Synthesis of nylon 66 composites containing natural organic nanomaterials

AUTHORS:
Lam Tan Hao, YoungHo Eom, Thang Hong Tran, JunMo Koo, SungYeon Hwang, JeYoung Park, DongYeop Oh

PRESENTED BY:

Lam Tan Hao

Researcher

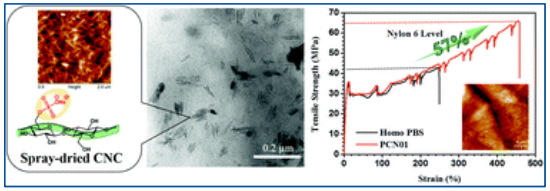
Korea Research Institute of Chemical Technology (KRICT)
University of Science and Technology (UST)

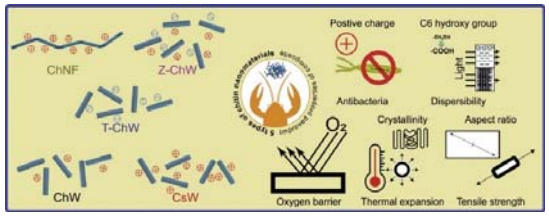
About me

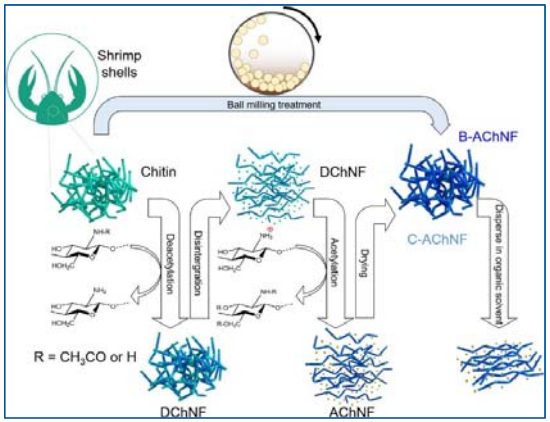
Lam Tan Hao

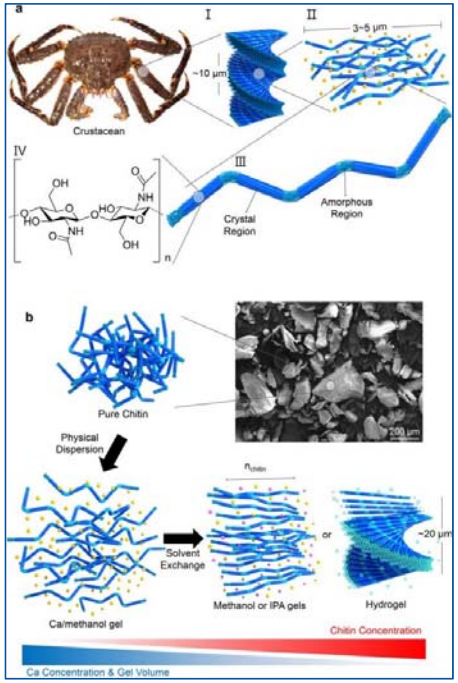
- Vietnamese student at Korea University of Science and Technology (UST)
- Researcher at Center for Bio-based Chemistry, Korea Research Institute of Chemical Technology (KRICT) in Ulsan
- Academic background: Biotechnology
- Research projects:
  - Bio-based nanocomposites
  - Natural nanomaterials for biomedical applications

Our research group: KRICT Biopolymer at Ulsan, South Korea









- *ACS Nano*, 2019, **13**:3796
- Carbohyd Polym, 2019, **205**:392
- Int J Biol Macromol, 2019, 125: 660
- RSC Adv, 2018, **8**:15389
- Sci Rep, 2016, **6**: 23245

Outline

- Why did we fabricate the bio-based composites?
- How did we do that?
- What are the properties of the composites?

Inorganic nanocomposites

Polymers

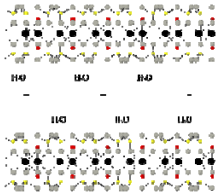
- *Synthetic polymers:* poly(ethylene glycol) (PEG); poly(vinyl alcohol) (PVA); poly(lactic acid) (PLA); poly(methyl methacrylate) (PMMA); poly(ethylene oxide) (PEO); natural rubber latex; polyamide (PA): nylon 66, nylon 610, nylon 1010
- *Natural polymers:* cellulose, chitosan, gelatin, silk, alginate, fibrin, starch, collagen, agarose

