PO Conference, February 2019

Sustainable Nanofibril Technology for Polyolefines with Superior Properties and Foaming Abilility

Chul B. Park

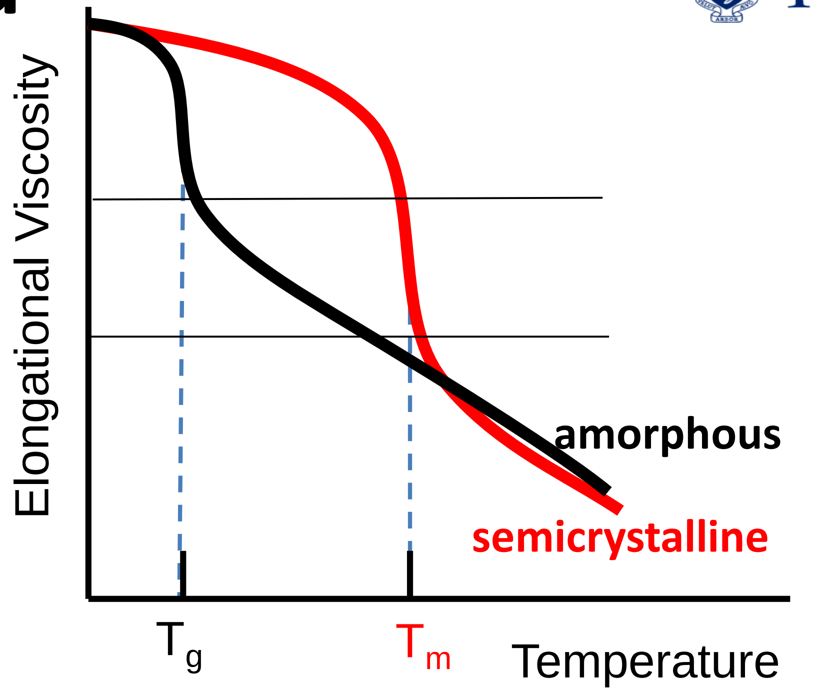
University of Toronto

Microcellular Plastics Manufacturing Laboratory

Background

Problem:

- **Semicrystalline polymers** exhibit **steep Elong. viscosity drop** around processing temperatures (~ T_m)
- **Narrow processing window** where **melt strength** is optimal for **foaming**

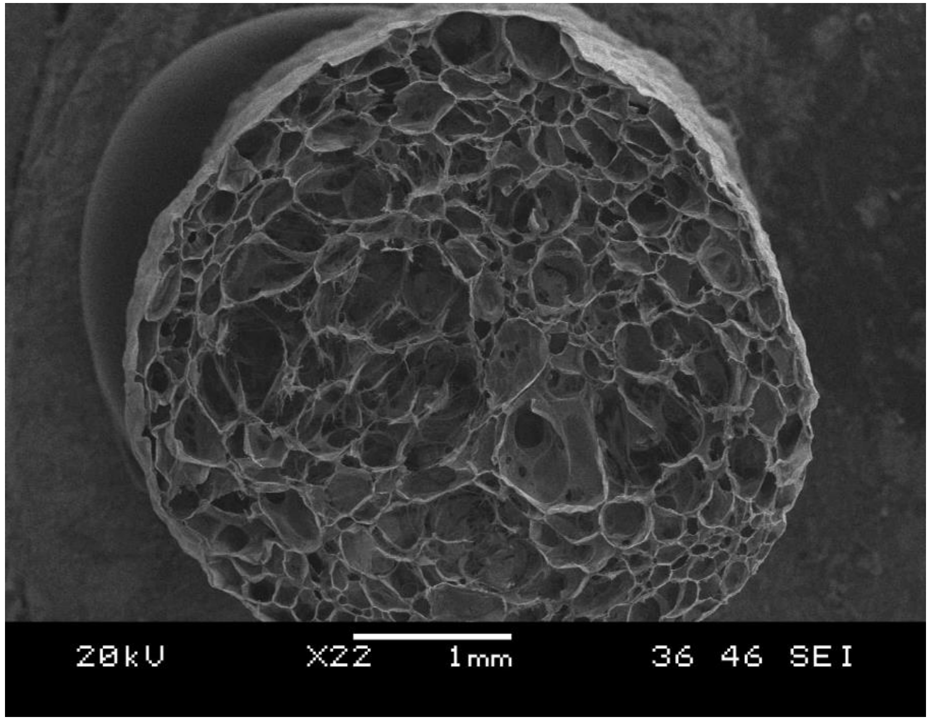


Current Solutions:

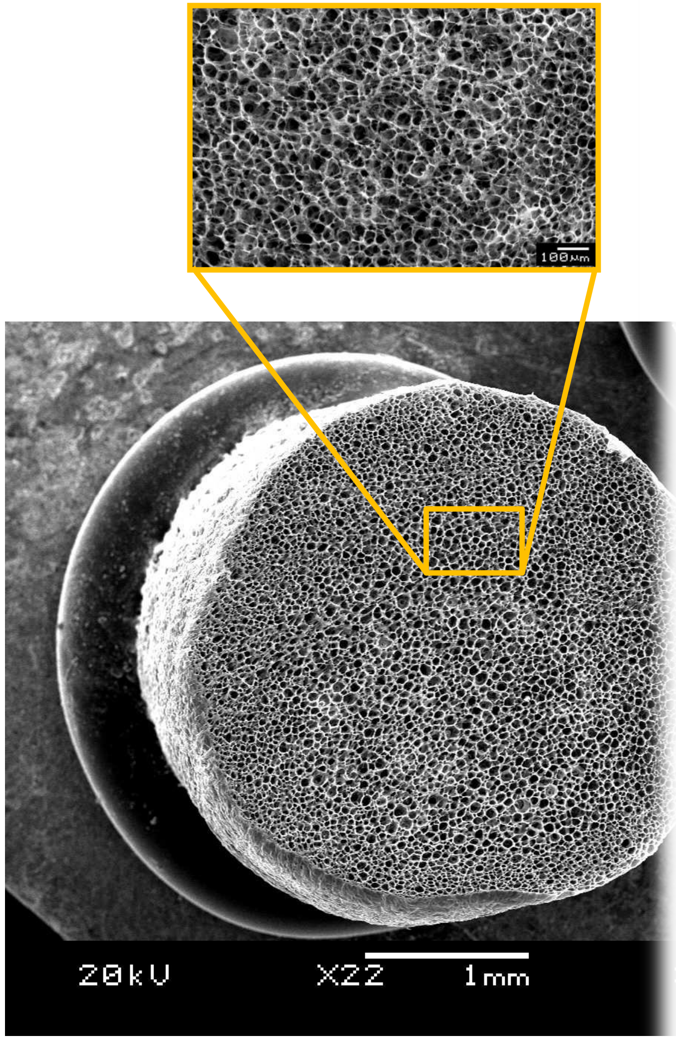
- **Long-chain branching:** Resin is at least **2x as expensive** as the linear counterpart for PP
- **Crosslinking:** Renders polymer **non-recyclable**
- **Nanofillers (e.g. nanoclay):** Modification of **surface chemistry** for uniform dispersion

