

Development of High Thermal Insulation and Compressive Strength PP Foams Blown in Injection Molding with Mold Opening

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Outline

■ Nano-Fibril Technology in Extrusion Foaming

- Use of PTFE to develop nano-fibrils in the PP matrix
- Effect of nano-fibrillated PTFE on the rheological behavior of PP
- Effect of nano-fibrillated PTFE on the extrusion foaming behavior of PP

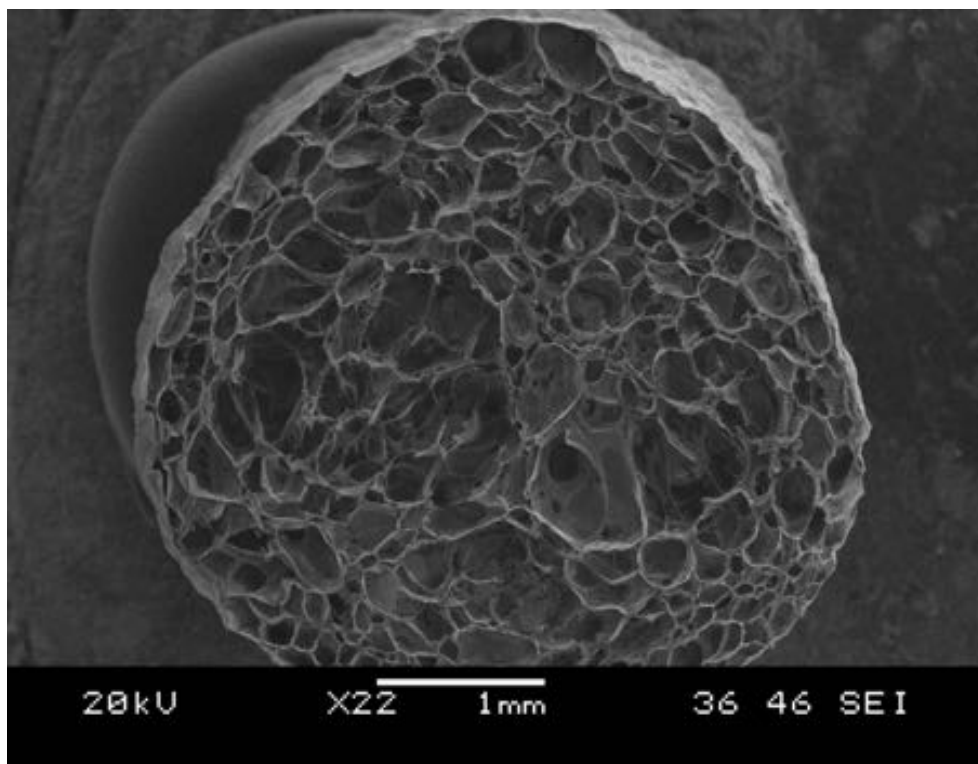
■ Application of the Nano-Fibril Technology to Injection Molding

- Effect of PTFE on the cellular structure of foam-injection-molded PP
- Effect of cell structure on thermal conductivity of PP foam below 40 W/m-K
- Effect of cell structure on mechanical properties of PP foam

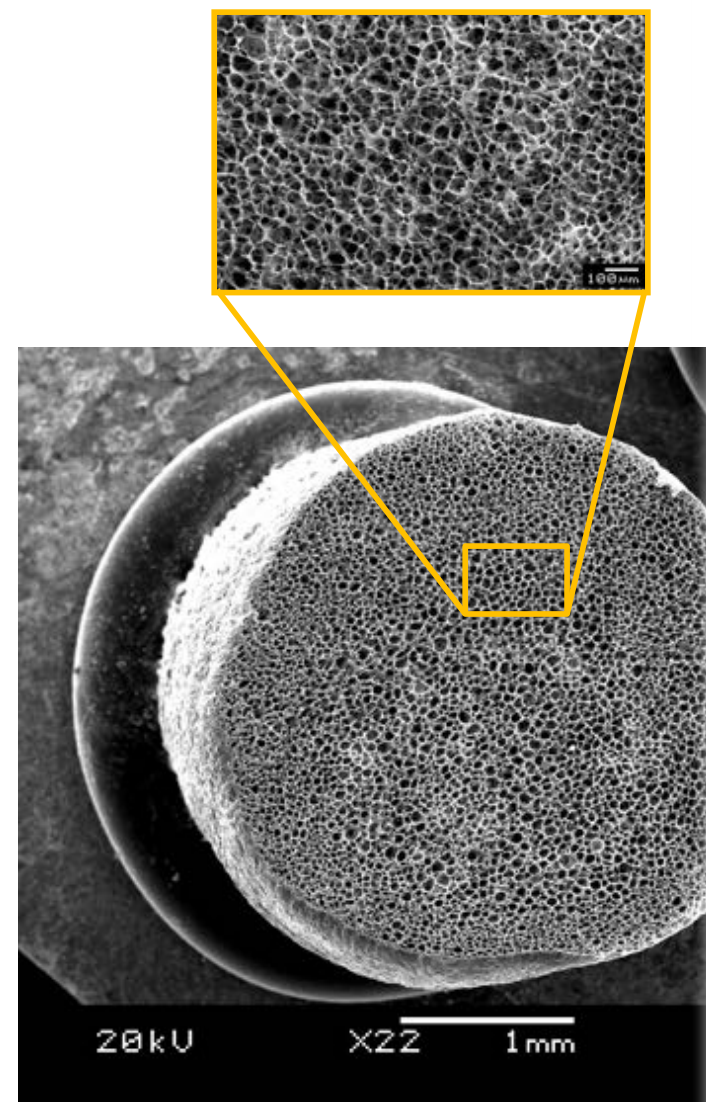
Nano-Fibril Technology in Extrusion Foaming

Development of PTFE as a foam enhancing additive

Linear PP



PTFE
3 wt%

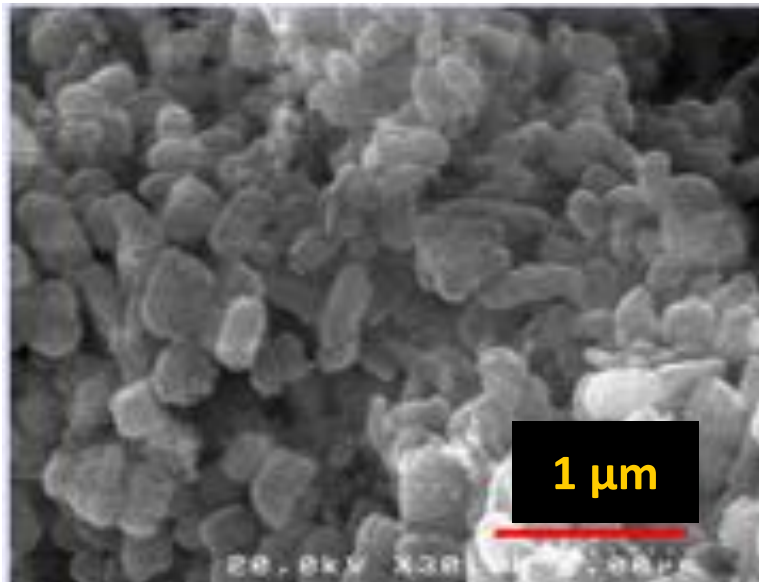


A. Rizvi, C.B. Park, M. Yamaguchi, **JP2013-514463**, 2013, and **WO2013137301**, 2013

A. Rizvi, A. Tabatabaei, R. Barzegari, H. Mahmood, C.B. Park, *Polymer*, **2013**, 54, 4645-4652

Morphology of PTFE in linear PP

Original PTFE granules

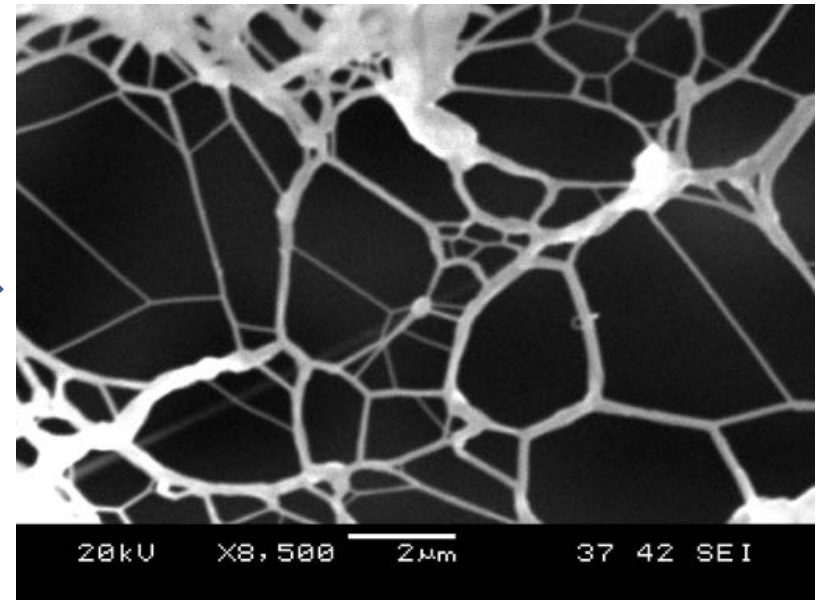


Spherical

Twin-screw
extrusion of PTFE
with PP

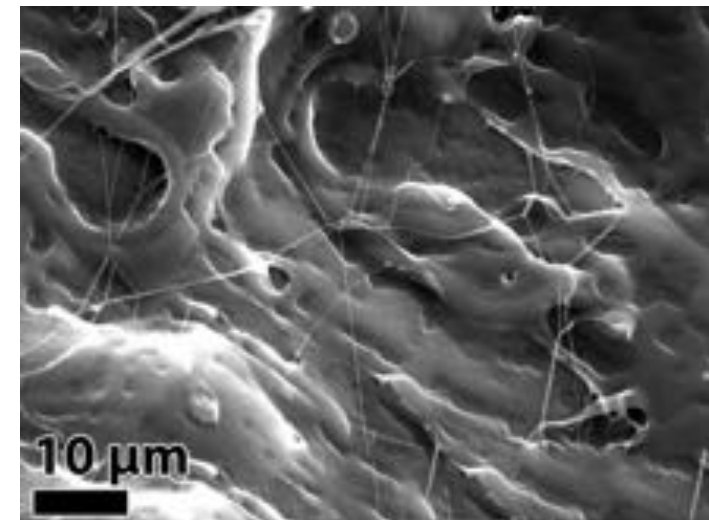


Residue of PP/PTFE (99.7/0.3 wt.%),
after dissolving in xylene

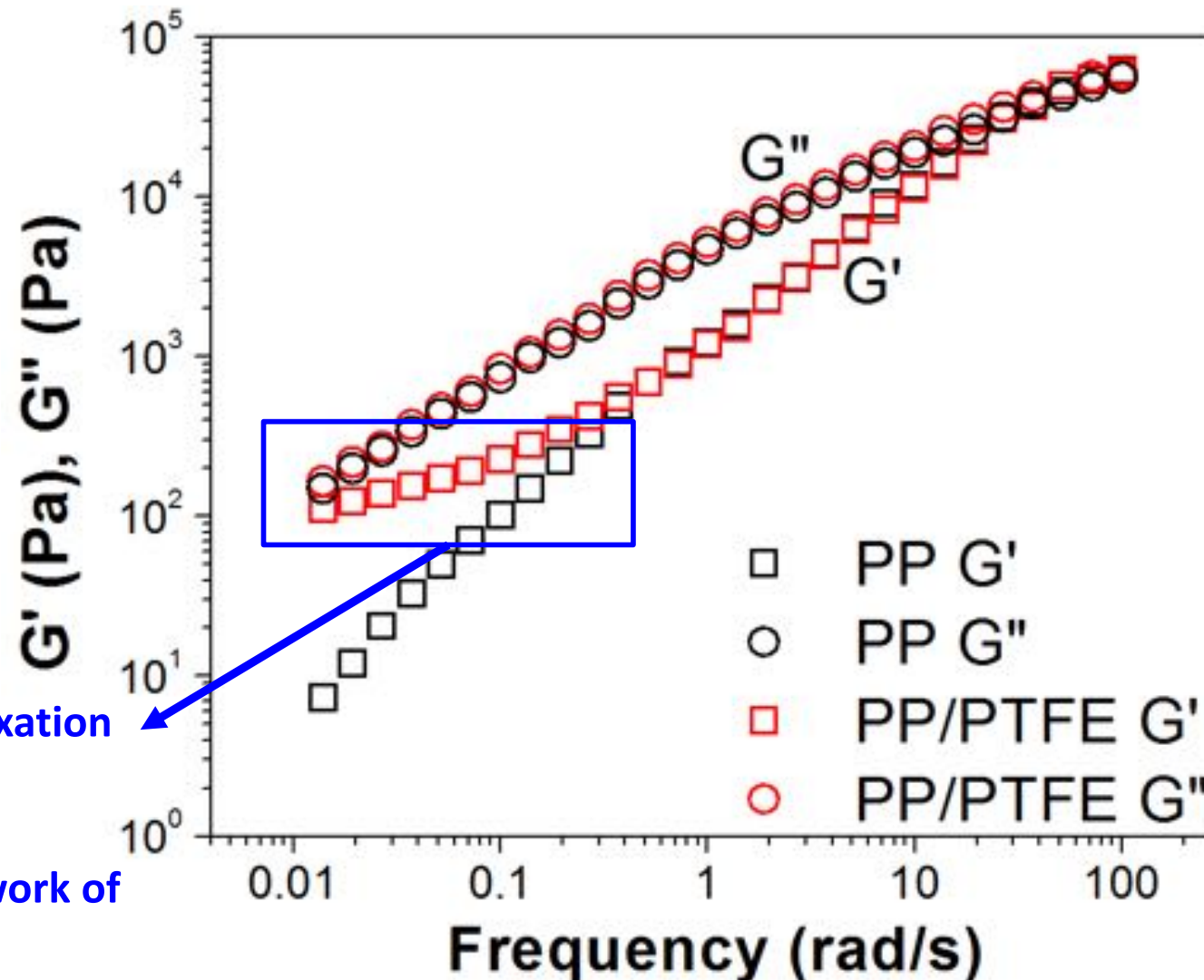


Fibrillar structure

- PTFE readily undergoes **plastic deformation**
- PTFE exhibits high **ultimate strain**
- Entangled fibrils enhance **melt strength** of matrix