+

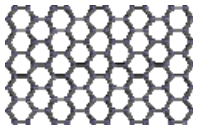
Inorganic nanoparticles

Metal-based

Clay



Carbon-based



Graphene

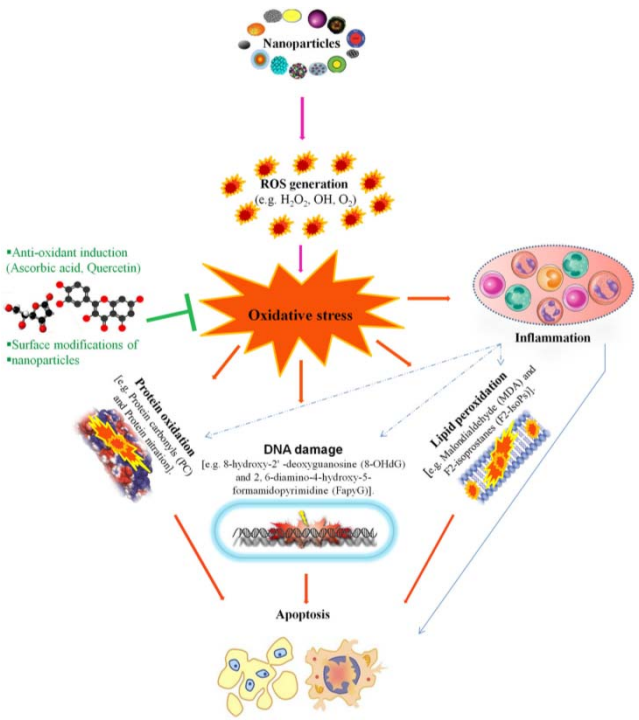
Carbon nanotube

Chem Soc Rev, 2011, **40**:696;
Adv Funct Mater, 2018, **28**:1704158

Limitations of inorganic nanomaterials

- Health problems
  - Non-pyrolyzed, fine particulates are generated when burning inorganic nanocomposites. (Chemosphere, 2010, **80**:193)
  - Exposure to the particulates leads to pulmonary effects, inflammation, and cancer. (Biointerphases, 2007, **2**:MR17; Science, 2006, **311**:622)
- Technical problems
  - Inorganic nanoparticles are poorly dispersed in polymeric matrices due to density difference and weak interfacial interaction.

RESEARCH GAP!



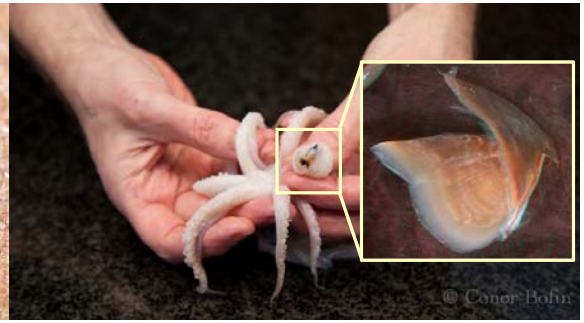
Nanotoxicity due to overproduction of free radicals (oxidative stress)

Front Pharmacol, 2017, **8**:606

Tough, bio-inspired hybrid materials

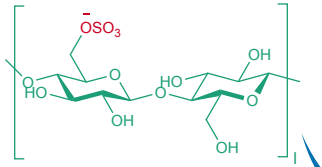
The hard shell of tunicates
Cellulose + protein complex

The exoskeleton of insects



The beak of cephalopods (squid/octopus)

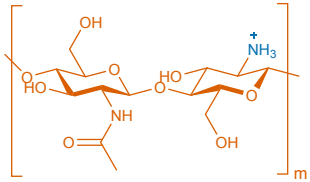
Chitin + protein complex



Cellulose nanocrystal
(CNC)

Bio-nanomaterials

- Excellent mechanical properties
- Abundant
- Biodegradable
- Biocompatible
- Sustainable



Chitosan nanowhiskers
(CSW)

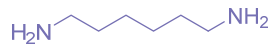
ACS Appl Mater Interfaces, 2014, **6**:6127;
Science, 2008, **319**:1816;
Arthropod Struct Dev, 2004, **33**:187;
Carbohydr Polym, 2019, **205**:392

Schematic illustration for preparation of nylon 66 nanocomposites

In situ interfacial polymerization

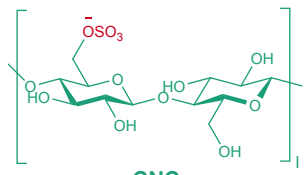
Solution Blending

Aqueous phase



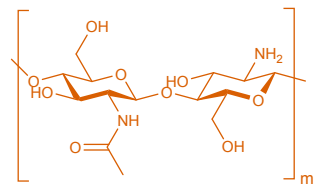
Hexamethylenediamine (HMDA)

+



CNC

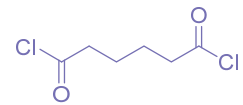
or



(CSW)