Development of PTFE as a foam enhancing additive

Linear PP



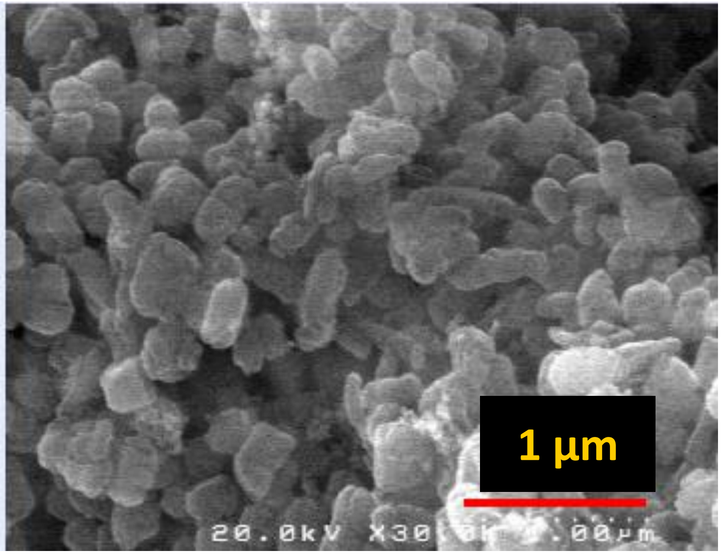
PTFE
3 wt%



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

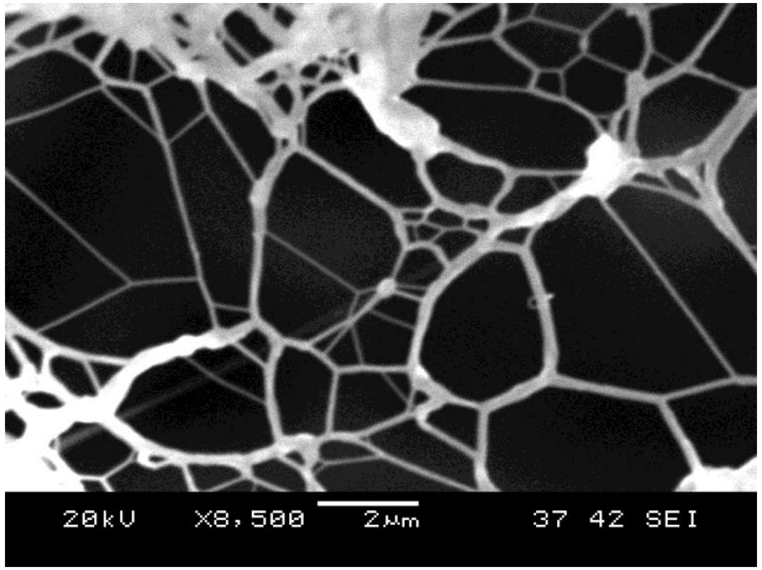
Original PTFE granules



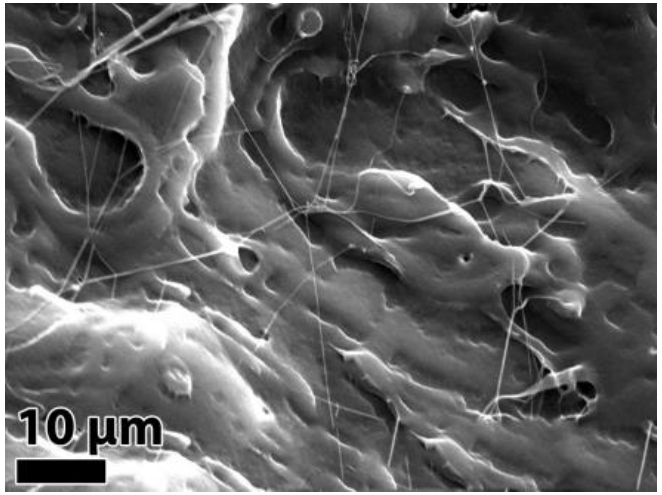
Spherical

Twin-screw extrusion of PTFE with PP

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