Frequency dependence of elastic and shear moduli at 190°C (PTFE 3 wt%)



Long-time relaxation

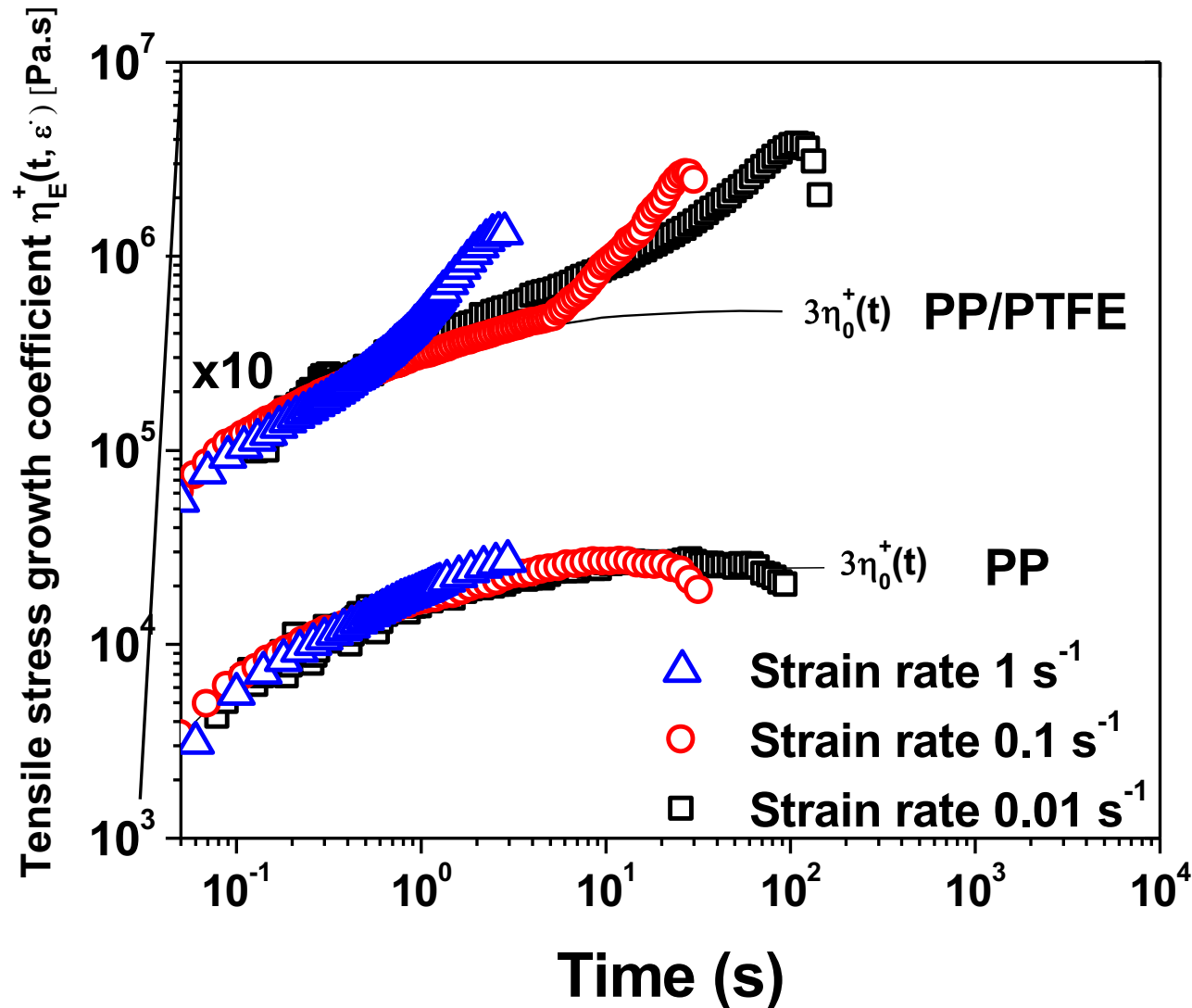


Entangled network of
fibers

A. Rizvi, C.B. Park, M. Yamaguchi, **JP2013-514463**, 2013, and **WO2013137301**, 2013

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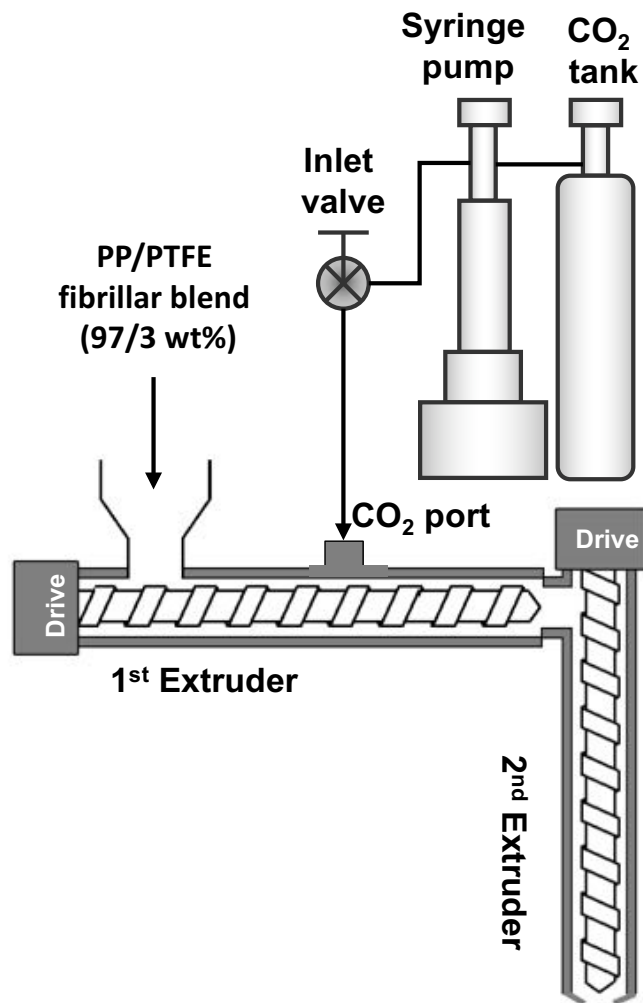
Strain-induced hardening in uniaxial elongational flow (PTFE 3 wt%)



A. Rizvi, C.B. Park, M. Yamaguchi, **JP2013-514463**, 2013, and **WO2013137301**, 2013

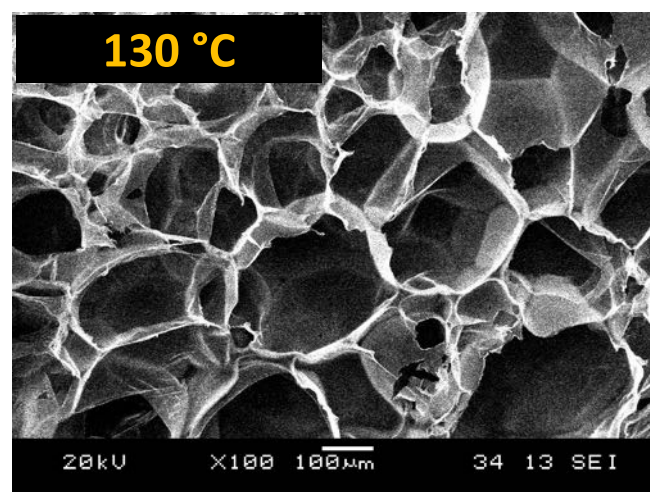
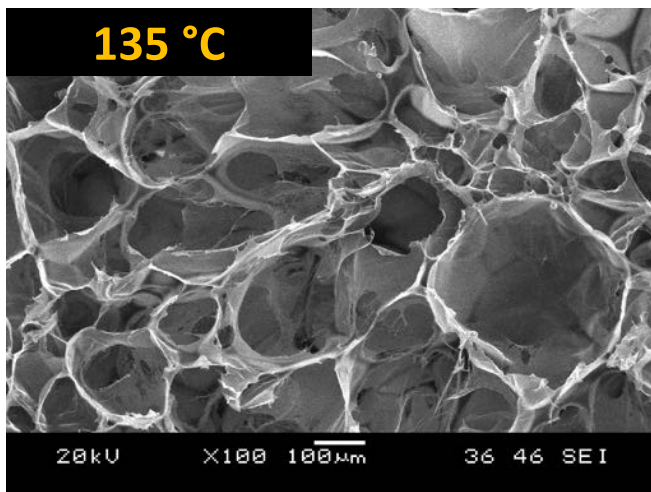
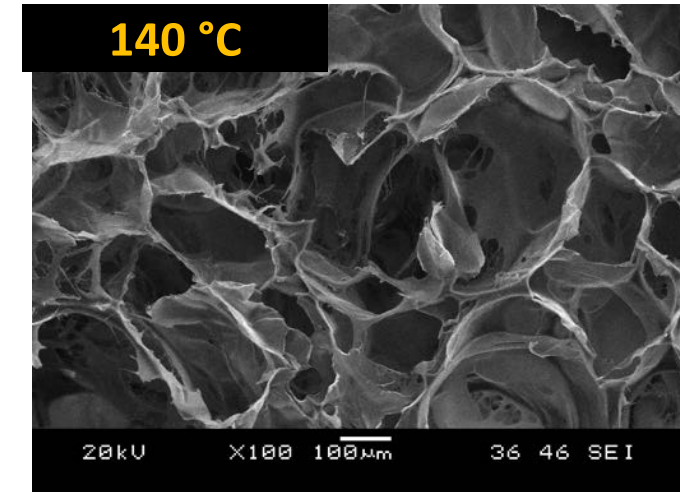
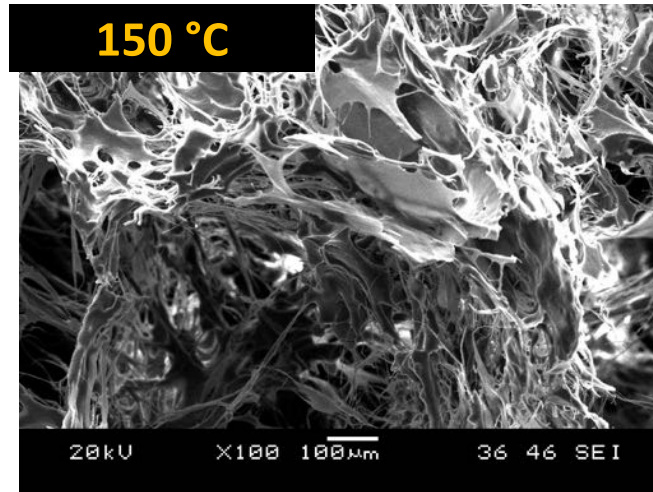
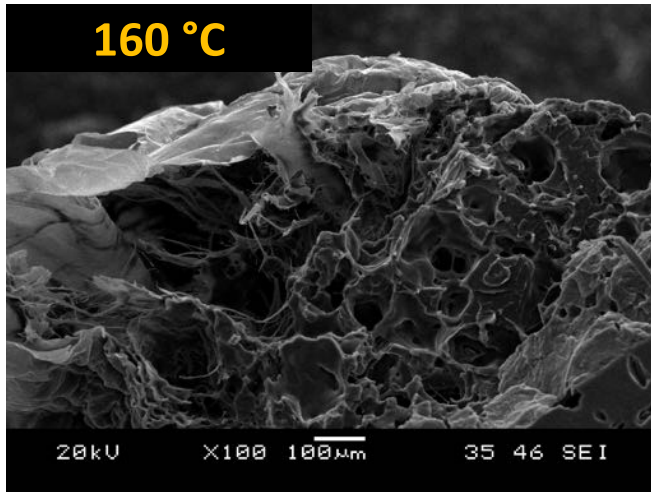
A. Rizvi, A. Tabatabaei, R. Barzegari, H. Mahmood, C.B. Park, *Polymer*, **2013**, 54, 4645-4652