+

Organic phase (1,2-dichlorobenzene)



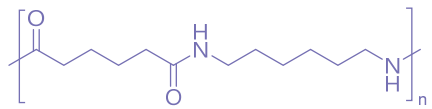
Adipoyl chloride (AdCl)

In situ Nylon 66/CNC and Nylon 66/CSW nanocomposite: **I-NC*n*** and **I-NS*n***

Filler loading: ***n* = 0.1–0.5 wt%** per total mass of the nanocomposite

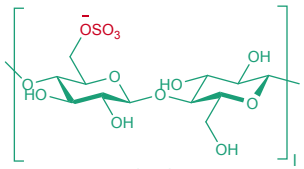
Solution-Blended Nylon 66/CNC and Nylon 66/CSW nanocomposite: **B-NC*n* and B-NS*n***

Formic acid



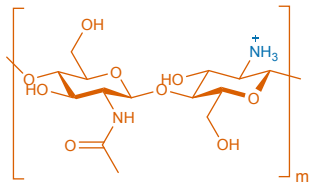
Nylon 66

+



CNC

or



CSW

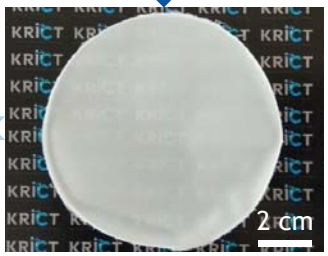
Processing and characterization of nylon 66 nanocomposite films

❖ Film processing

6.5 wt% nylon 66 solution (formic acid)

Solution casting

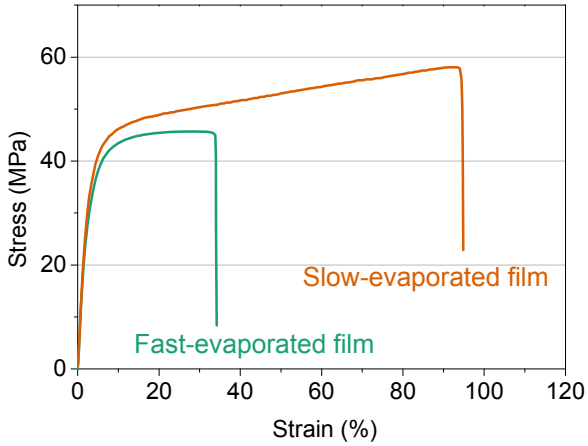
Solvent evaporation
- Fast: for 2 days
- Slow: for 5 days



Slow-evaporated nylon 66 film

Cut into a dumbbell specimen

❖ Effect of solvent evaporation rate



- The retarded evaporation rate of formic acid increased the mechanical properties of the film.

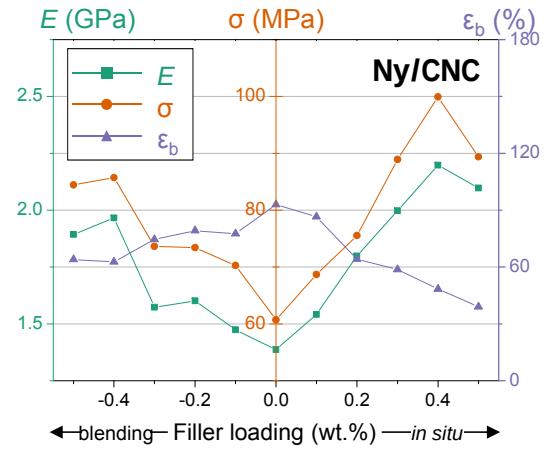
❖ Film characterization

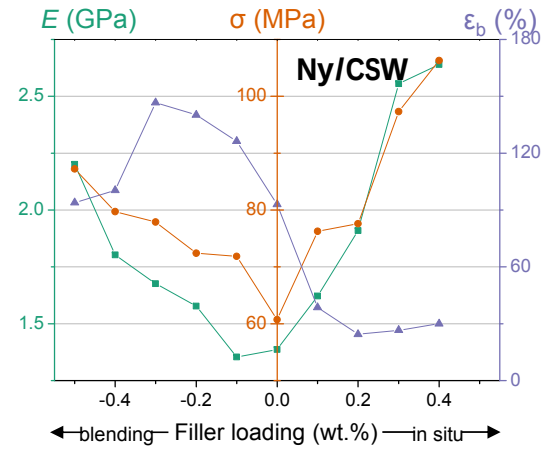
- Mechanical properties
- FTIR
- SEM
- Others (ongoing): TGA, DSC, XRD…