Fibrillar structure

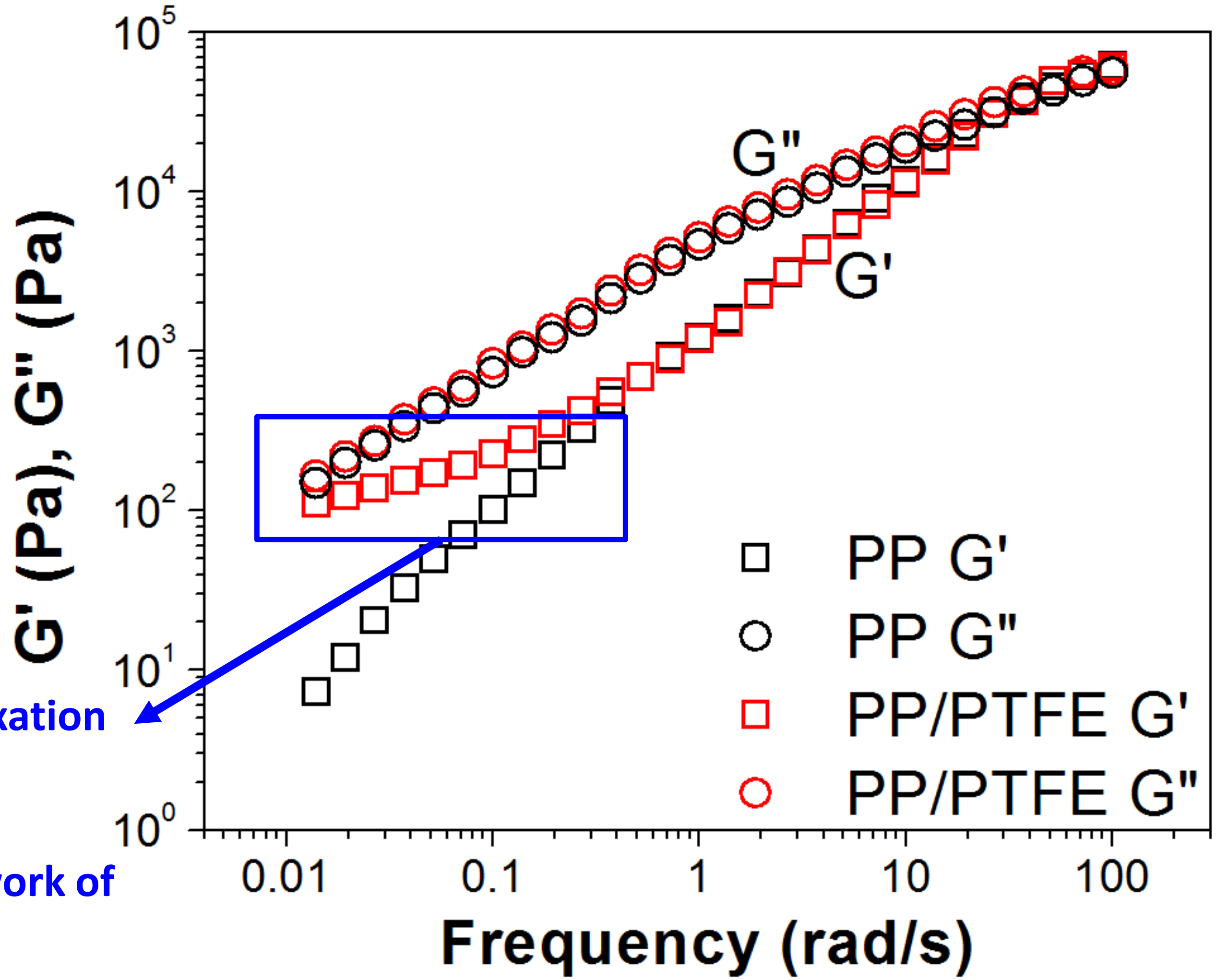


- PTFE readily undergoes **plastic deformation**
- PTFE exhibits high **ultimate strain**
- Entangled fibrils enhance **melt strength** of matrix

A. Rizvi, C.B. Park, M. Yamaguchi, JP2013-514463, 2013, & WO2013137301, 2013
A. Rizvi, A. Tabatabaei, R. Barzegari, H. Mahmood, C.B. Park, *Polymer,* 2013, 54, 4645-4652