Experiment: Tandem foam extrusion system

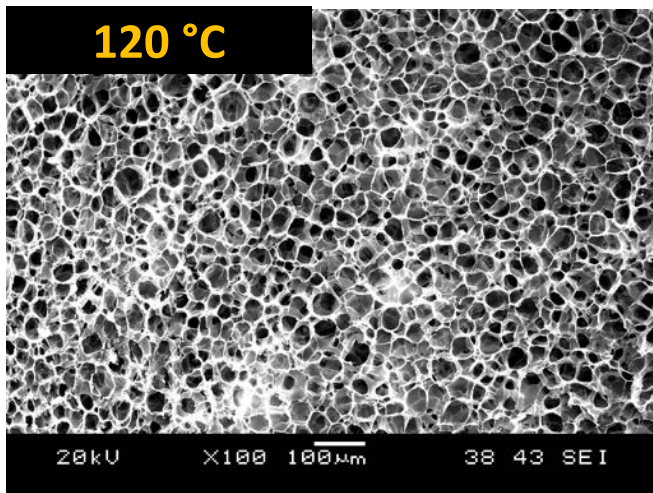
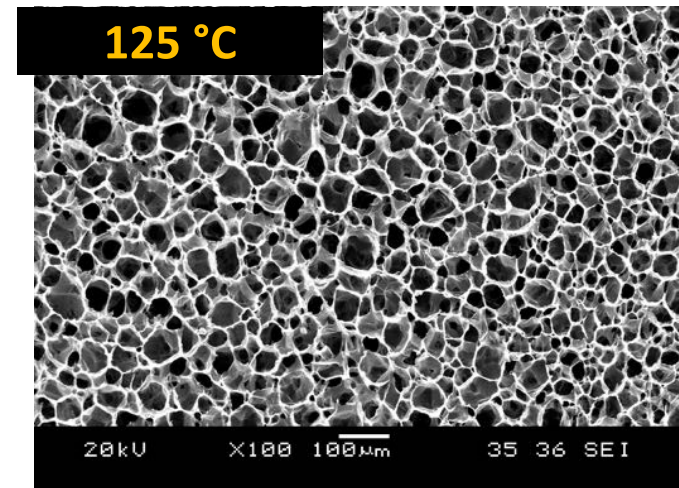
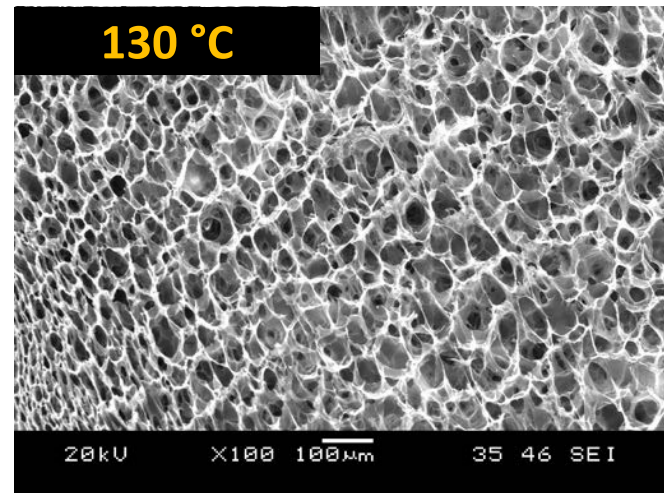
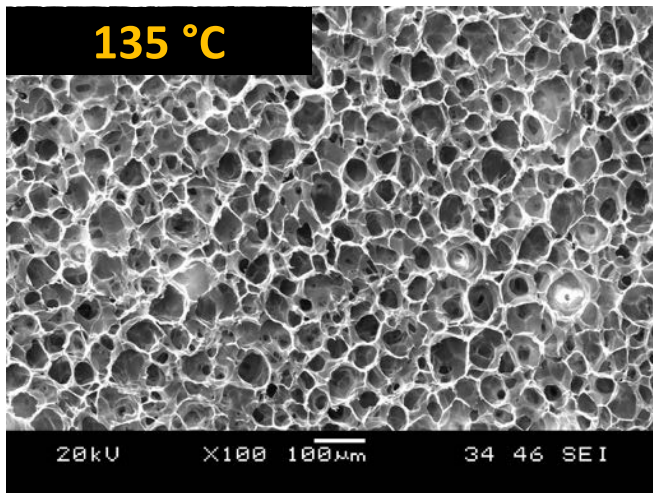
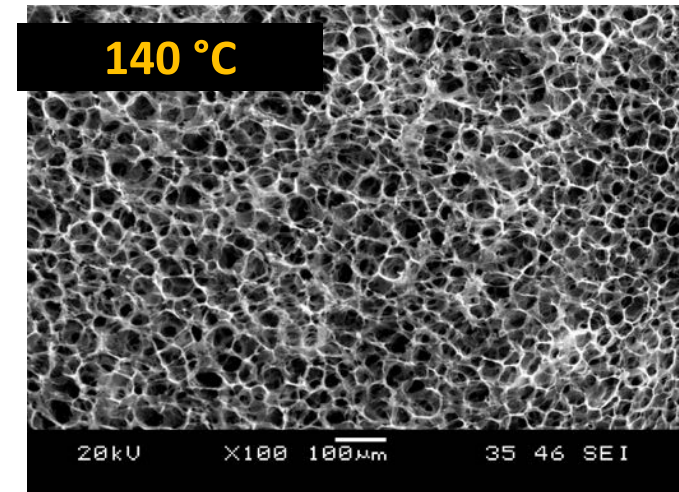
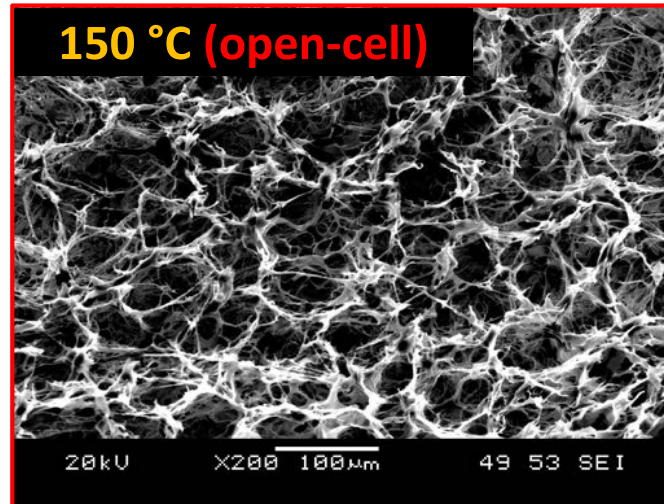
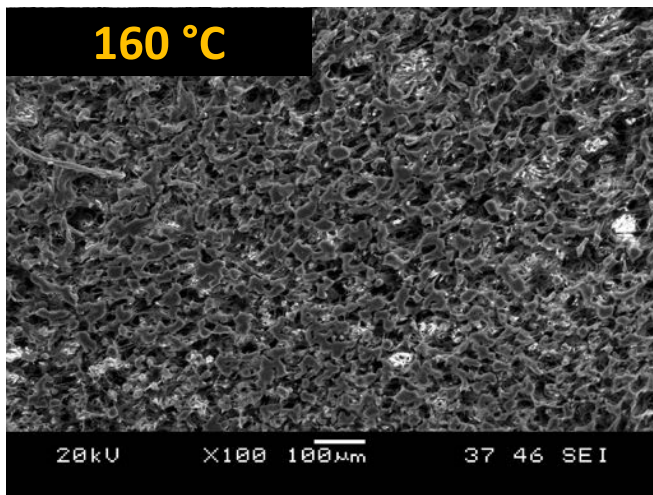


Material	1. Linear PP 2. PP/PTFE (97/3 wt%)
Die	L/D ~8.3 (L = 10 mm / ϕ = 1.2 mm)
CO ₂ Content	10 wt%
Equipment	Small tandem extruder (0.75" / 1.5")

SEM Images of extruded PP foams

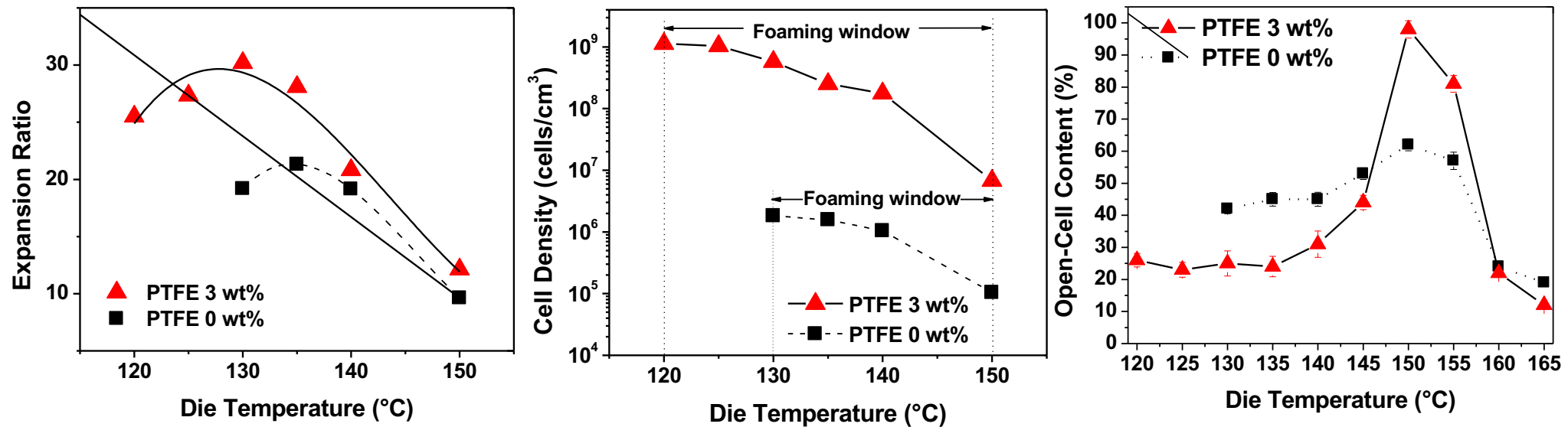


Die blockage occurred at
125°C



**SEM Images of extruded
PP/PTFE (97/3 wt%) foams**

Foam characterization



- **Expansion Ratio:** Up to **10-fold** increase
- **Cell Density:** Up to **2 orders of magnitude** increase
- **Open-cell content:** Up to **97.7%** at 150°C

Application of the Nano-Fibril Technology to Injection Molding

- Effect of PTFE on the cellular structure of foam-injection-molded PP
- Effect of cell structure on thermal conductivity of PP foam below 40 W/m-K
- Effect of cell structure on mechanical properties of PP foam

Introduction

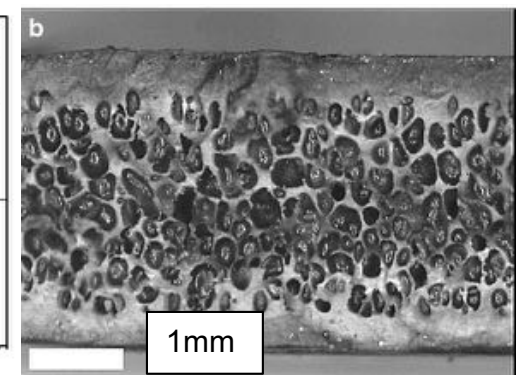
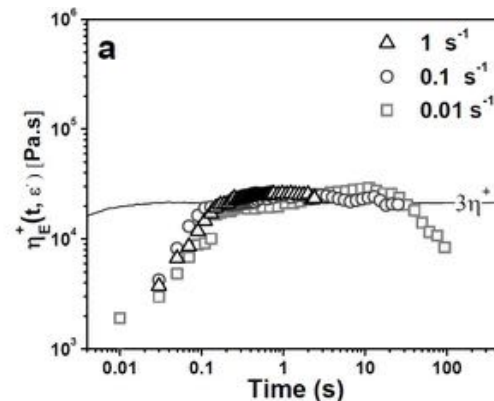
■ Advantage of PP foams

- Low price
- Low density
- High stiffness
- Good temperature stability
- High chemical residence



■ Difficulties to foam PP

- Weak melt strength

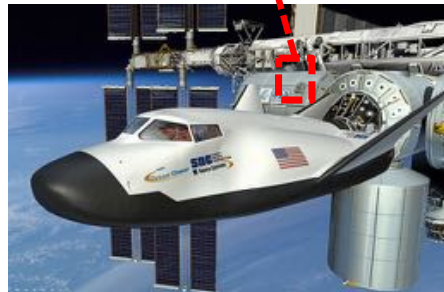


Apply PTFE to improve melt strength as well as crystallization, and to enhance strain hardening behavior in foam injection molding

