Unprecedented Ultrahigh Expansion Injection-Molded Polypropylene Foams with Hydrophobic-Modified Cellulose Nanofibers

Co-AUTHORS:

Long Wang, Yuta Hikima, Kiyomi Okada,
Takafumi Sekiguchi, Akihiro Sato, Hiroyuki Yano

PRESENTED BY:

Masahiro Ohshima

Professor, Chemical Engineering,
Kyoto University

Objective

- **We seek a potential of CNF as a multifunctional additive for thermoplastic polymers**

There have been many researchers who try to use CNF as a mechanical reinforcement agent

- **We focused upon the usage of CNF as a foaming agent of thermoplastic polymer**

Why Foaming?

Why foaming?

Plastic foams are the products which can fully enjoy the benefit of CNF

- **Car companies have been making big efforts of reducing the weight of parts**
  - **by replacing the iron parts with plastics**
  - **by either foaming or thinning the plastic parts.**
- **When the plastic is foamed, mechanical properties are dropped**

Glass fiber (GF) is used to compensate the reduction of mechanical strength. Decrease the weight by foaming

Car Needs thermal and sound insulations

increase the weight by adding the GF to foamed plastics.

Characteristics of CNF

- **Light weight**

  Its Density is lower than those of Glass fiber & Carbon fiber

- **Good mechanical strength**

  Mechanical strength is higher than those of Glass fiber

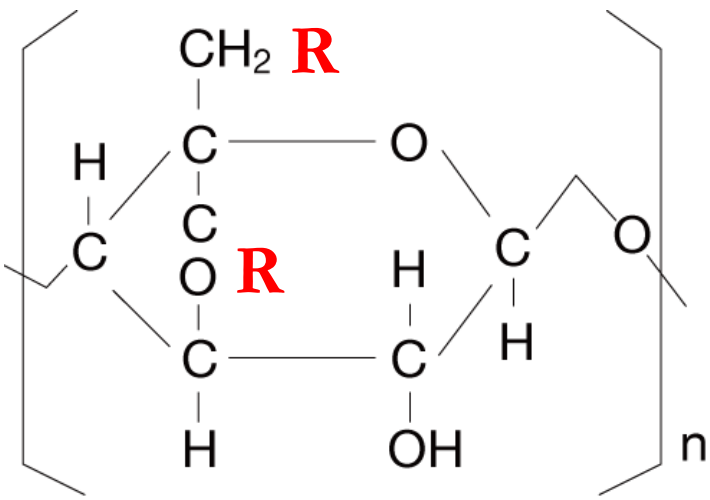
	CNF	Glass Fiber(GF)
Density [g/cm^3]	1.5	2.55
Elastic Modulus [GPa]	140	74

■ **By taking advantages of the light weight and strength of CNF, GF can be replaced with CNF and further weight reduction can be achieved.**

Merit of CNF Chemical Modification

- Chemical Modification

  We can modify CNF easier than Glass fibers and Carbon fibers.



glucose.

The hydrophobicity of CNF is changed

- by replacing some of the OH groups with alkyl group (R)
- by choosing the (R)

The hydrophobicity/hydrophilicity are tuned by The degree of substitution.

Degree of Substitution (OH⇒R)	**Increase**
Affinity between polymer and CNF	increase ↑
Dispersity of CNF in polymer	increase ↑
Performance of Crystal agent : of Foaming agent	decrease decrease ↓