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

UNIVERSITY OF TORONTO



Long-time relaxation

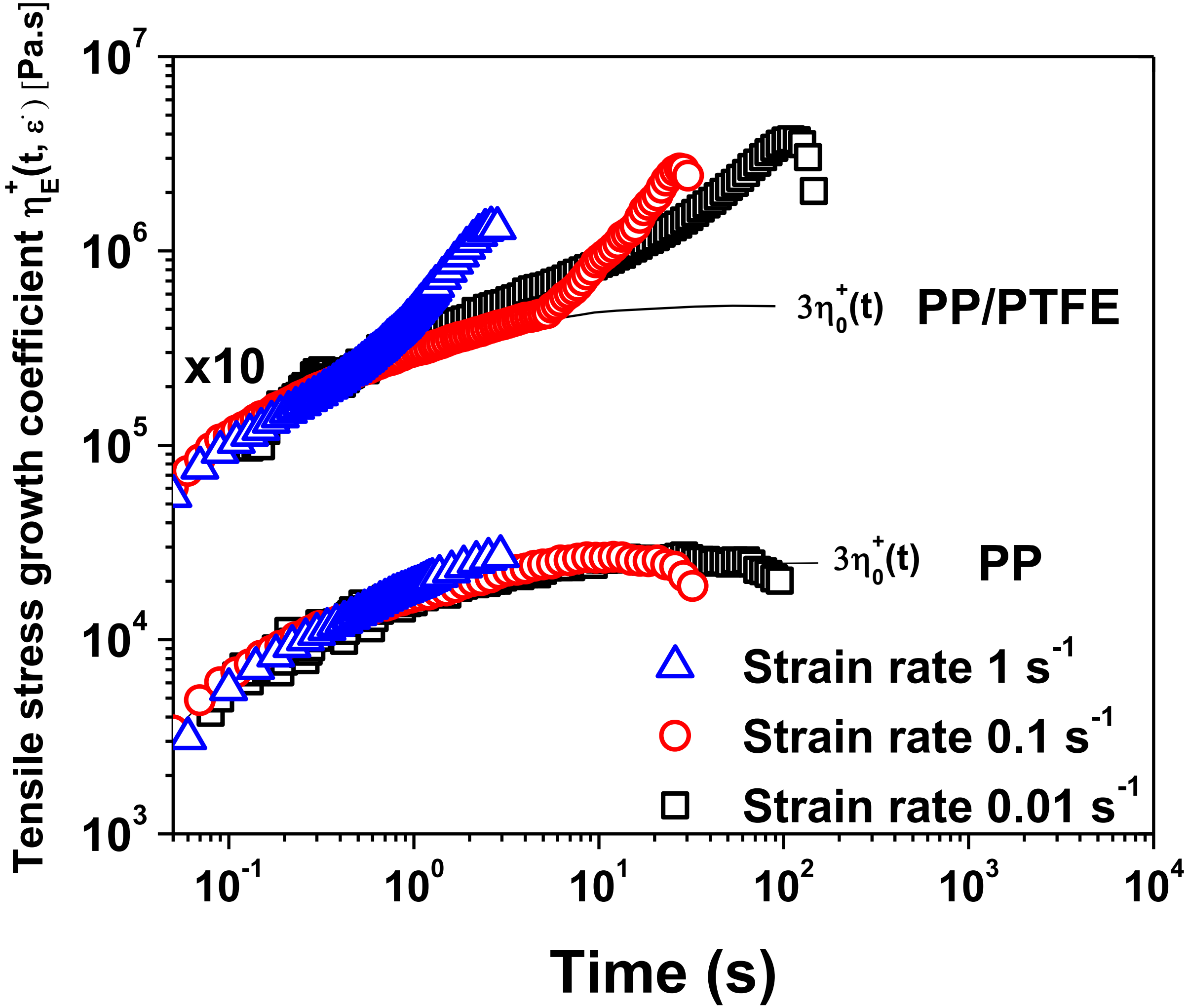
⬇

Entangled network of fibers

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

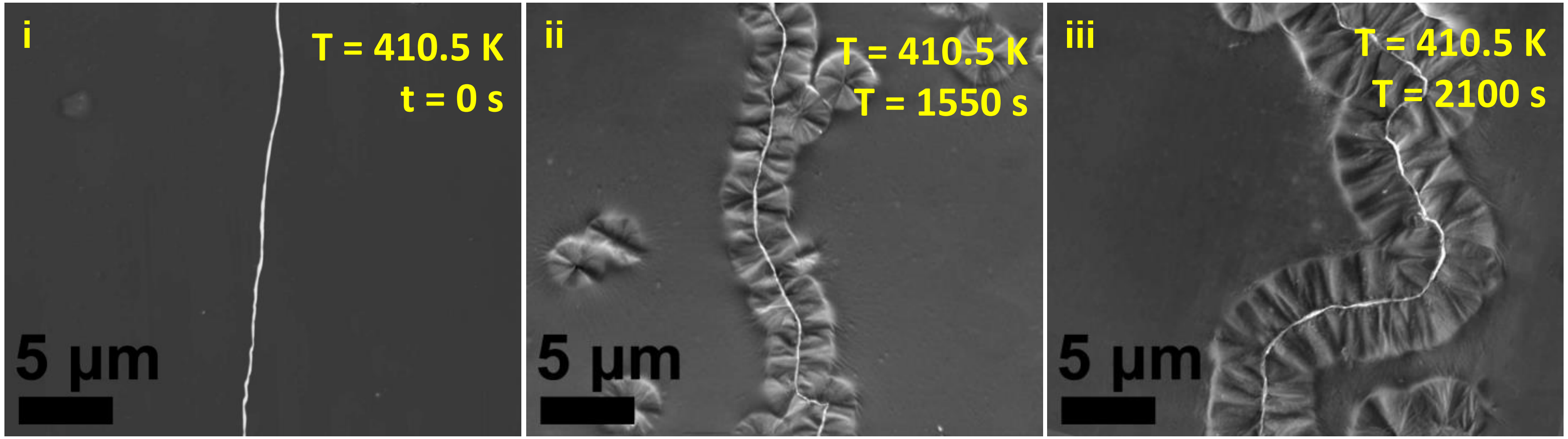
Strain-induced hardening in uniaxial elongational flow (PTFE 3 wt%)

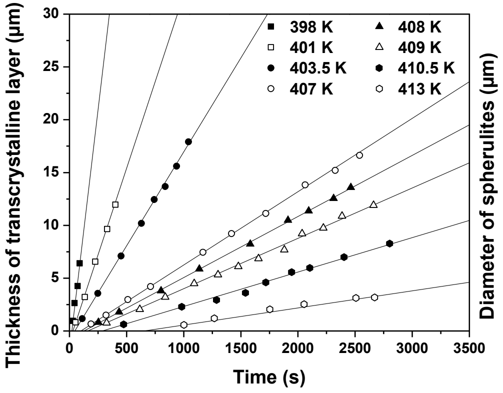


A. Rizvi, C.B. Park, M. Yamaguchi, **JP2013-514463**, 2013, and **WO2013137301**, 2013

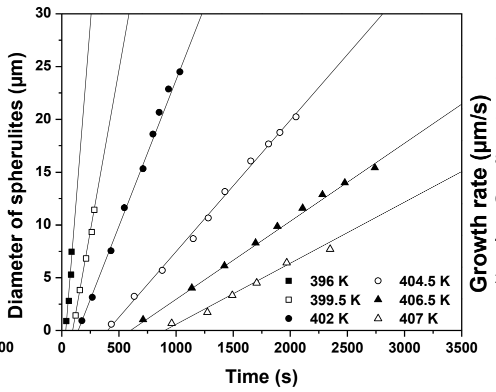
A. Rizvi, A. Tabatabaei, R. Barzegari, H. Mahmood, C.B. Park, *Polymer,* **2013**, 54, 4645-4652