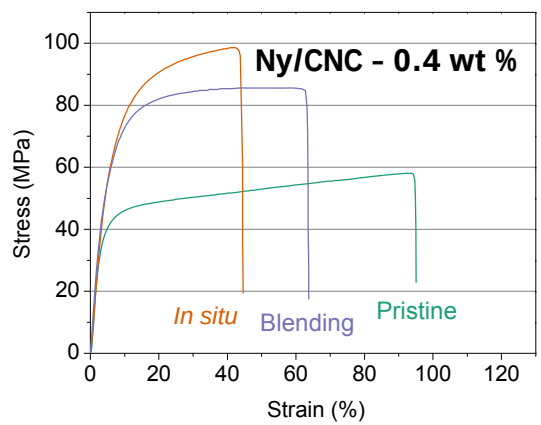
Mechanical properties of the films

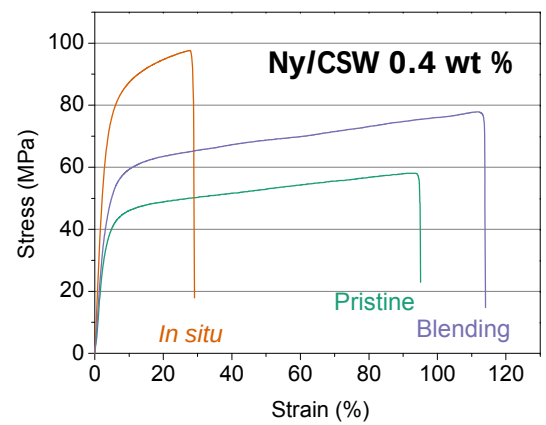
- *In situ* films:
  - Both nanofillers increased Young's modulus (*E*) and tensile strength (σ) but reduce the elongation at break (ε_b).
  - Optimal loading: 0.4 wt%.
- Solution-blended films:
  - CNC showed a similar trend as in *in situ* films.
  - CSW increased all the mechanical parameters.
  - Optimal loading: 0.4 wt% (CNC) and 0.5 wt% (CSW)

→ different kinds and/or degree of interactions between CNC and CSW with nylon 66