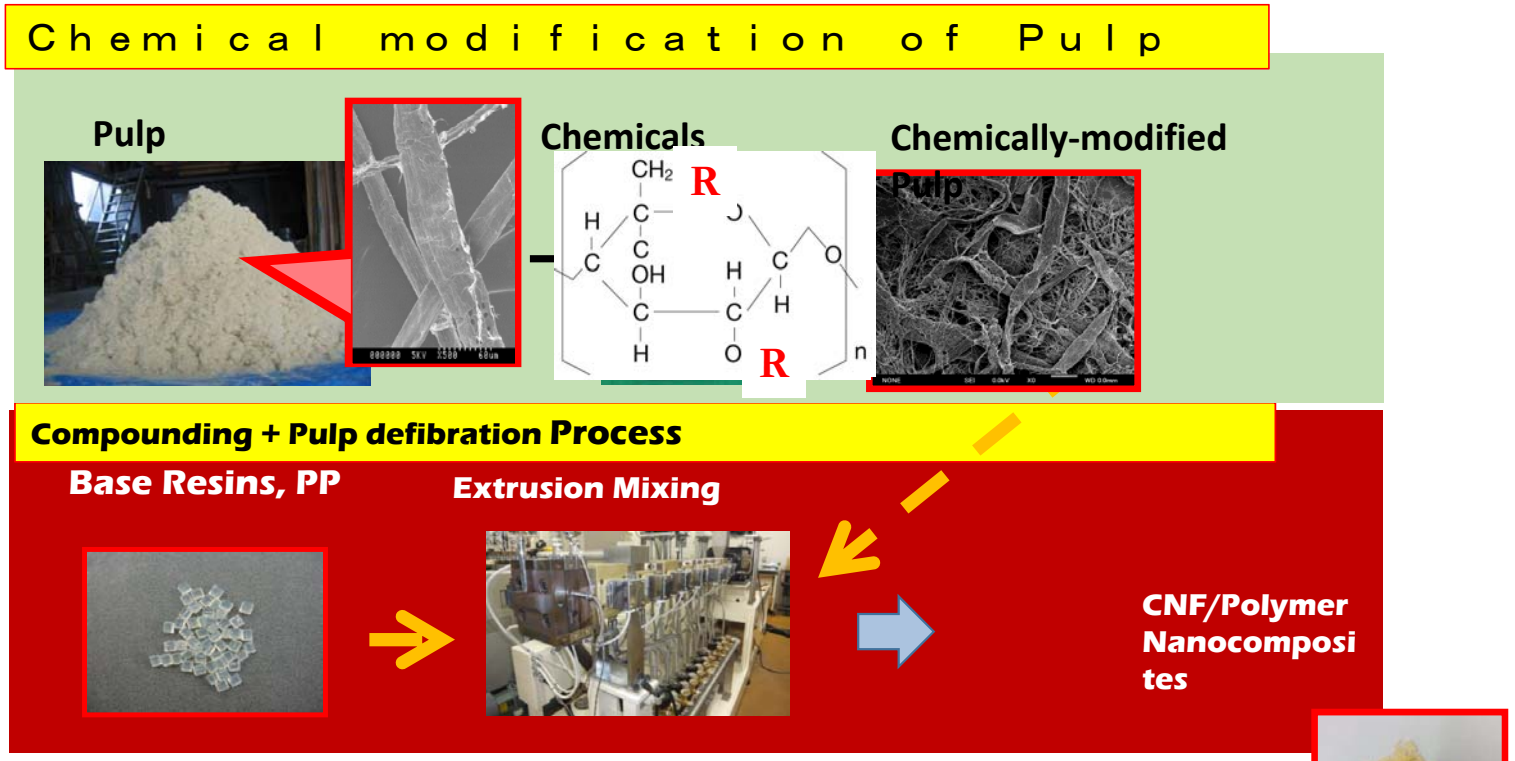
Aim of this presentation

- Show how this tunability can be beneficial for preparing microcellular (fine) polymer foams

- Discuss the benefit of using CNF for polymer foams
  - Rheology view point
  - Crystallinity view point

CNF/Polymer composite issue

Preparation of Polymer(PP)/CNF composite (KYOTO Process)



CNF /polymer composite was prepared in KYOTO Process by chemical m the pulp and de-bundling (defibrating) the pulp into nanocellulose fibrils in extrusion

By giving shear force, de-bundling of pulp into CNF is conducted

Materials in detail

Polypropylene

iPP(F133A, Prime Polymer)

tacticity：97 mmmm%

MFR ：3.0 g/10min

370,000 =Mw

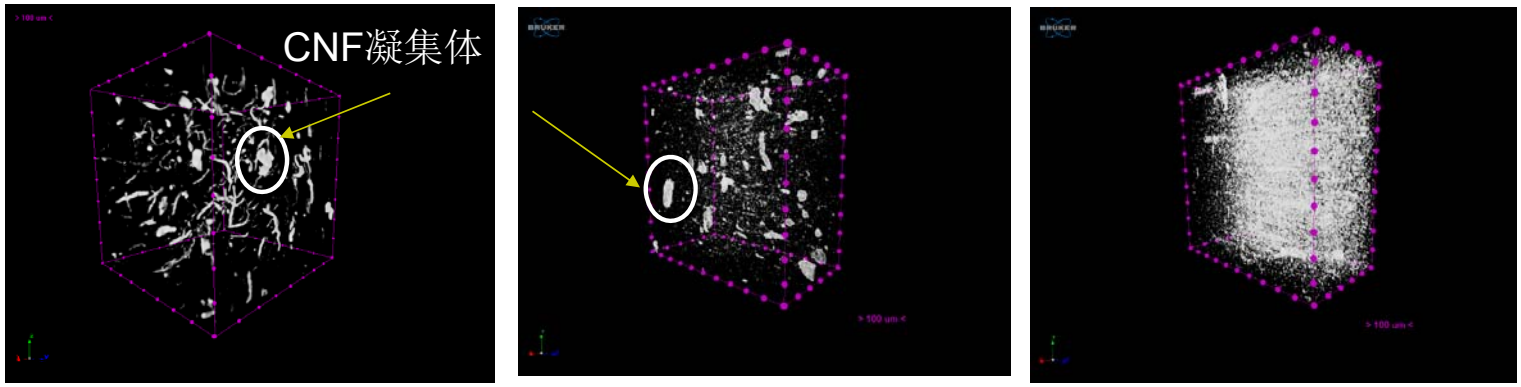
CNF modified with alkenyl succinic anhydride (ASA) (T-NC124, Seiko PMC)

Degree substitution of OH = 0, 0.2, 0.4

To conduct Foaming Experiments, the master batch (CNF 17 wt %) was firstly prepared and dry-blended with iPP (F133A) at the given weight ratio.