Kinetics of Transcrystalline Growth

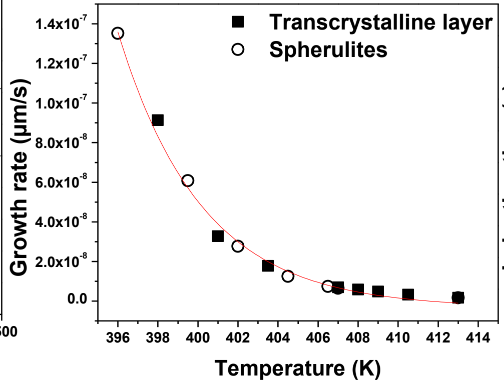




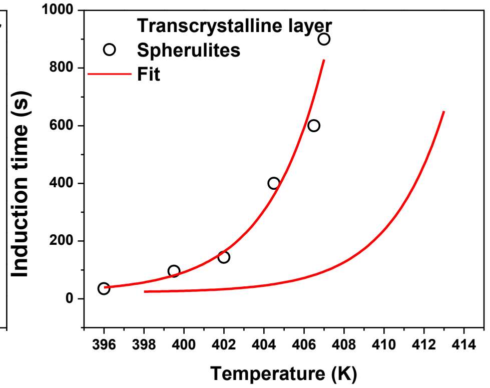
Thickness of TCL as a function of **time** for various $T_{crystallization}$



Diamater of spherulite as a function of **time** for various $T_{crystallization}$



Growth rate for
TCL≈ spherulites

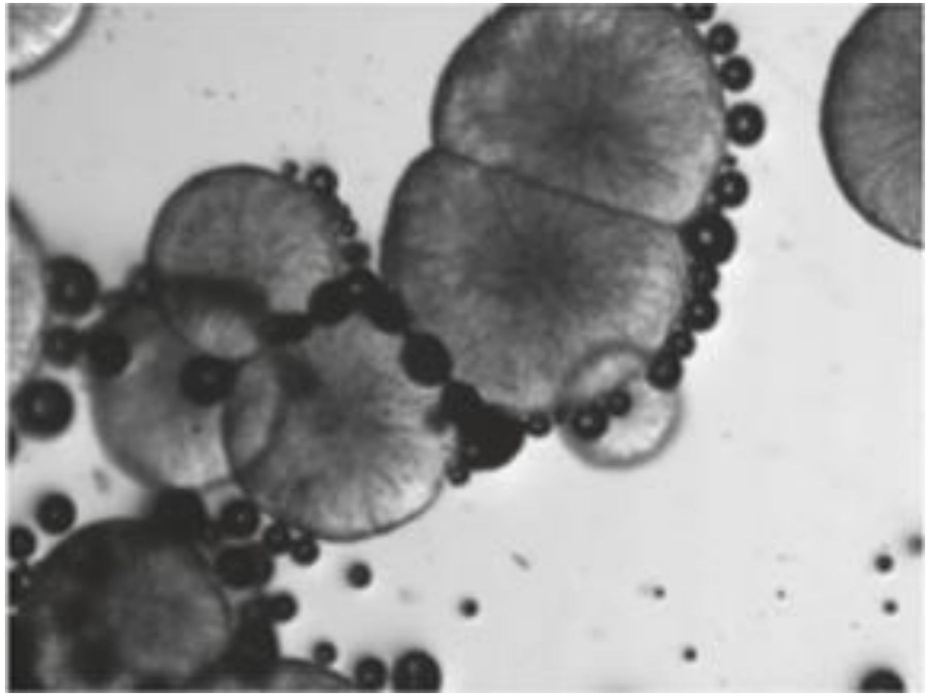


Induction time for
TCL < spherulites

A Rizvi, A Tabatabaei, P Vahedi, SH Mahmood, CB Park, *Polymer,* 135, 185-192, 2018

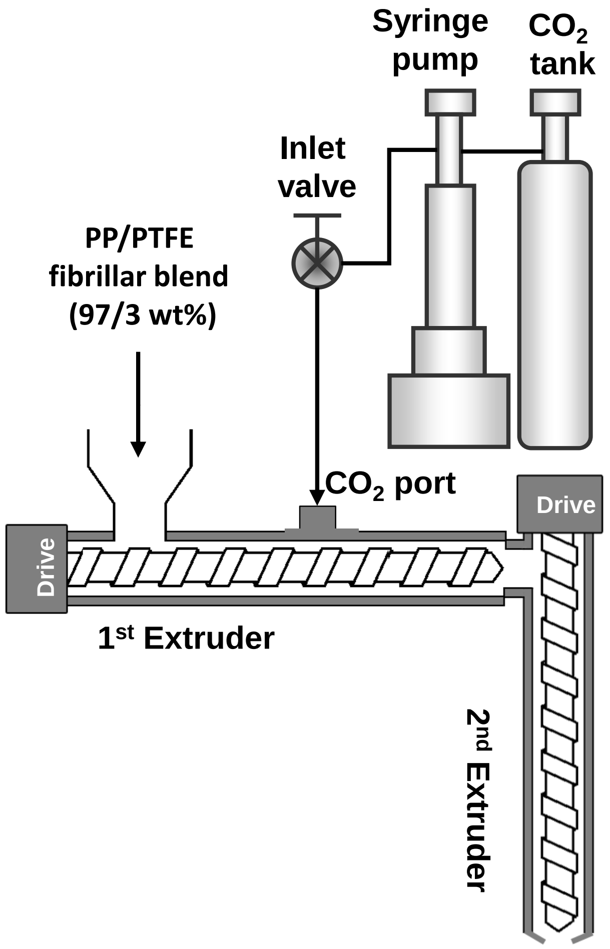
Effect of Crystals on Foaming

1. Gas is expelled from growing crystals into the boundary of crystal and amorphous region: supersaturation (Taki)
2. Crystallization causes shrinkage, and therefore, tensile stresses are applied on the polymer melt by the crystals. (Wong)
3. The rigid body motion of crystals generates local tensile stresses generated around the polymer crystals (Wong)