Introduction

■ The Requirements for Thermal Insulation Materials

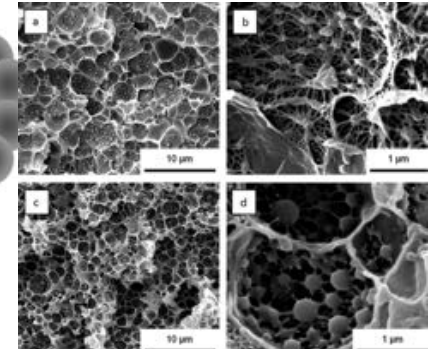
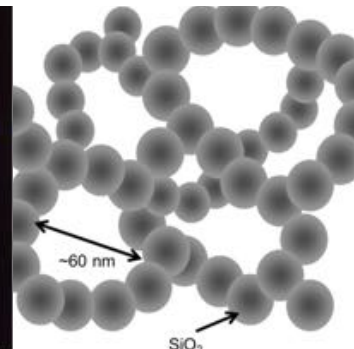
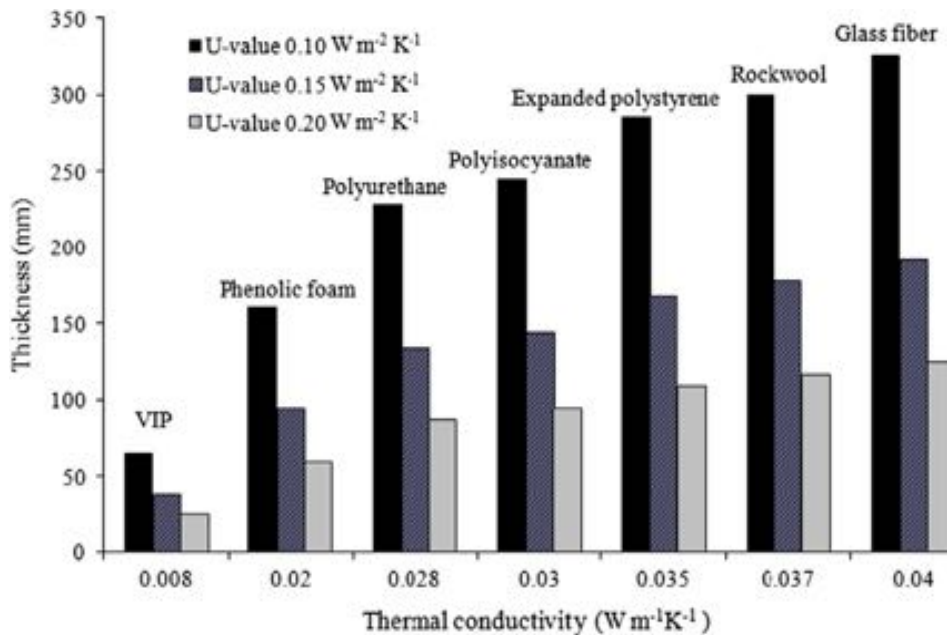
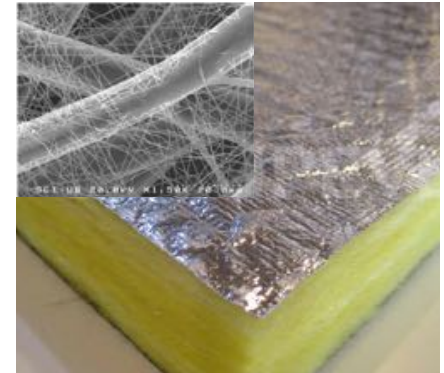
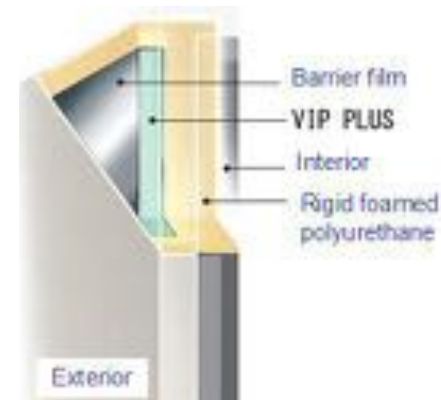
- Housing
 - Walls
 - Roofs
- Space
 - Space suit
 - Spacecraft
 - Space station
 - Space probe
- Airplane
- Transport pipelines
- Storage tanks



Introduction

■ Methods for thermal Insulation

- ❑ vacuum insulation panels (VIPs)
- ❑ Foams
- ❑ Glass fiber
- ❑ Aerogel materials



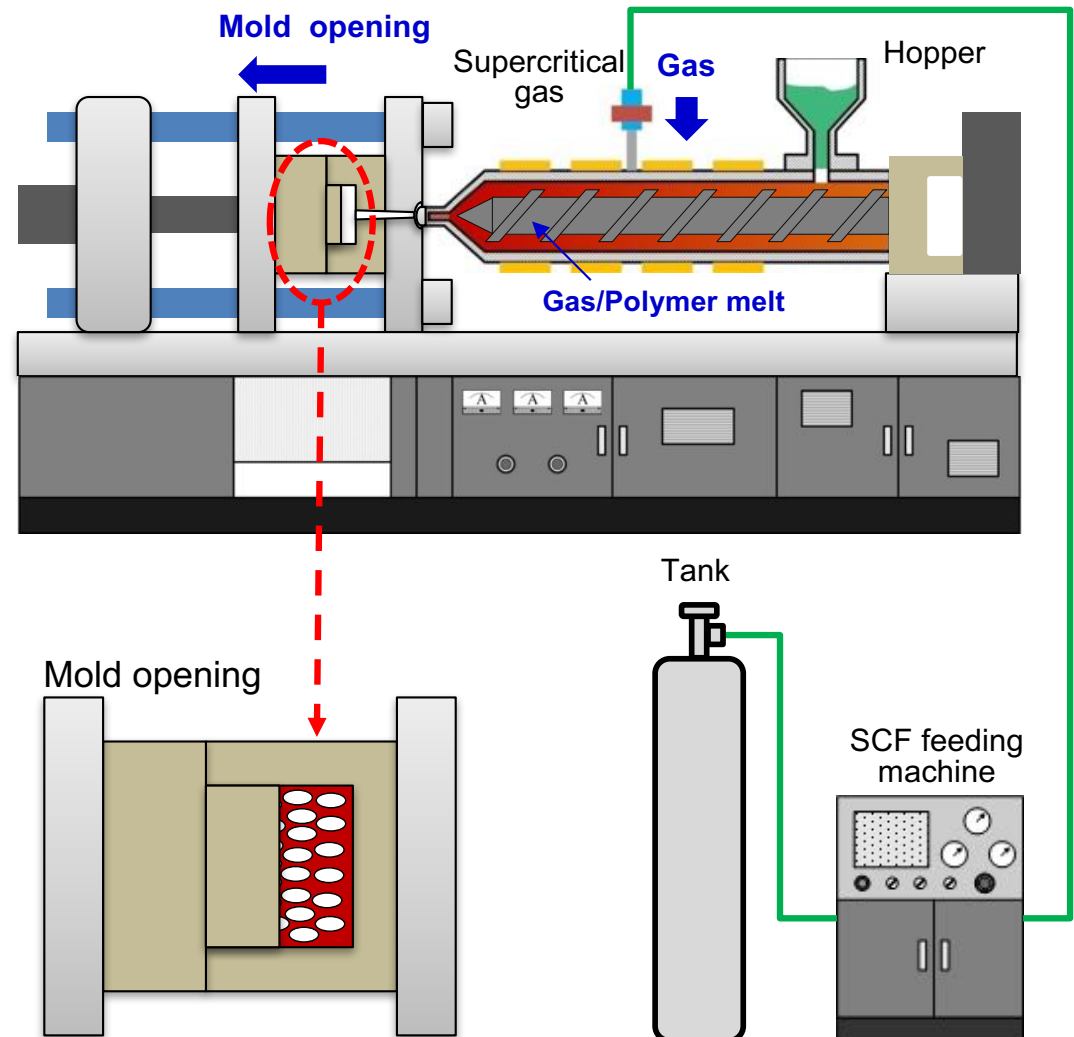
■ Foams:

- ❑ Lower price
- ❑ Good processability
- ❑ Highly efficient thermal insulation

Methodology

■ High- P Foaming Approach

- Close the mold
 - Metering the polymer
 - Dissolving supercritical CO₂
- Inject the gas/polymer mixture
 - Completely filling the mold cavity
 - Packing with high pressure
- Dwelling time
 - Allowing the material to cool
- Mold opening to cause foaming
 - Nucleation and growth occurring



Experimental

■ Materials

□ Polypropylene

- Homopolymer
- Novatec FY4, supplied by Japan Polymer Corp.
 - MFR = 5 kg/10min (230°C, 2.16kg)

□ Polytetrafluoroethylene (PTFE)

- METABLEN A-3000, Mitsubishi Rayon

□ Blowing agent

- 8 wt.% CO₂, supplied by Linde Gas

Experimental

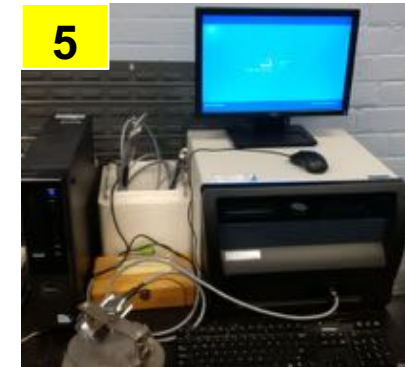
■ Experimental equipment

- 50-ton MuCell FIM equipment
 - Arburg Allrounder 270^[1]
 - Mucell SC feeding machine^[2]



■ Characterization and Rheology measurement

- SEM JEOL JSM-6060^[3]
- ARES-G2 Rheometer^[4]
- Hot Disk Thermal constant analyser^[5]



Experimental

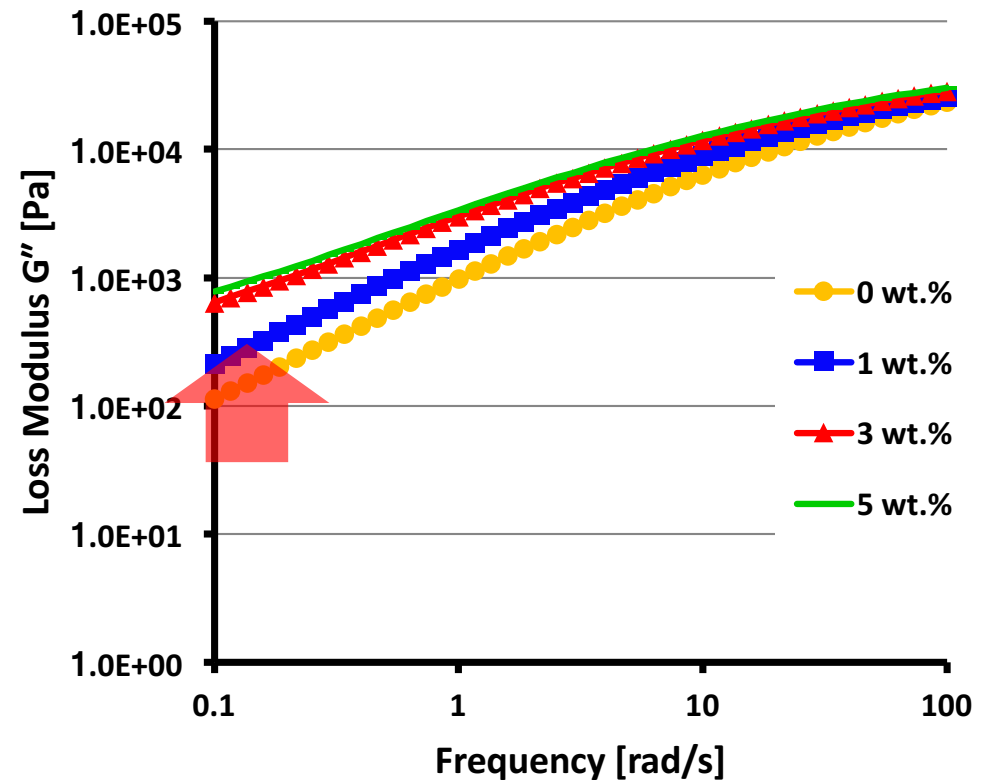
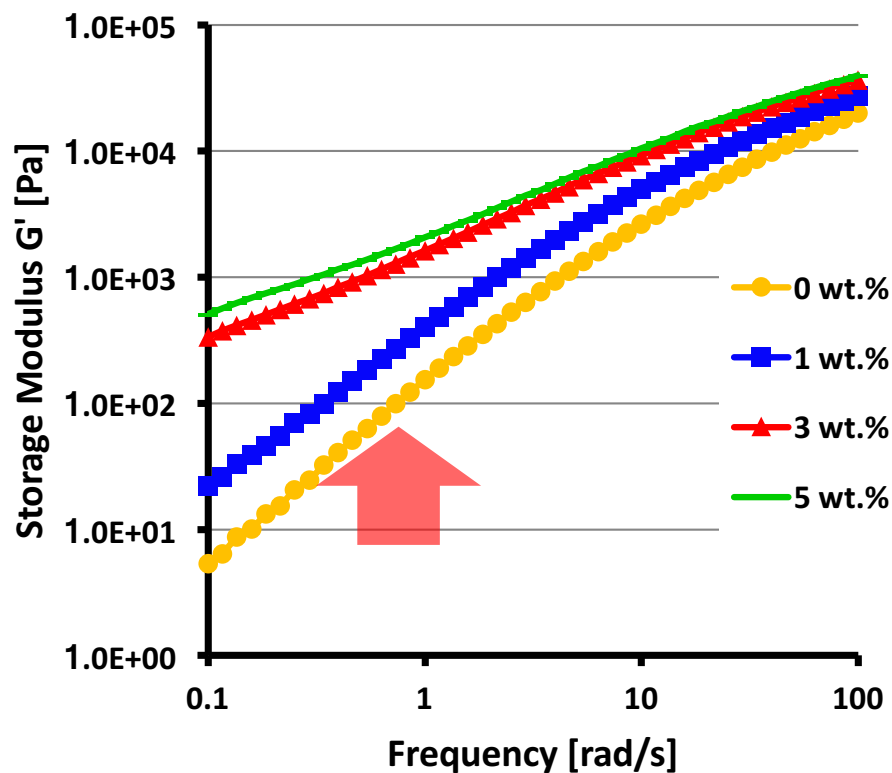
■ Processing conditions for injection molding