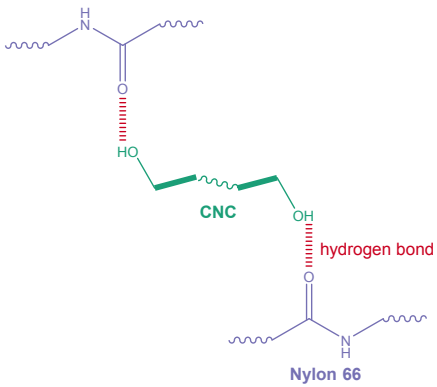




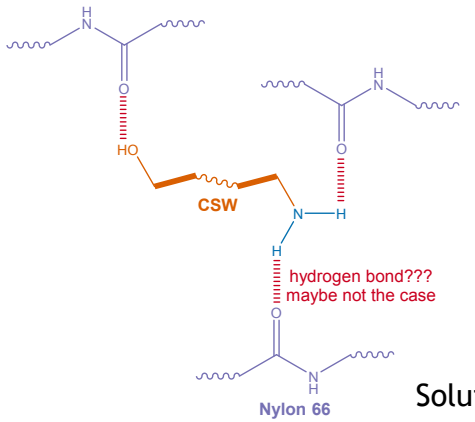




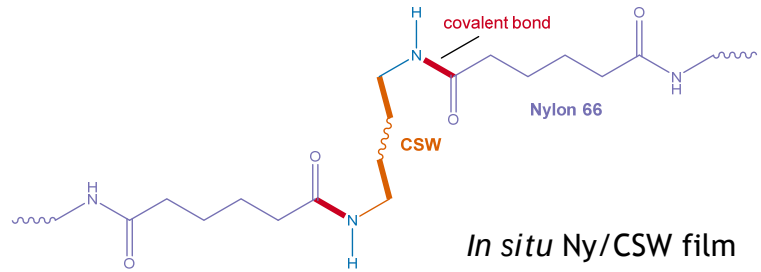
Possible filler-matrix interaction



In situ and solution-blended Ny/CNC film

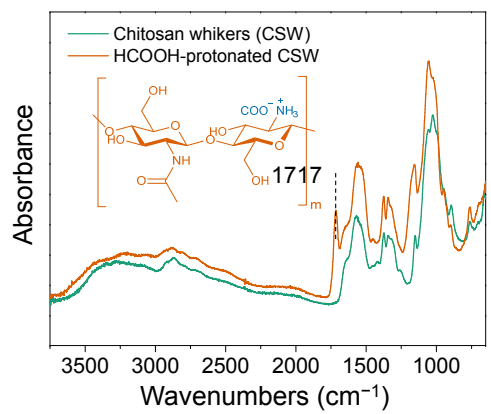


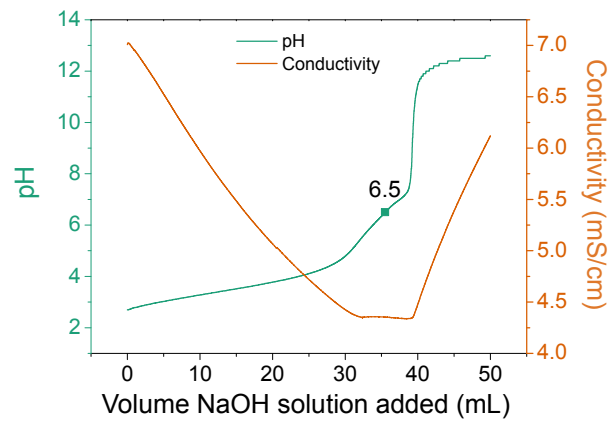
Solution-blended Ny/CSW film



In situ Ny/CSW film

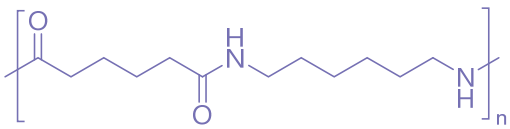
- Ionization of CSW during film processing of solution-blended Ny/CSW samples (FTIR and titration assay)
- Weaker CSW-nylon 66 interaction
- → Lower modulus and higher elongation at break of B-NS series