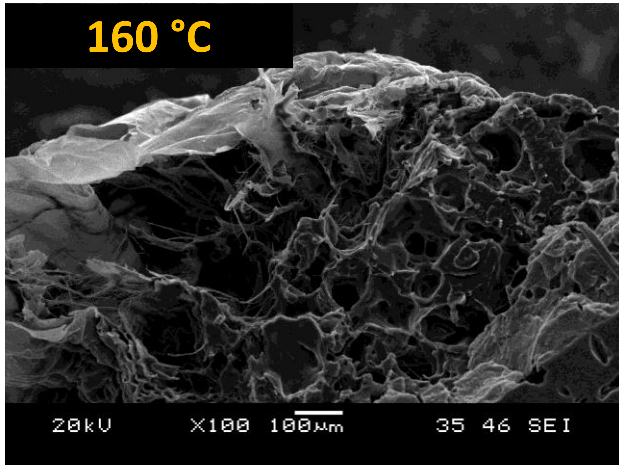
Taki K., Kitano D., and Ohshima M., *Ind. Eng. Chem. Res.*, 2011. 50(6): p. 3247-3252
Wong A., Guo Y., and Park C.B., *J. Supercrit. Fluids.*, 2013. 79: p. 142–151

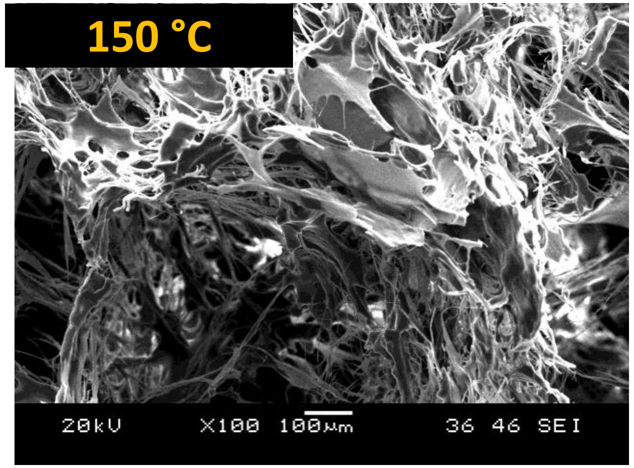
Experiment: Tandem foam extrusion system

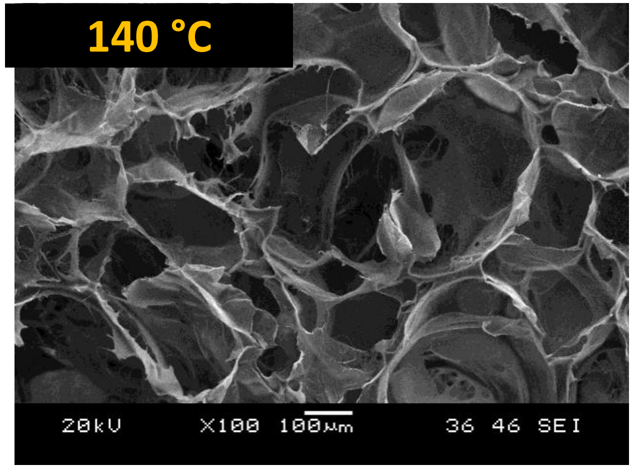


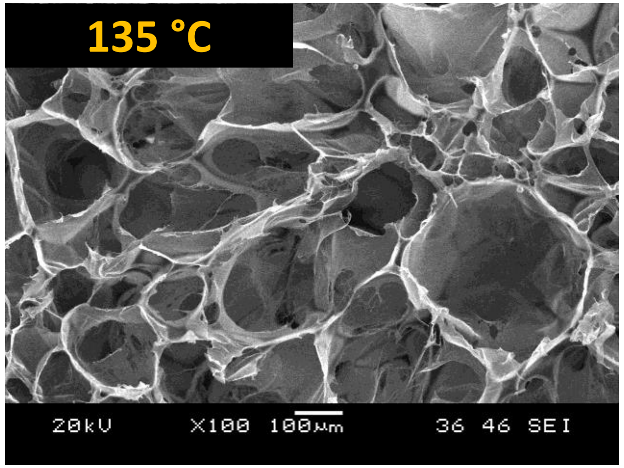
Material	1. Linear PP 2. PP/PTFE (97/3 wt%)
Die	L/D ~8.3 (L = 10 mm / ø = 1.2 mm)
CO_2 Content	10 wt%
Equipment	Small tandem extruder (0.75"/ 1.5")