- A full factorial experiment was used and the processing conditions below were conducted for PP/PTFE (0%wt, 1%wt, 3%wt, 5%wt)

Parameters	Values
CO ₂ content (%)	8.0
Melt temperature (°C)	230
Mold temperature (°C)	80
Injection speed (cm ³ /s)	100
Dwelling time (s)	30, 32.5, 35, 37.5, 40, 42.5
Shot size (cm ³)	60
Packing pressure (MPa)	30
Mold opening distance (mm)	12, 15, 18, 21, 24

Results and discussion

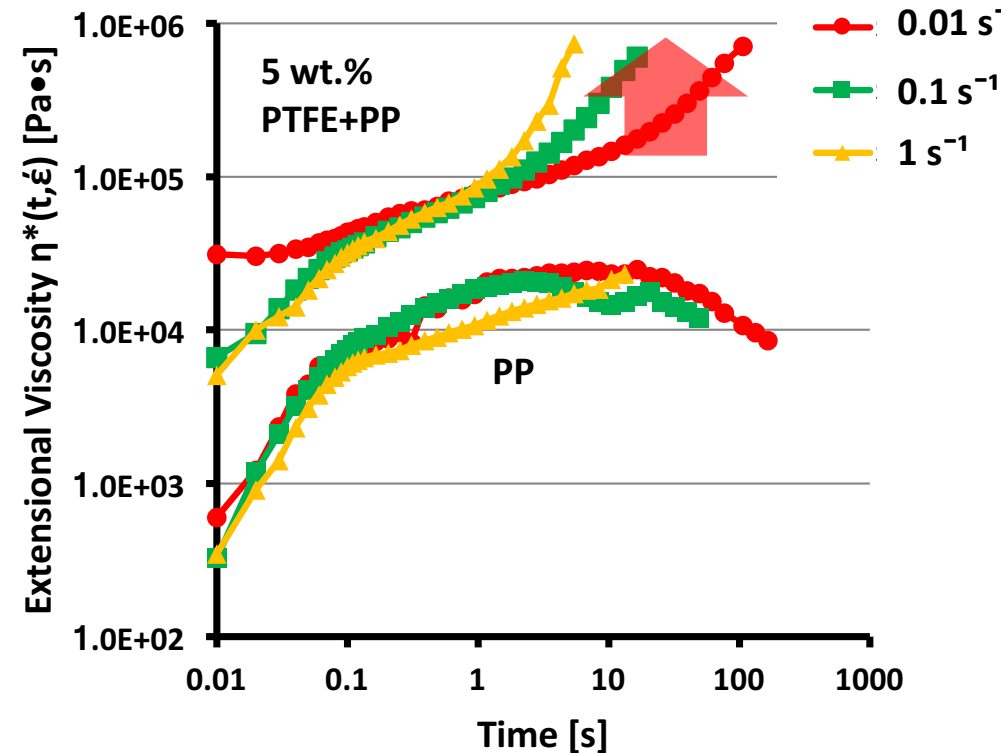
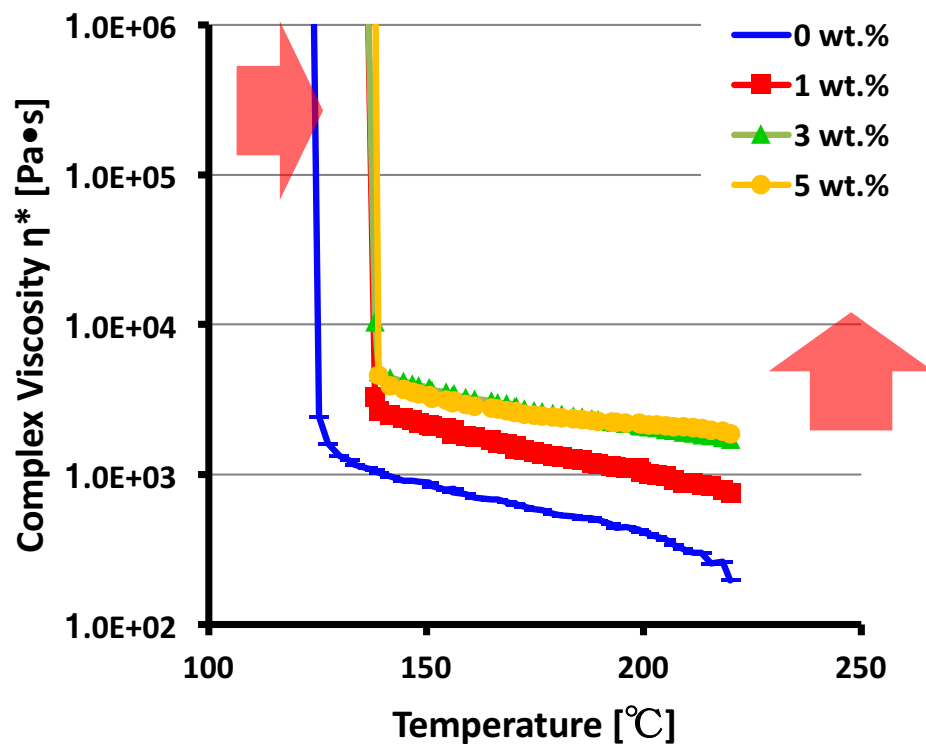
■ Rheological Properties of PP/PTFE blend: Effects of PTFE on Rheological Property



- In the low shear rate region, G' and G'' increased, as the PTFE content increased.
- Indication of a network structure formed

Results and discussion

■ Rheological Properties of PP/PTFE blend: Effects of PTFE on Rheological Property

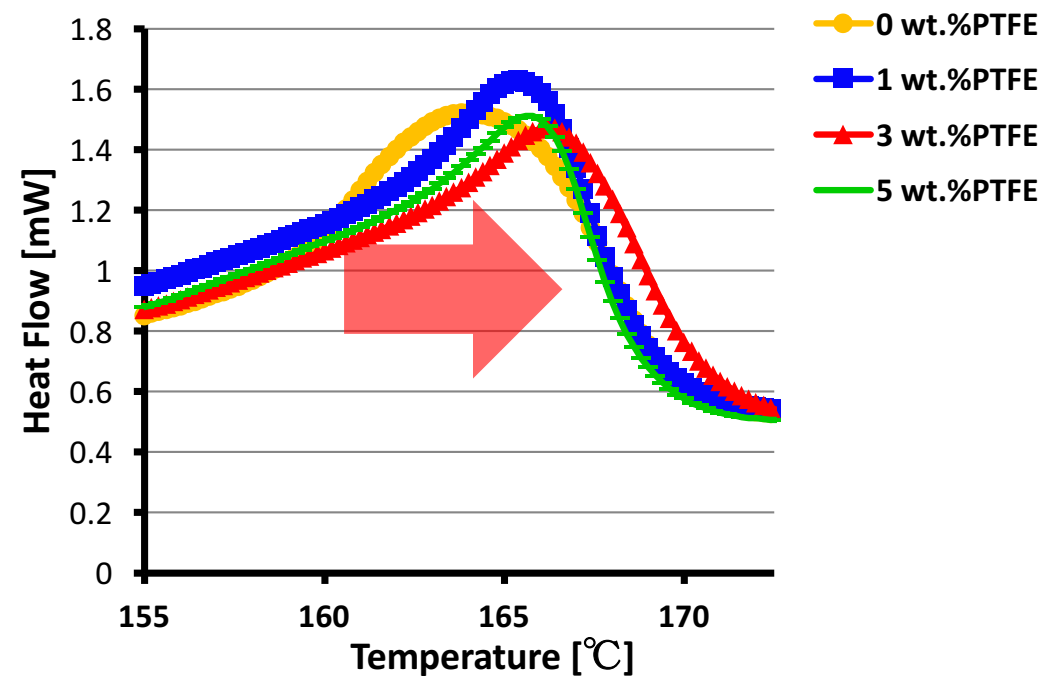
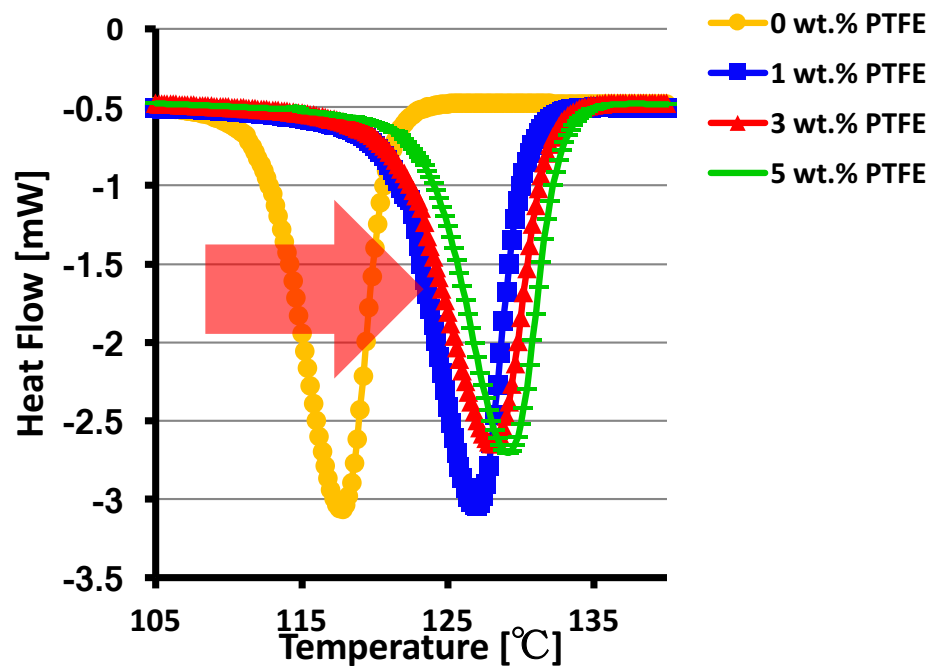


- The crystallization temperature and the viscosity increased with an increased PTFE content.
- PTFE dramatically enhanced the strain hardening behavior.