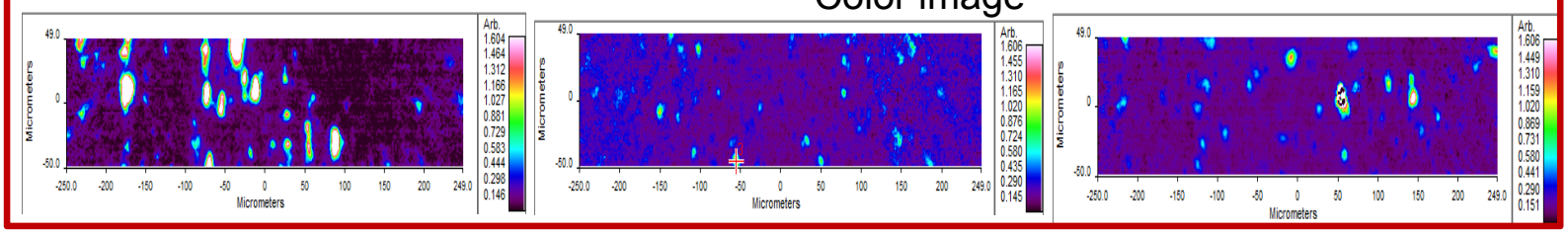
CNF dispersiveness in iPP(X-ray CT＆FTIR)

DS=0 **DS=0.2** **DS=0.4**



FTIR

Color image



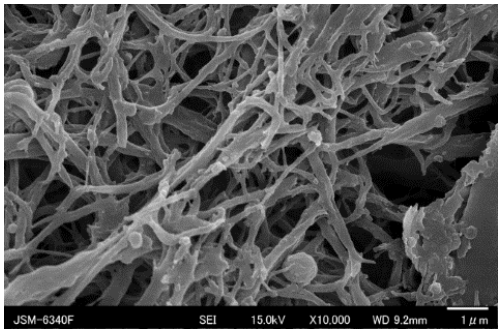
Red/yellow indicate CNF chunk

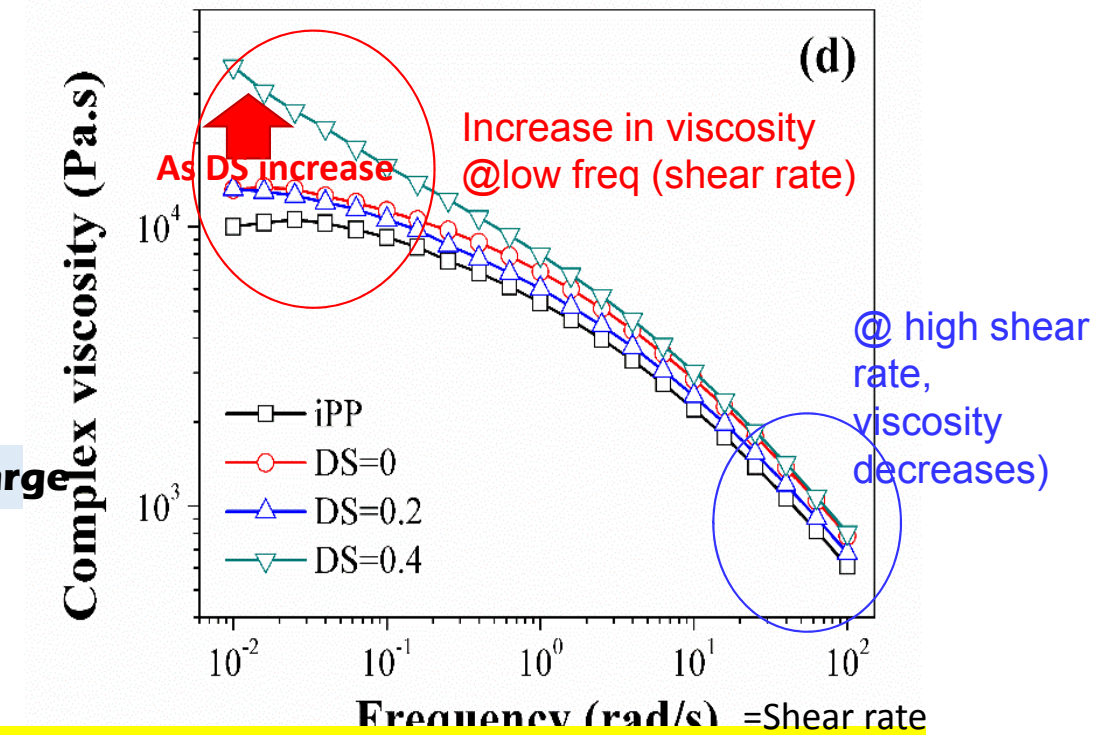
- ❑ **DS=0 : Big chunk (agglomeration) of CNF**
- ❑ **DS=0.2 : Size of agglomeration is reduced.**
- ❑ **DS=0.4 : Dispersiveness is improved**

AS the DS increases, the dispersiveness of CNF is improved

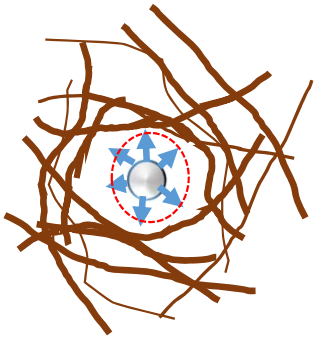
Advantage of CNF for Foaming (Higher viscosity at low shear rate)

CNF forms a Network structure in polymer





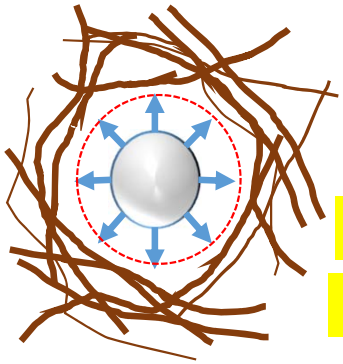
@ Bubble radius R is sma



$$\frac{1}{R}\frac{dR}{dt} = Shear\ rate$$

= Shear rate is high

@ Bubble radius R is large



$$\frac{1}{R}\frac{dR}{dt} = Shear\ rate$$

= Shear rate is low

As bubbles grow, the polyme viscosity increases

Prevent bubble from coalescence or further growth

Bubble size is reduced.