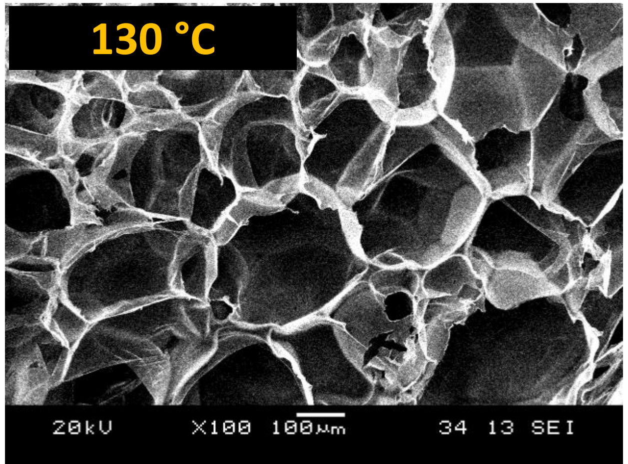
SEM Images of extruded PP foams



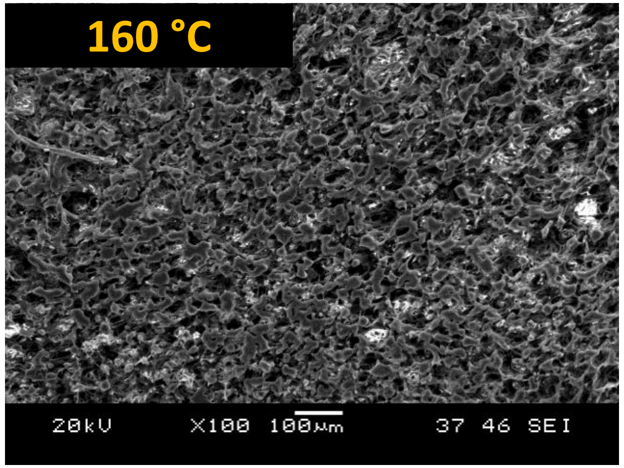


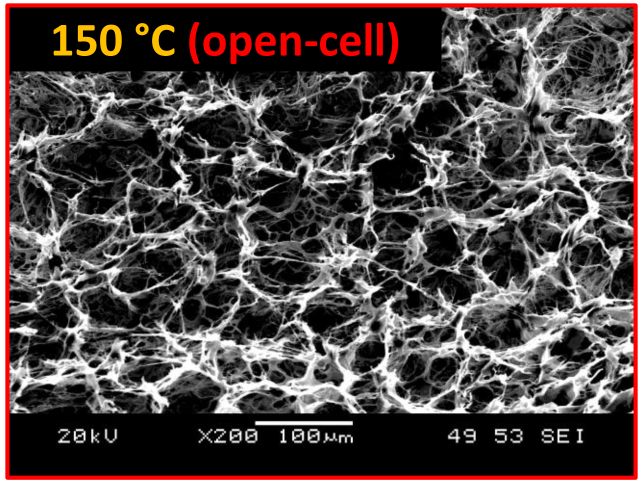


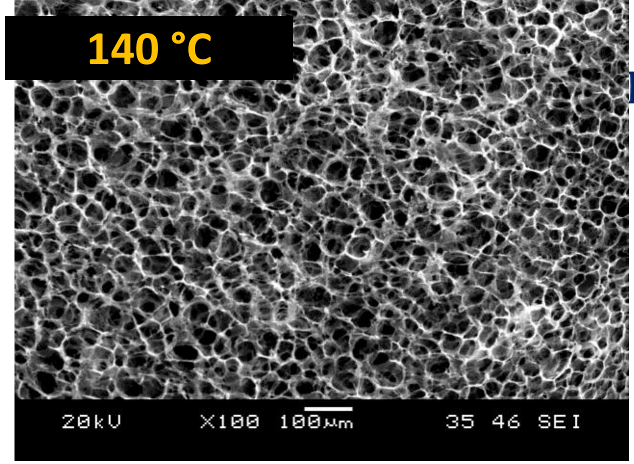




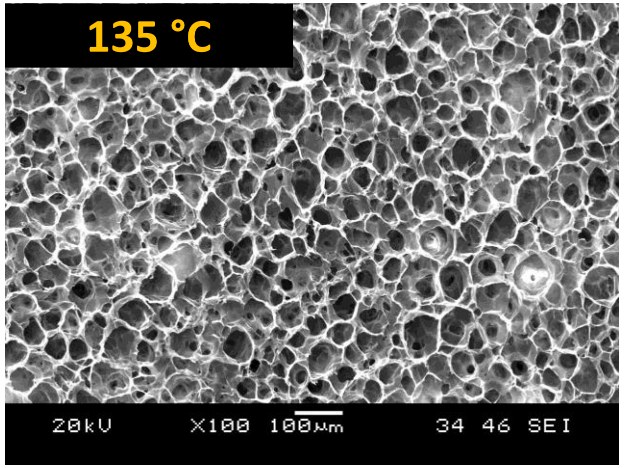
Die blockage occurred at 125°C

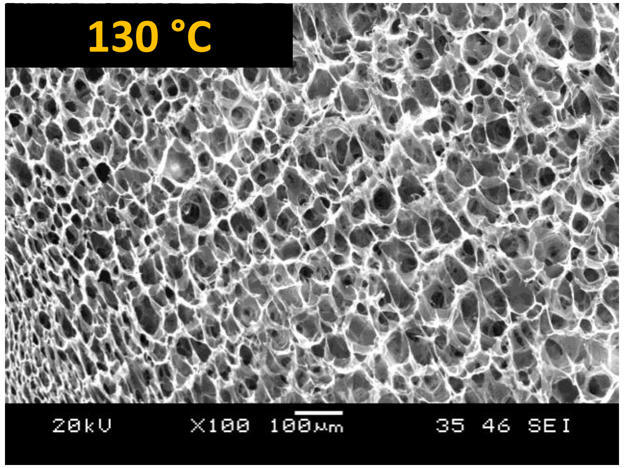


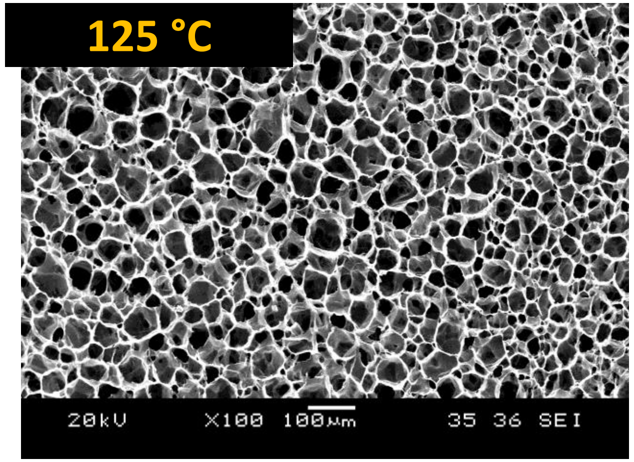


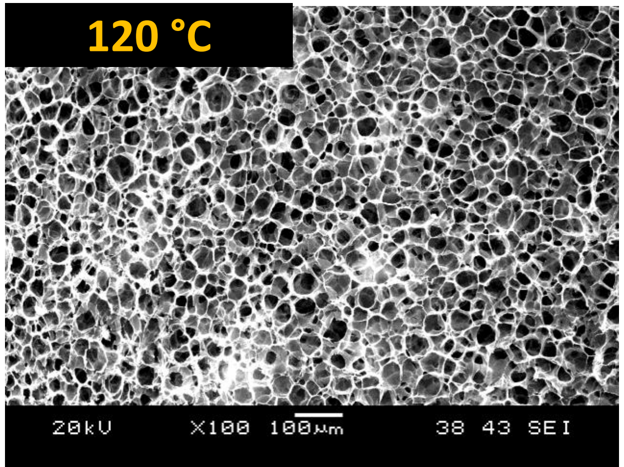