Results and discussion

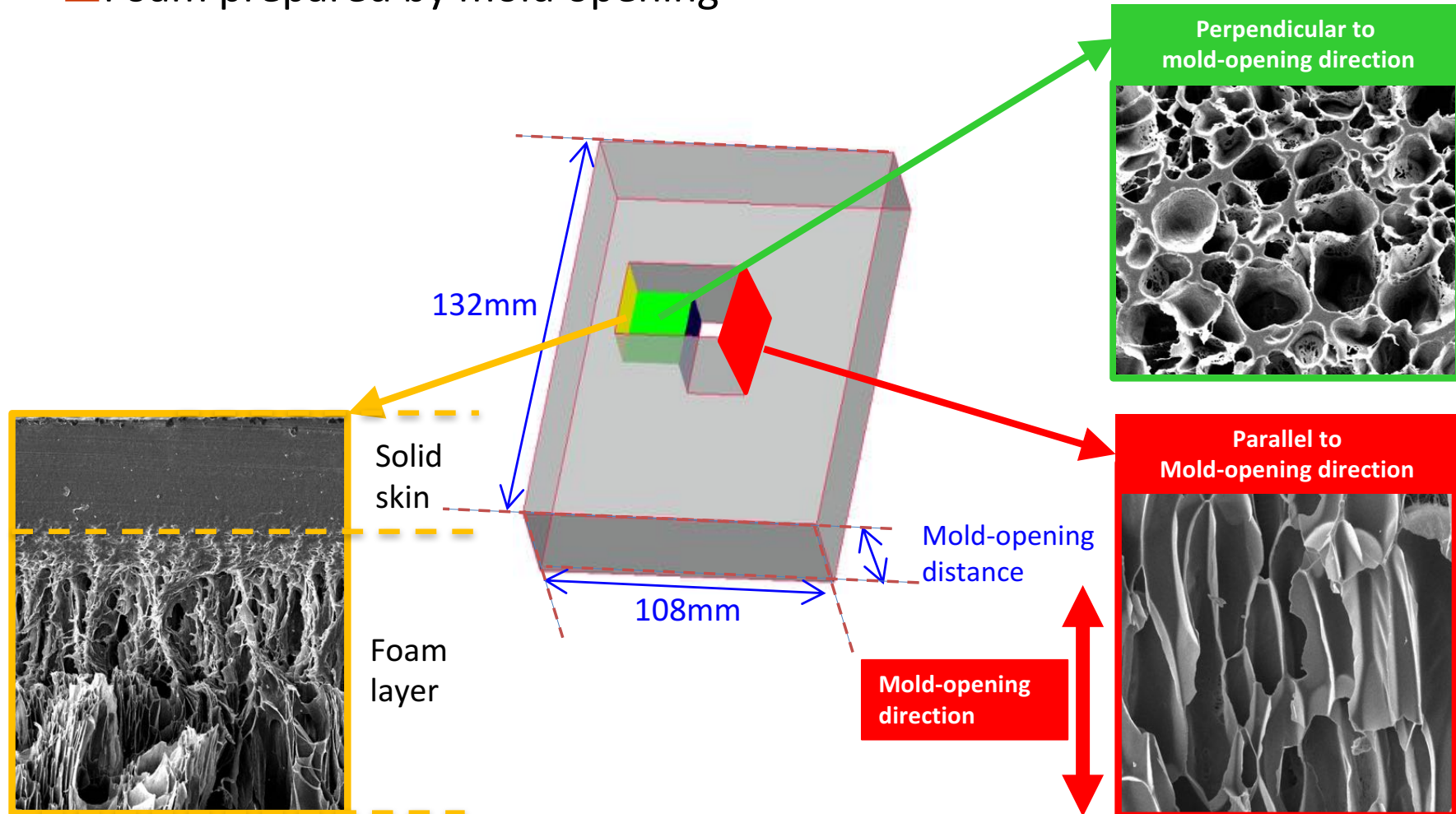
■ Thermal Properties of PP/PTFE blend: Effects of PTFE on Crystallization

	crystallization peak	enthalpy-heating	melt temperature	degree of crystallinity
PP-FY4	117.82	74.82	163.79	0.3614
PP+1PTFE	126.94	81.61	165.36	0.3982
PP+3PTFE	128.19	80.68	166.13	0.4018
PP+5PTFE	128.89	75.38	165.77	0.3833



Results and discussion

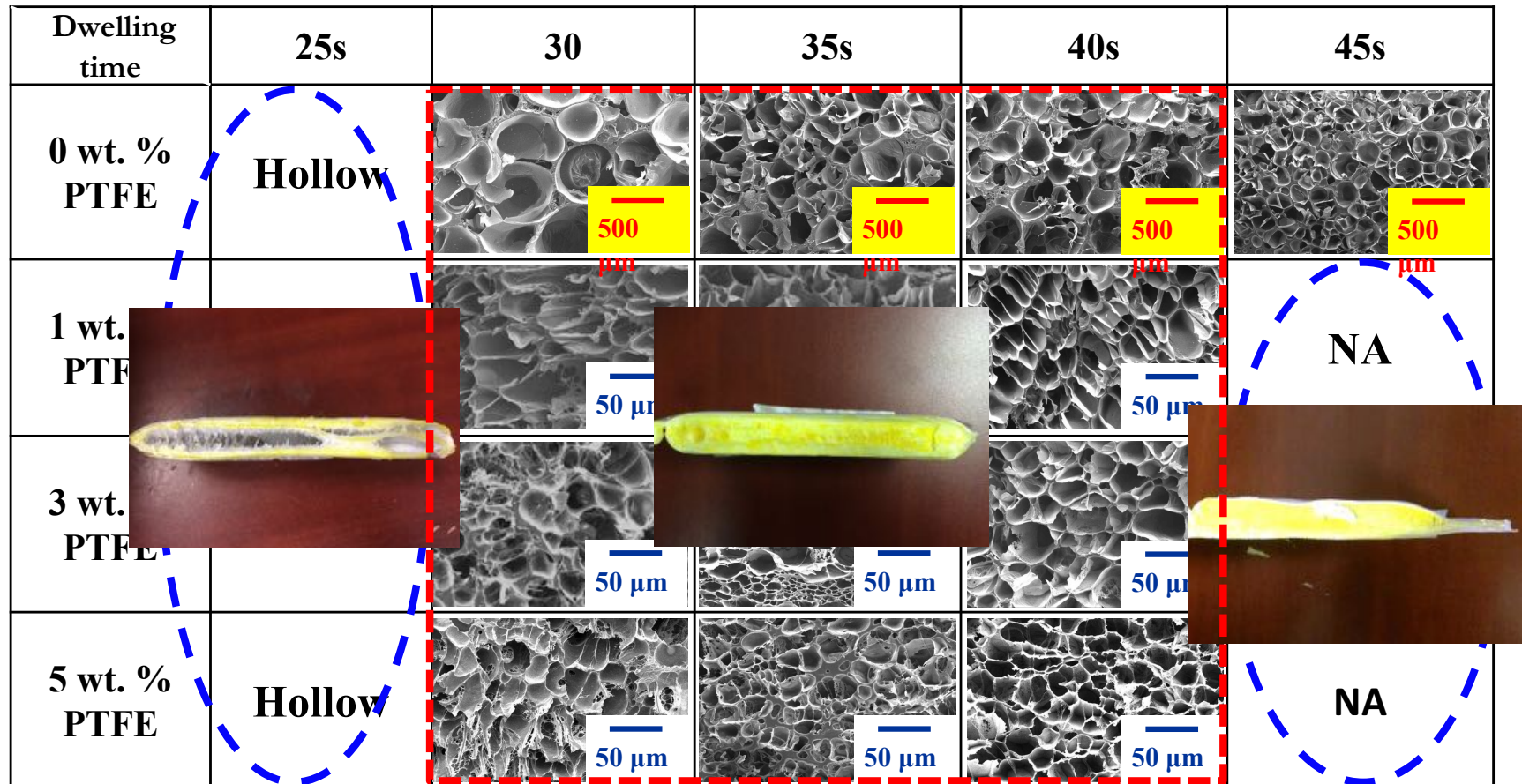
- Cell structure of foam with PTFE
 - Foam prepared by mold opening



Results and discussion

■ Cell structure of foam with PTFE

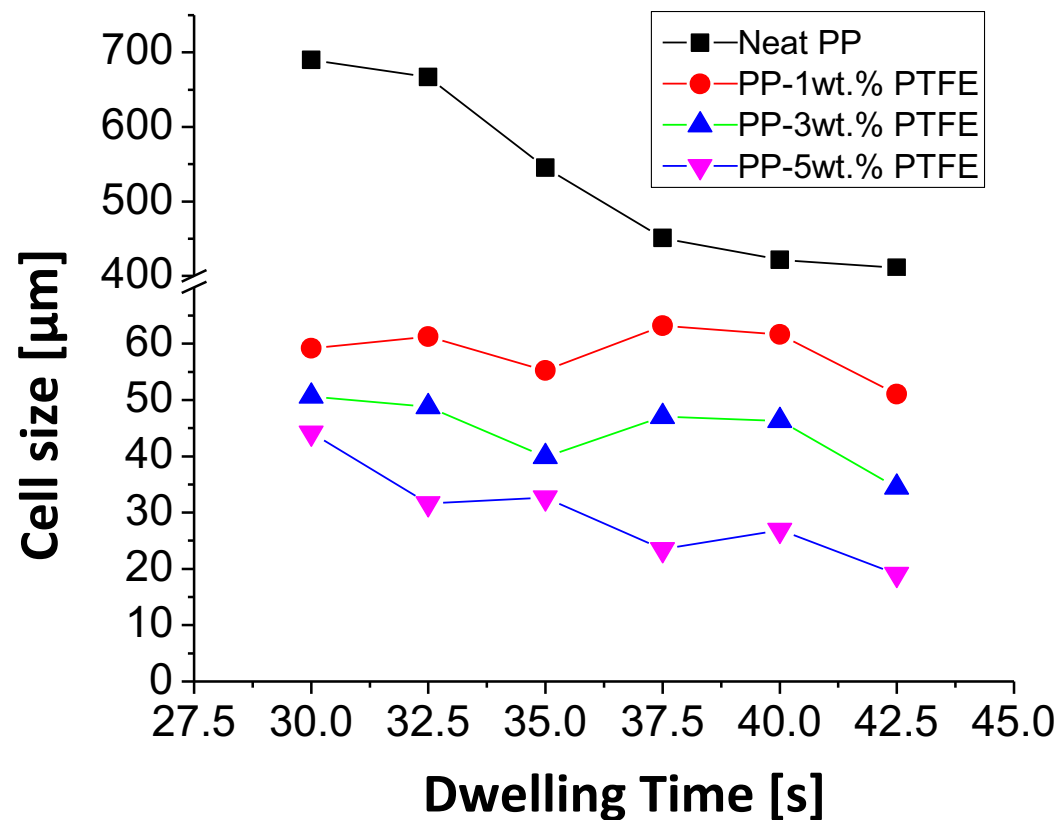
□ SEM Images (perpend. to Mold-opening) of Foam (Expansion ratio 7.5)



Results and discussion

■ Cell structure of foam with PTFE

□ Effect of dwelling time on cell morphology (perpend. to Mold-opening)

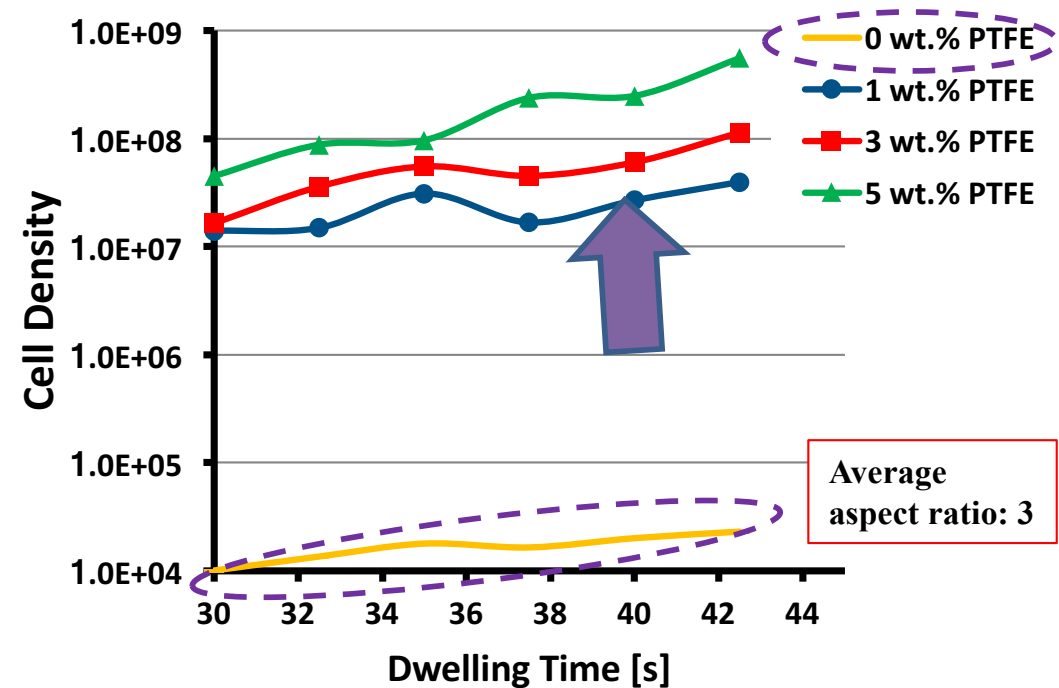
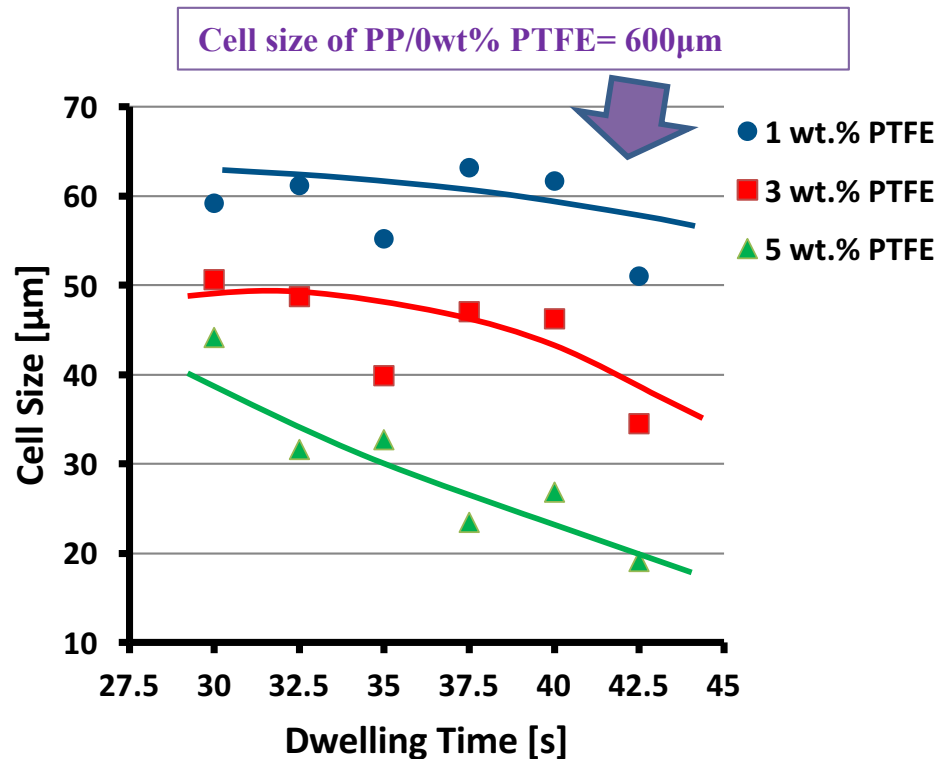