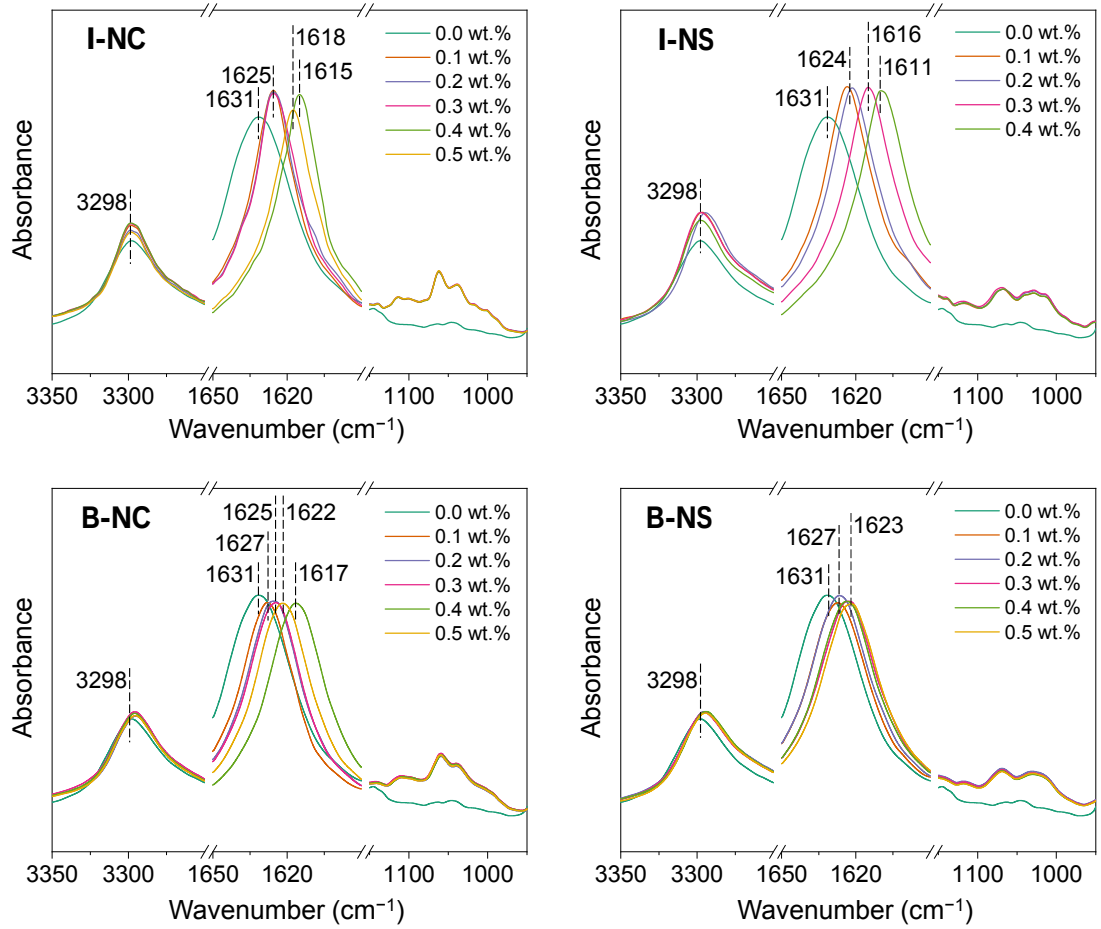


FTIR spectra of nylon 66 nanocomposites

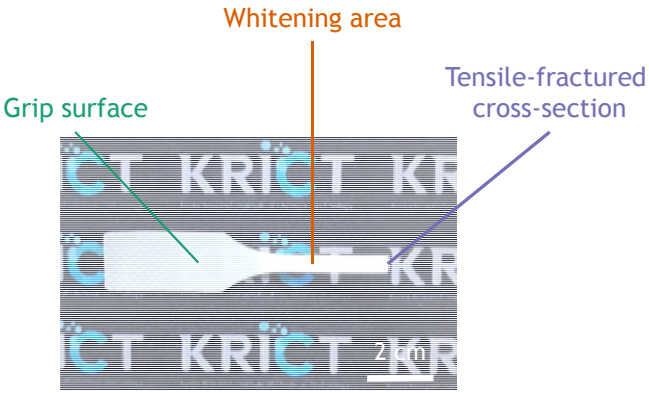
- Fundamental peaks of nylon 66
  - N-H stretching (3295-3300 cm^{-1})
  - C=O stretching (~1631 cm^{-1})
  - In-plane N-H deformation (1530-1550 cm^{-1}) *(not shown)*
- Shift of amide CO from 1631 cm^{-1} to a lower wavenumber → possible hydrogen bonding with the nanofiller OH groups (Polymer 2016, **101**:75; RSC Adv, 2016, **6**:87405; Biophys J, 2005, **88**:2833)
- Extra peaks within 950-1150 cm^{-1}



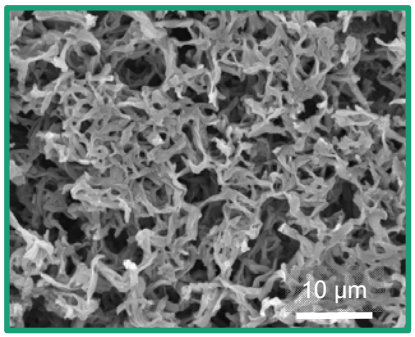
Nylon 66

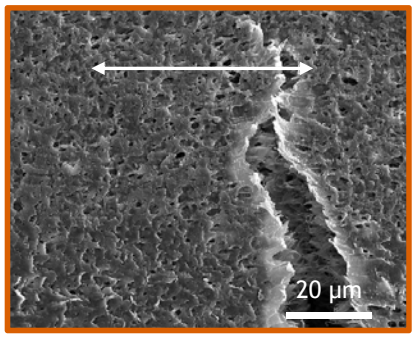


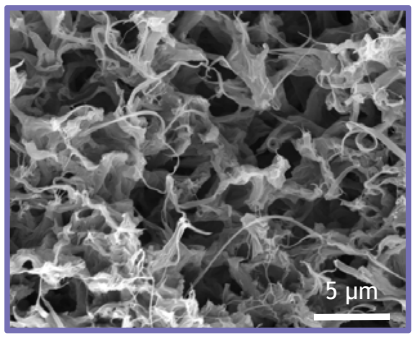
SEM images of tensile-fractured films (pristine samples)