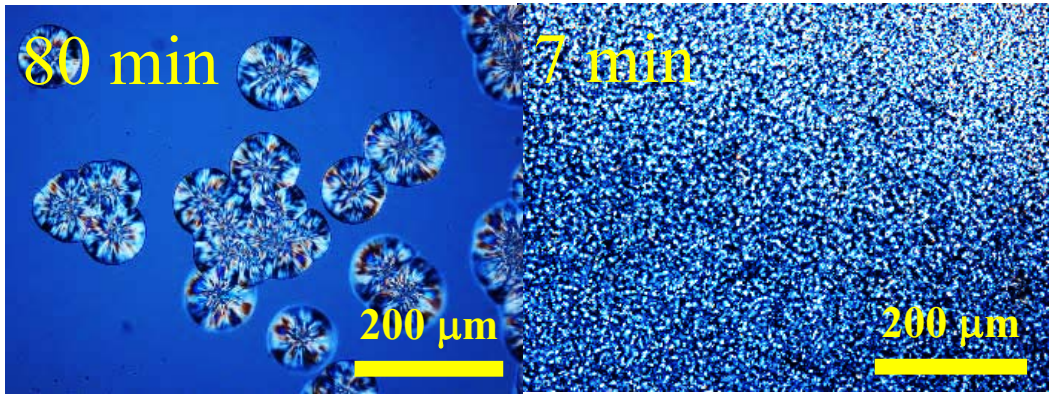
Mechanical strength of foam will not be

Advantage of CNF for Foaming (Crystals is for bubble nuc. agent)

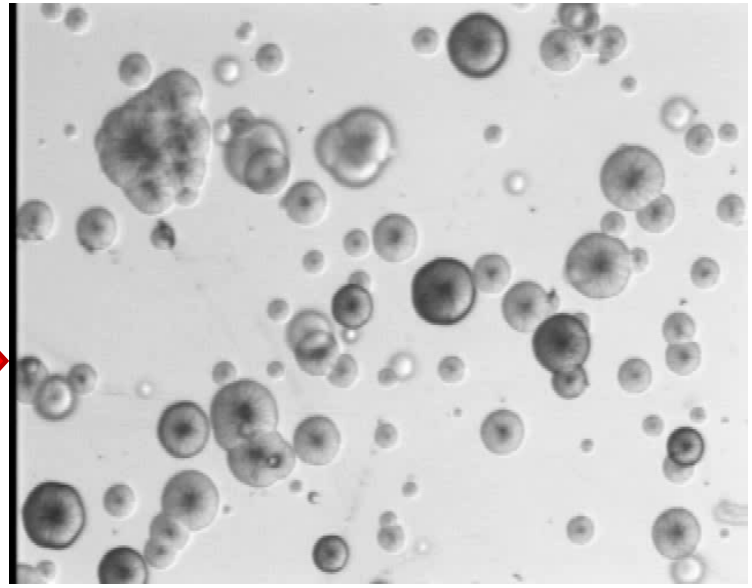
- **CNF is a Foreigner to PP**
- **Heterogeneity enhances Crystal nucleation**
- **Crystal size is made smaller by CNF**