Volume
Expansion
Ratio: 7 ± 1

Results and discussion

Cell structure of foam with PTFE

Effect of dwelling time on cell morphology (perpendicular to mold-opening),

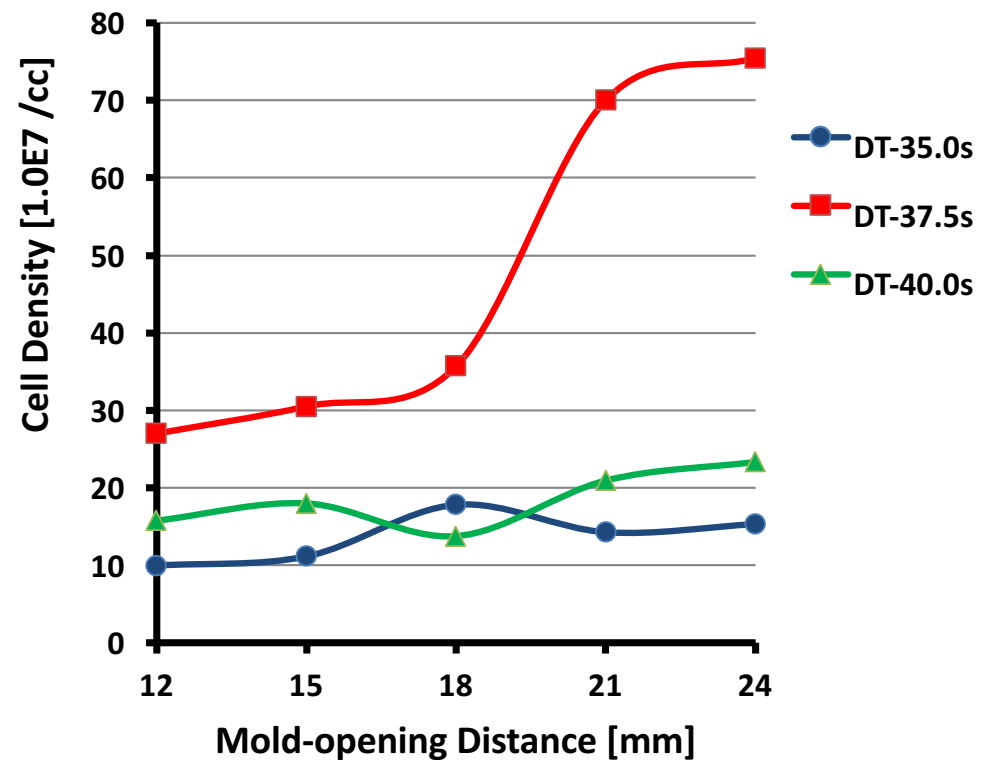
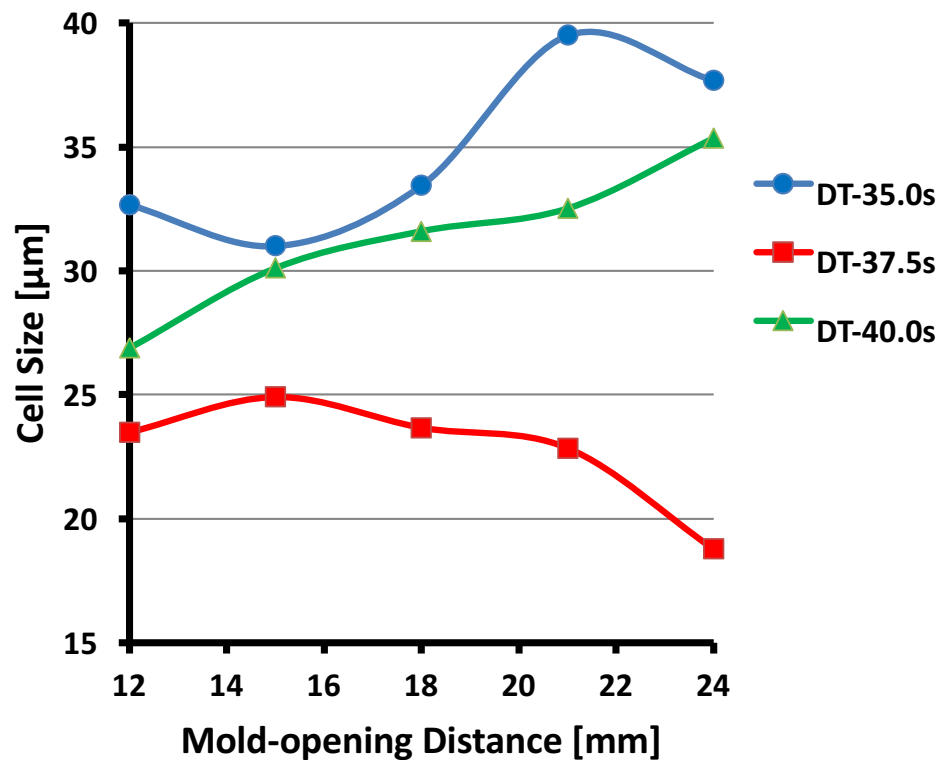


- PTFE improved the cell morphology significantly
 - Cell density: 3-orders of magnitude increased
 - Cell size: 1-order of magnitude decreased ($\sim 600\mu\text{m} \rightarrow 50\mu\text{m}$)

Results and discussion

■ Cell structure of foam with PTFE

□ Effect of Mold-opening distance (expansion ratio) on cell morphology

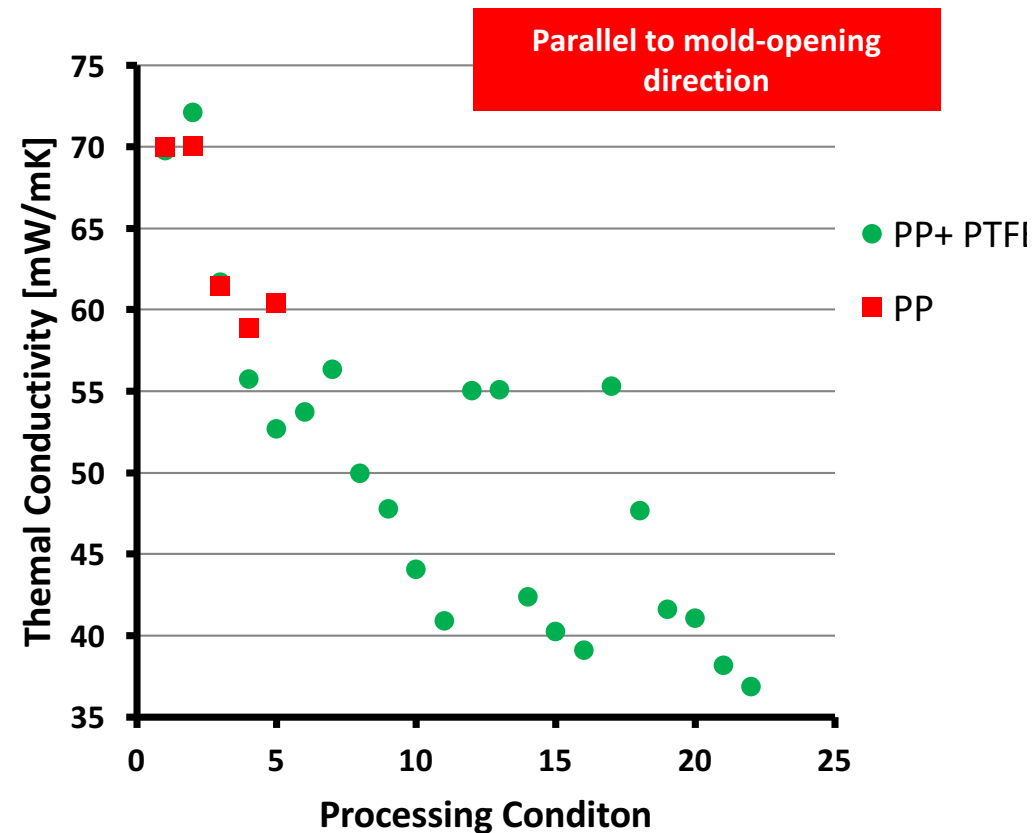
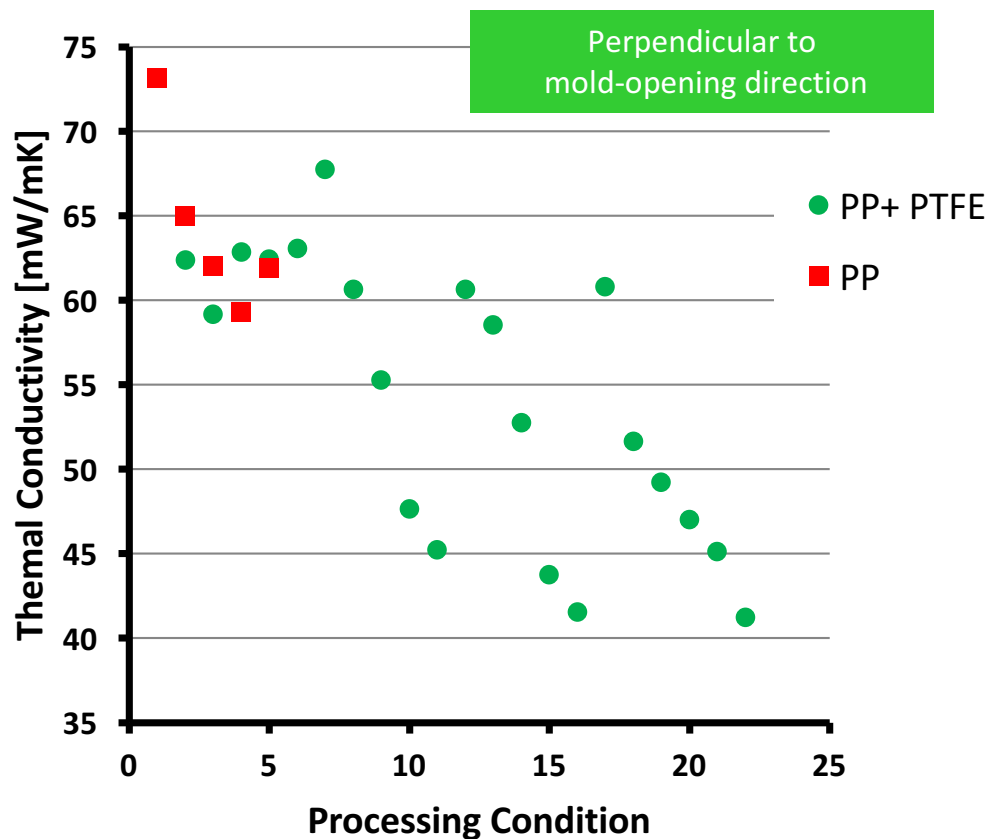


- There was little effect of the mold-opening distance on the cell size and cell density of PP/PTFE foams