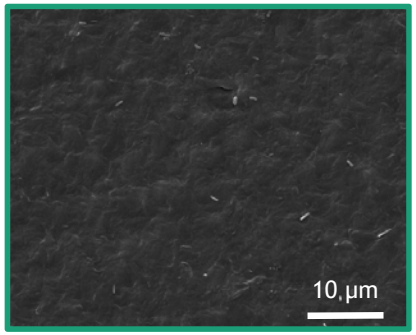
❖ Fast evaporated film

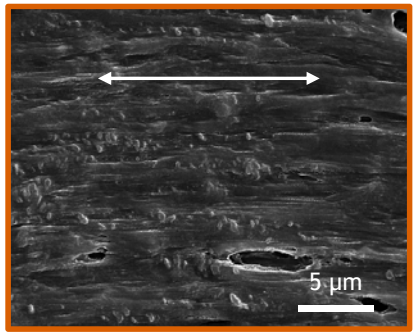


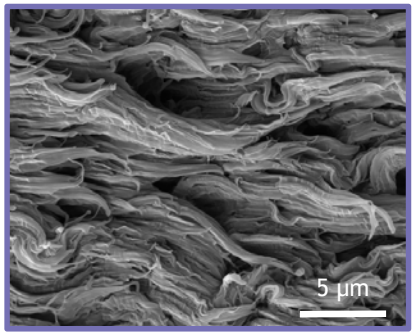




❖ Slow evaporated film





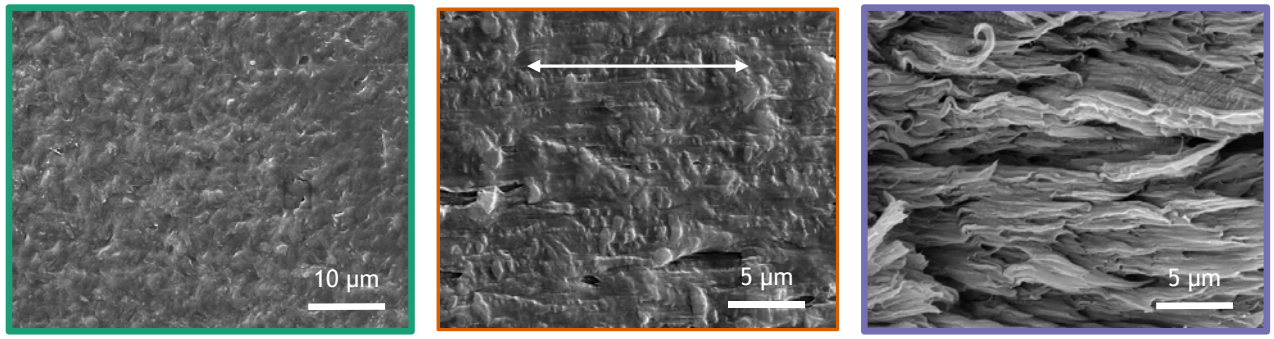


- Fast evaporated film → non-continuous, highly porous, bead-like surface, entangled fibers
- Slow evaporation → continuous surface, regularly aligned fibers

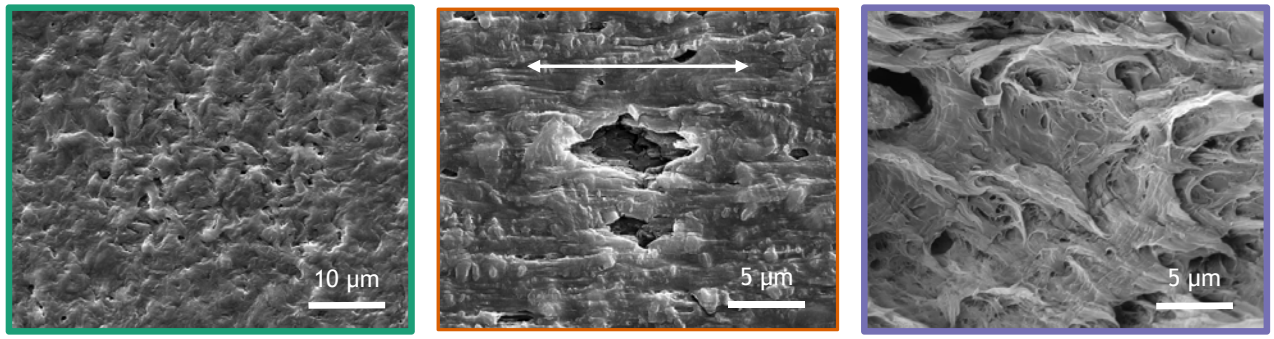
SEM images of tensile-fractured films (*in situ* samples)

- Rougher surface than the pristine film
- Uniaxial stretch-induced alignment of nylon 66 fibers → ordered self-assembly of polymer chains during the film processing
- The polymer is highly deformed across the fractured surface with different fracture propagation.