Crystals play a role of bubble nucleating ag

iPP PP/CNFs



isothermal crystallization at 135 °C

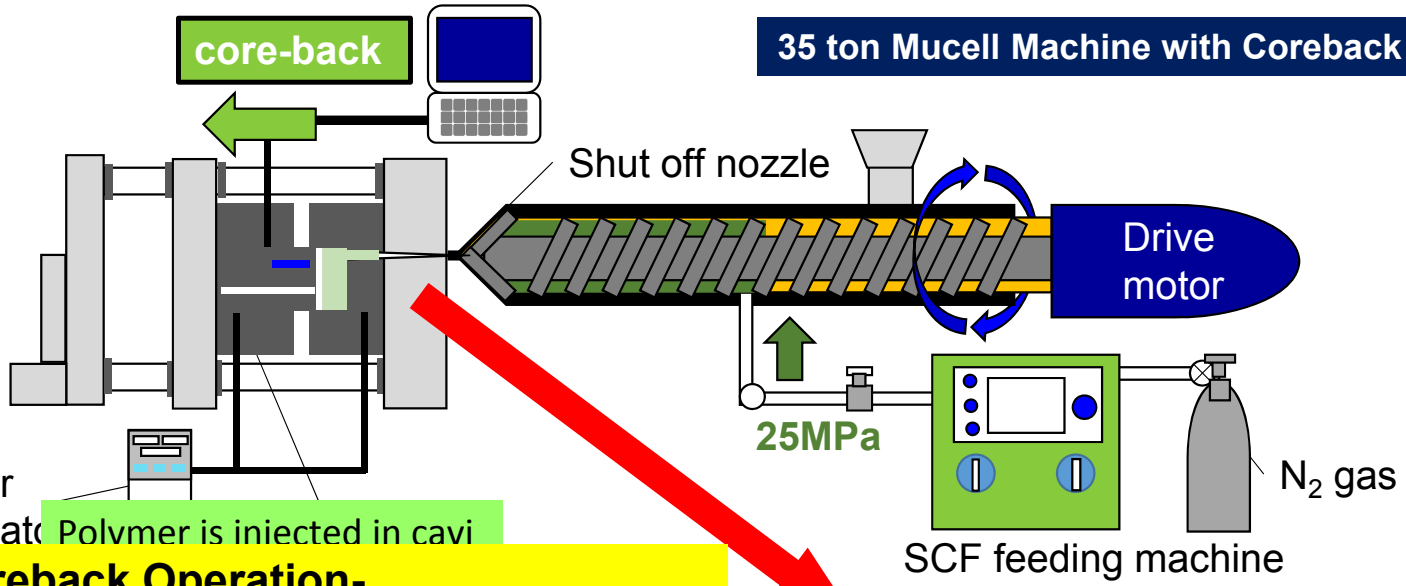


PLA crystals

The smaller and larger number of crystals make bubble nucleation sites smaller and increase the site number

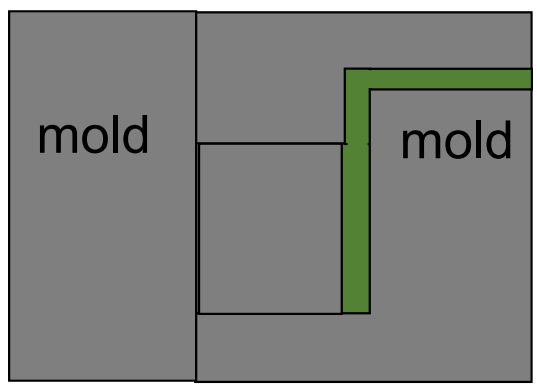
Let’s move to a foam injection molding to prepare the industrial size nanocomposite foams

Foam Injection Molding (FIM) Machine



-Coreback Operation-

1. **Close the mold**
2. **The screw is moved for metering the polymer**
3. **Introduce PBA (N2) and dissolve**
4. **Inject the polymer**
5. **A part of the mold is moved to expand the cavity volume**

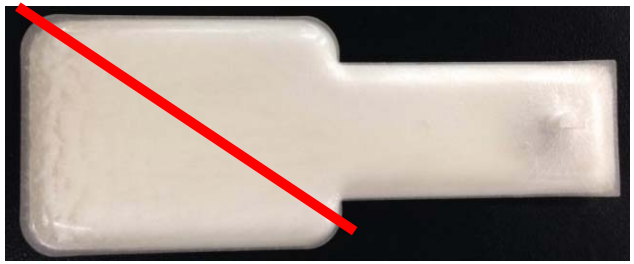


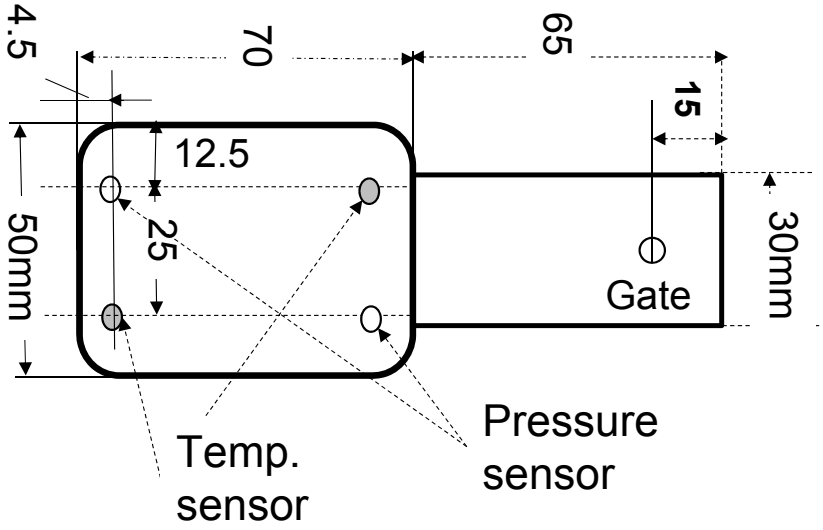
Digital Camera Image of cross sectional area cut along the red line