Results and discussion

■ Thermal insulation properties

□ Effect of PTFE on thermal conductivity

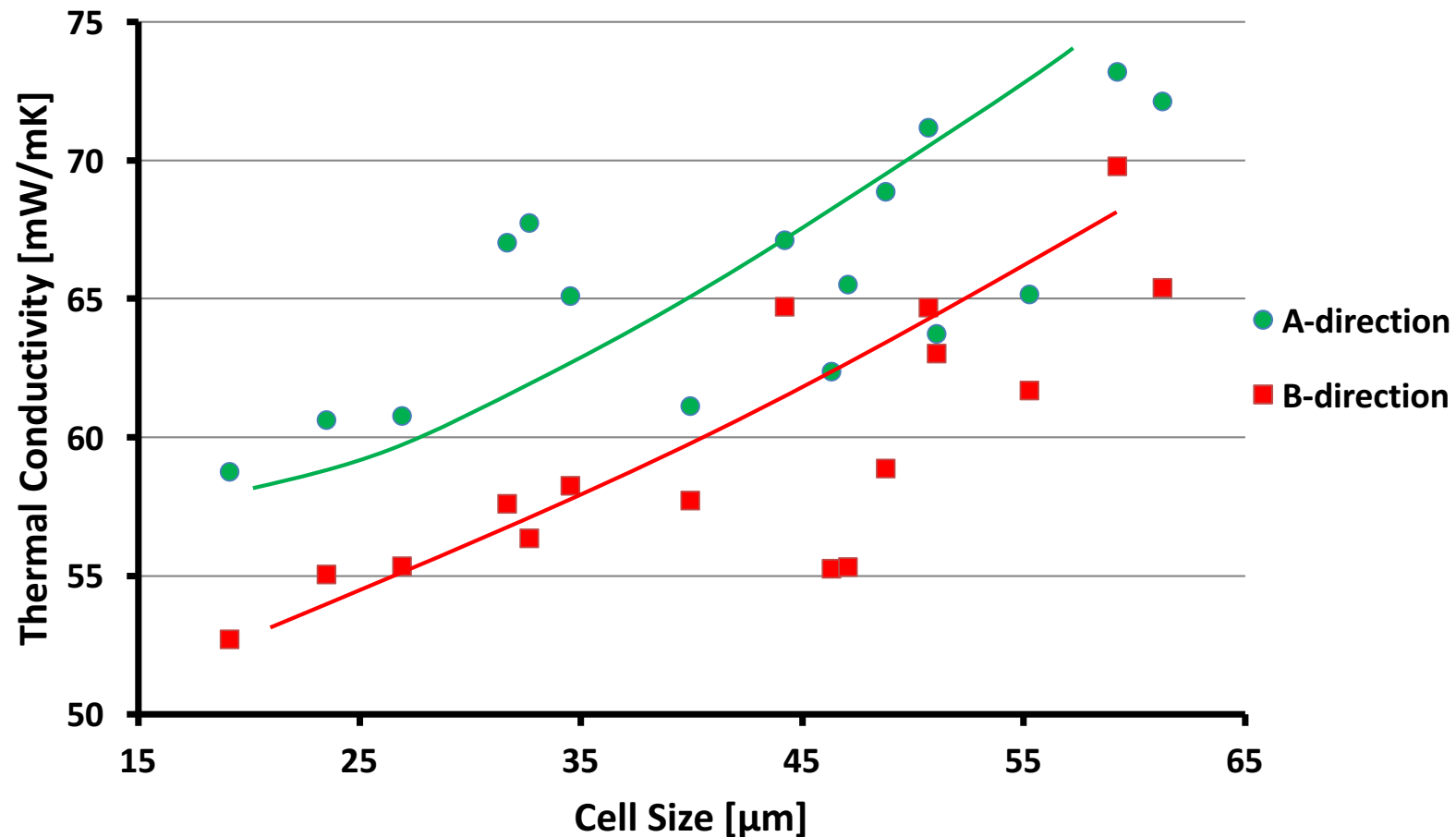


● PTFE enhanced the thermal insulation significantly!

Results and discussion

■ Thermal insulation properties

□ Effect of cell size on thermal conductivity

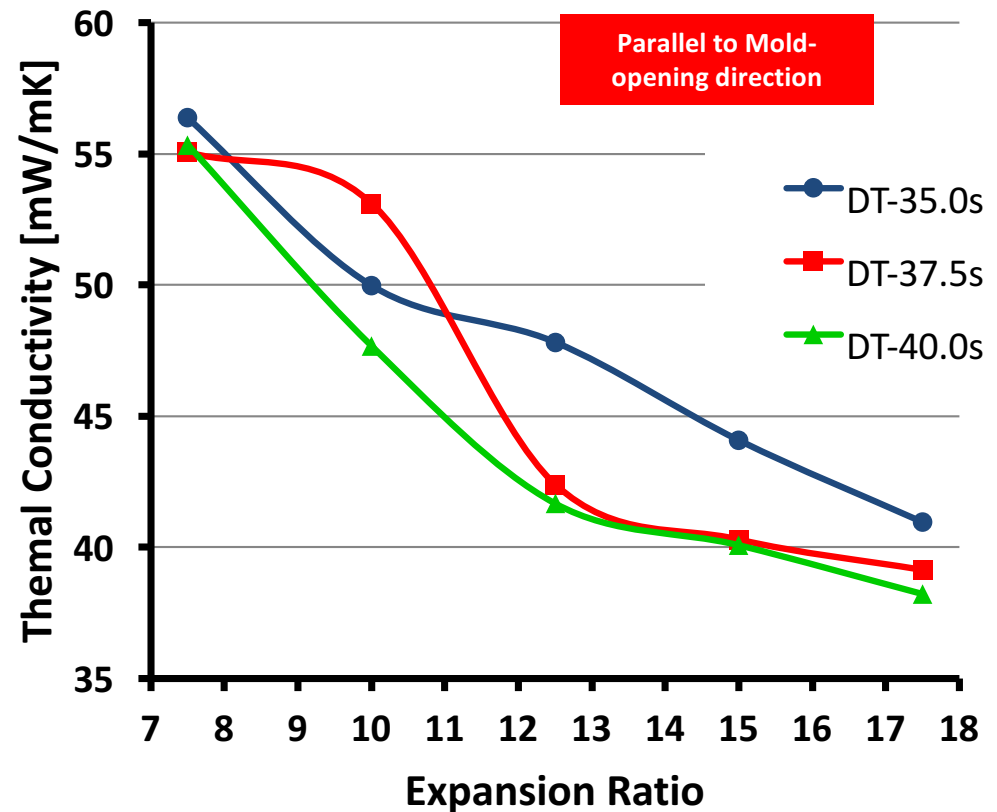
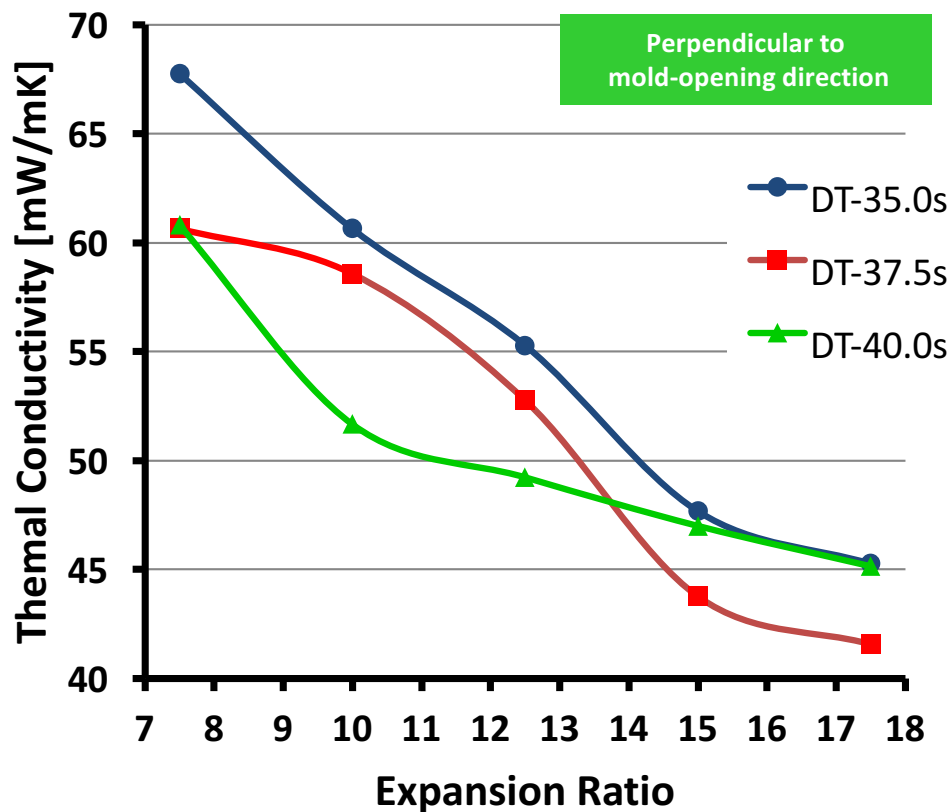


- Thermal conductivity is increased as the expansion ratio increase

Results and discussion

■ Thermal insulation properties

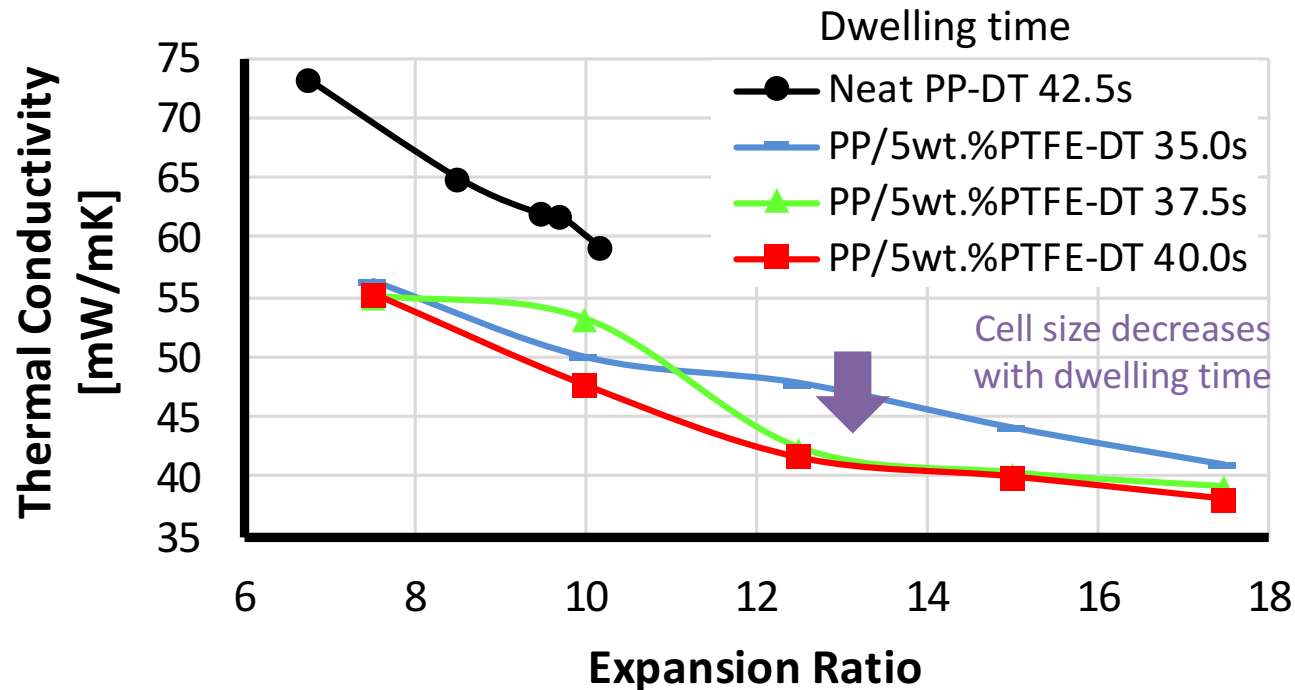
□ Effect of expansion ratio (Mold-opening distance) on thermal conductivity



- Thermal conductivity is decreased as the expansion ratio increase

Results and discussion

■ Thermal insulation properties



- Presence of fibrillated PTFE enables FIM PP parts to attain higher quality foam structures (more uniform, higher expansion, much smaller cell sizes)
 - FIM PP/PTFE parts possess better thermal insulation properties

Summary

- Effect of PTFE on rheological properties
 - Increased G' , G'' , and η^* at low frequency range
 - Improved the strain hardening behavior
 - Increased crystallization temperature and enhanced Heterogeneous crystal nucleation
- Effect of PTFE on cellular structure
 - Decreased the cell size from $600\mu\text{m}$ to $20\mu\text{m}$
 - Increased the cell density from 10^4 cells/cm³ to 10^9 cells/cm³
- Effect of cell structure on thermal conductivity
 - Dramatically enhanced the thermal insulation, decreasing thermal conductivity from 70 mW/mk to 40 mW/mk