❖ Ny/CNC



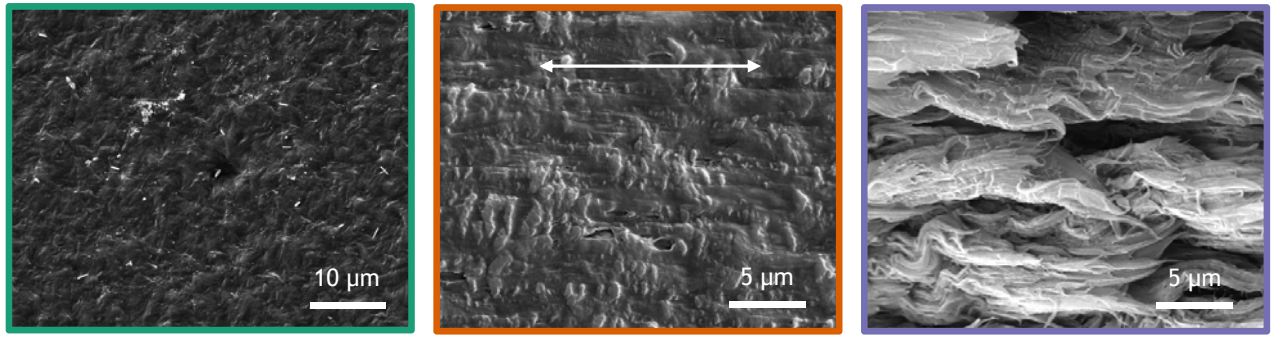
❖ Ny/CSW



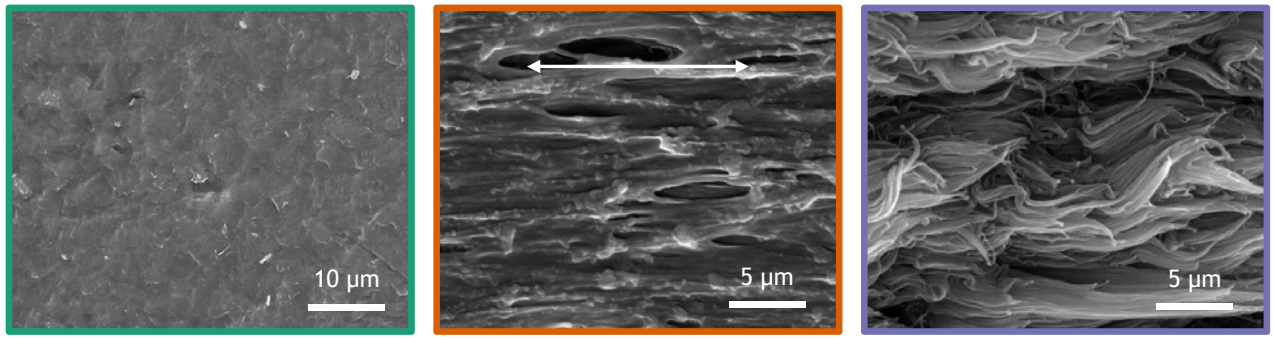
SEM images of tensile-fractured films (solution-blended samples)

- In solution blended Ny/CSW films:
  - Plastic deformation occurs extensively along the stress direction
  - Microvoid formation → "stabilizes" the deformation → higher elongation at break

❖ Ny/CNC



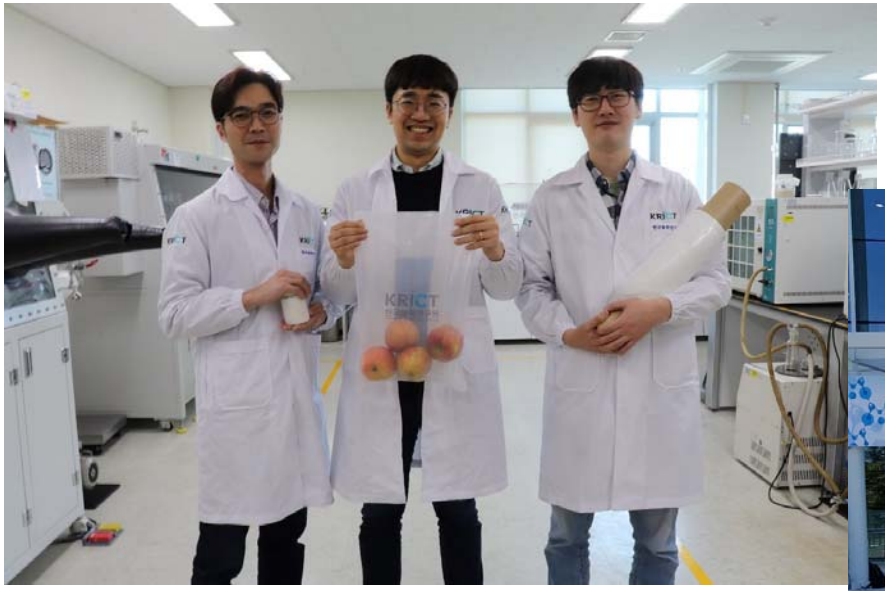
❖ Ny/CSW



Result Highlights and Perspectives

- Nature-inspired nylon nanocomposites with cellulose nanocrystals or chitosan nanowhiskers was synthesized
  - *In situ* polymerization
  - Solution blending with formic acid
- Mechanical properties of the composites
  - Enhanced at low filler loading level (0.1–0.5 wt%)
  - Tunable using CSW and proper preparation methods
- Different kind and/or degree of filler-matrix interactions was speculated.
- Further study on crystallinity and thermal behaviors of the composites are being conducted.

Acknowledgments



https://sites.google.com/site/krictbiopolymer/

Thank you

PRESENTED BY:

Lam Tan Hao

Researcher

Korea Research Institute of Chemical Technology (KRICT)
University of Science and Technology (UST)

tanhao@krict.re.kr