Injection molded foam without CNF

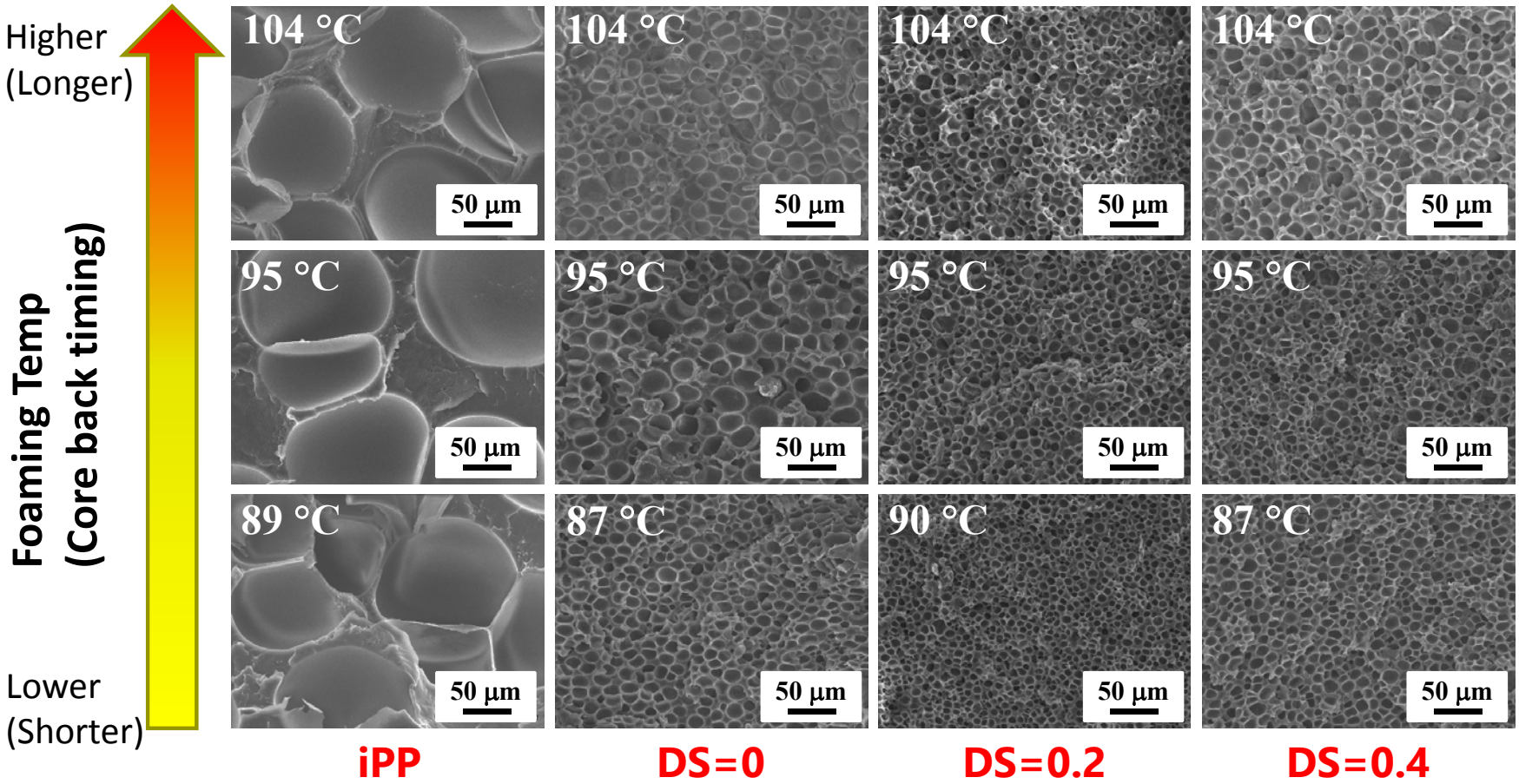
CNF(5%)/PP nano-composite foams

Cut line



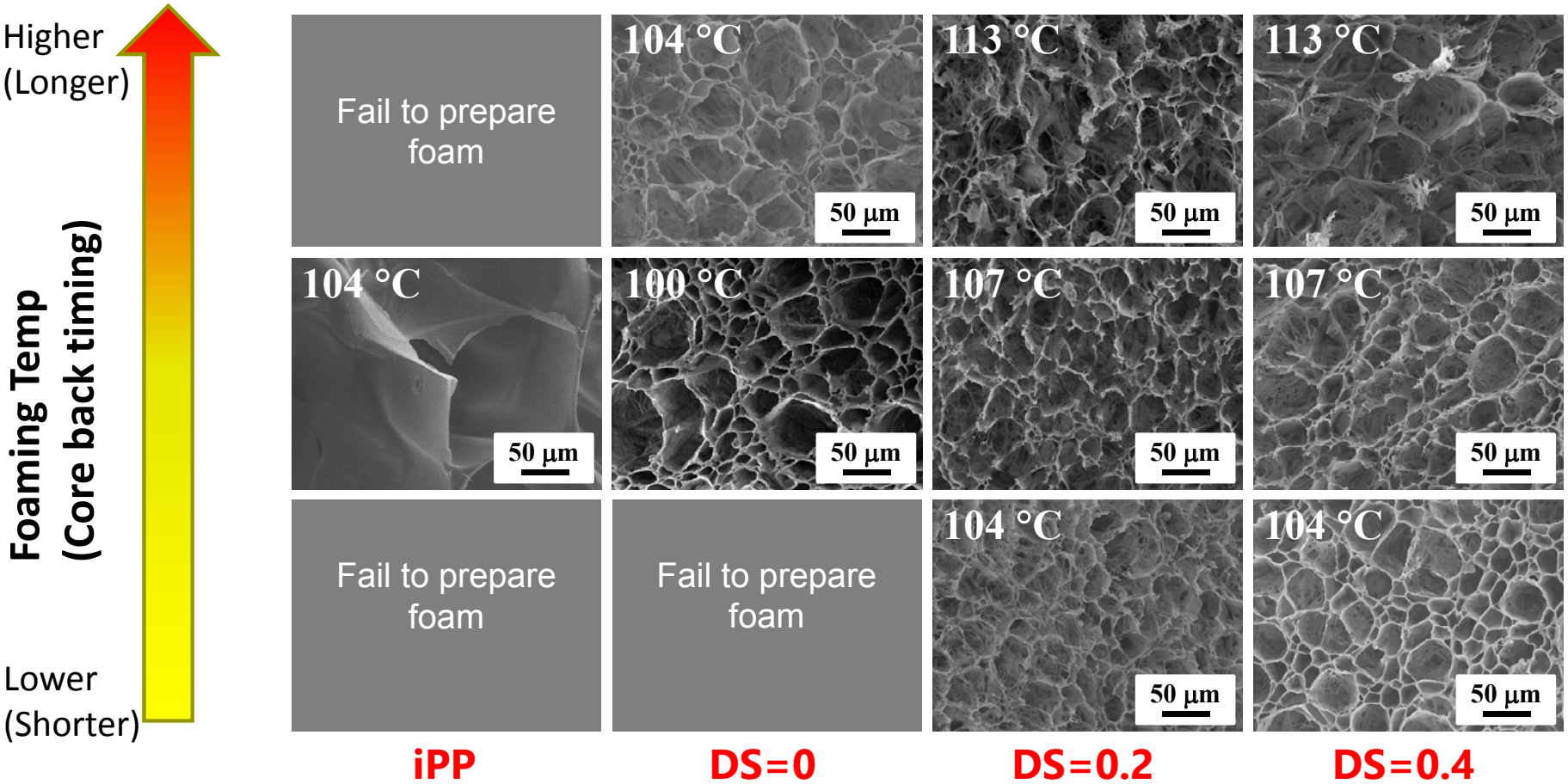


