetron sputtering
  - Pulsed DC magnetron sputtering
  - Reactive sputtering
- Nano particle deposition system (NPDS)

* Spray pyrolysis is in between solution and vapor base

Fabrication methods for electrochromic devices

© Sung-Hoon Ahn
Fabrication method of ECW (NPDS)

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

Nano Particle Deposition System (NPDS): WO₃ 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 $\text{WO}_3$ films was also measured by a SEM.
- A cross-section image of a specimen was used.
- The thickness of an FTO coating and $\text{WO}_3$ film is 750 nm and 141.7 nm respectively.
Coloring/Bleaching

**Transmittance**

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