Cellular structures at the expansion ratio of 2-fold PP/CNF(5wt%)



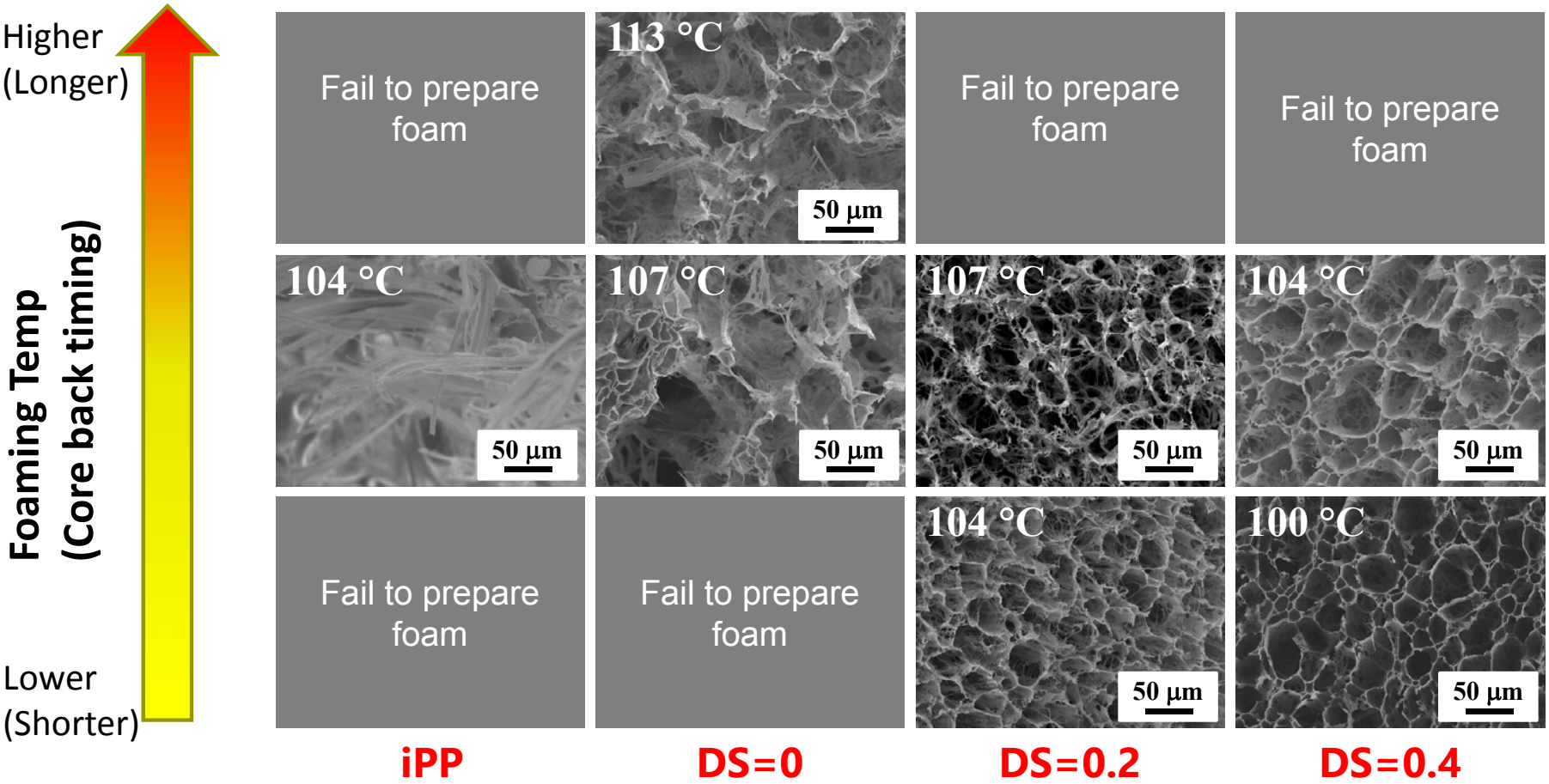
As we expected, CNF with any DS reduced the cell size and increase the cell number

Cellular structures at the expansion ratio of 7-fold (PP/CNF(5wt%)



As the expansion ratio increased, the operating window became smaller.
But, the presence of CNF could help widening the window

Cellular structures at the expansion ratio of 10-fold (PP/CNF5wt%)



DS= 0.2 provides finer cell than DS=0.4

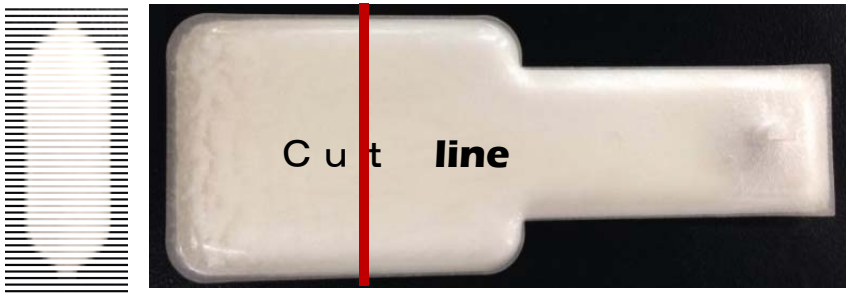
DS=0.4 provides wider operating windows and higher expansion foams

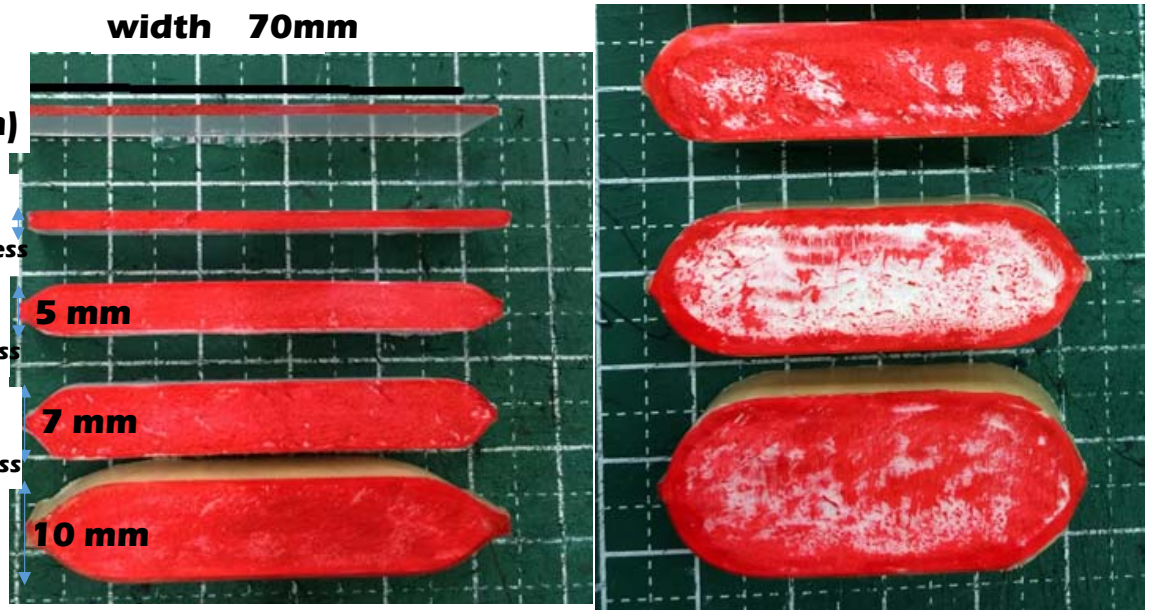
High Expansion ratios Foam

CNF（5wt%）/PP Composite Foam

DS=0.4 CNF

Cross-sectional area of foam





Painted with red ink

Conclusion

- **CNF can provide some benefits to polymer (PP) foaming.**
  - **Modification of Rheological behavior of PP, which is useful to reduce the cell size.**
  - **Enhancement of Crystallization behavior and reduction of crystal size, which are useful to Increase the number of bubble nucleation site.**

These benefits come from the heterogeneity of CNF (hydrophilicity).

- **To obtain a uniform cellular structure in foam, good dispersiveness of CNF is inevitable.**
- **The optimal chemical modification exists. i.e., The performance of foaming is tunable by DS (chemical modification)**

Thank you for your kind attention

PRESENTED BY:

Masahiro Ohshima

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