UNIVERSITY OF TORONTO



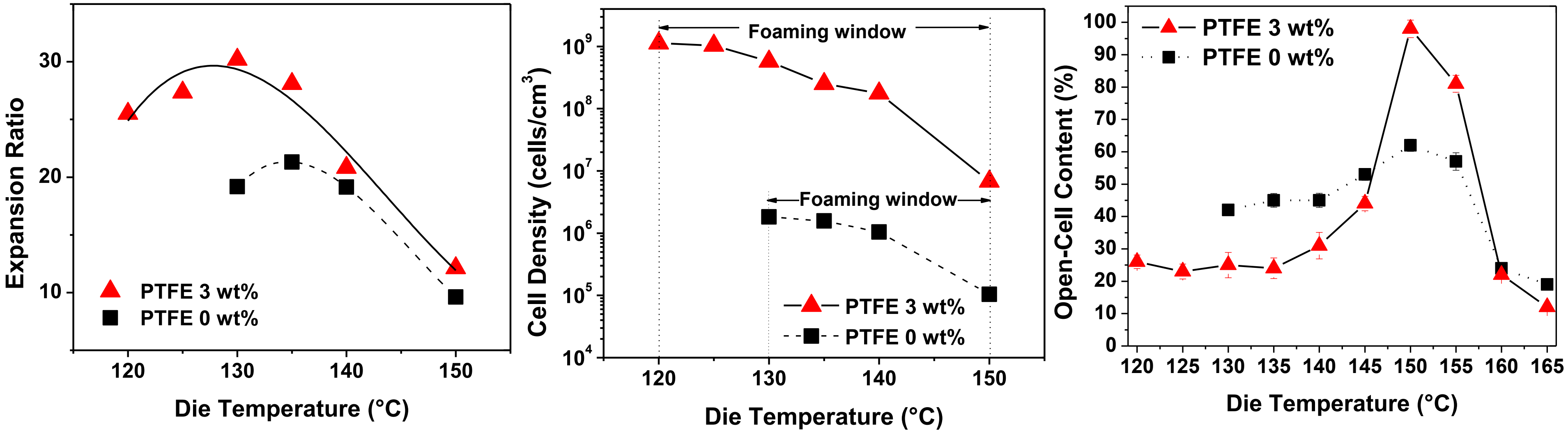






SEM Images of extruded PP/PTFE (97/3 wt%) foams

Foam characterization

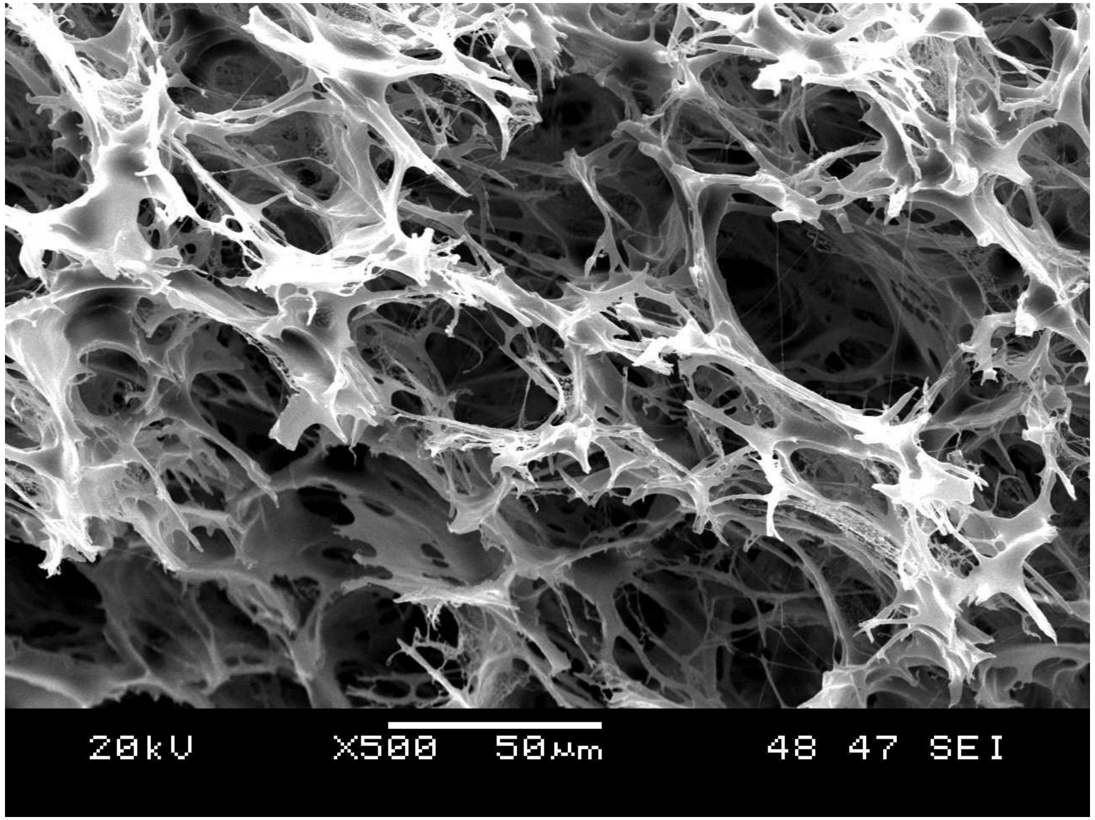


- **Expansion Ratio:** Up to **10-fold** increase
- **Cell Density:** Up to **2 orders of magnitude** increase
- **Open-cell content**: Up to **97.7%** at 150°C

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

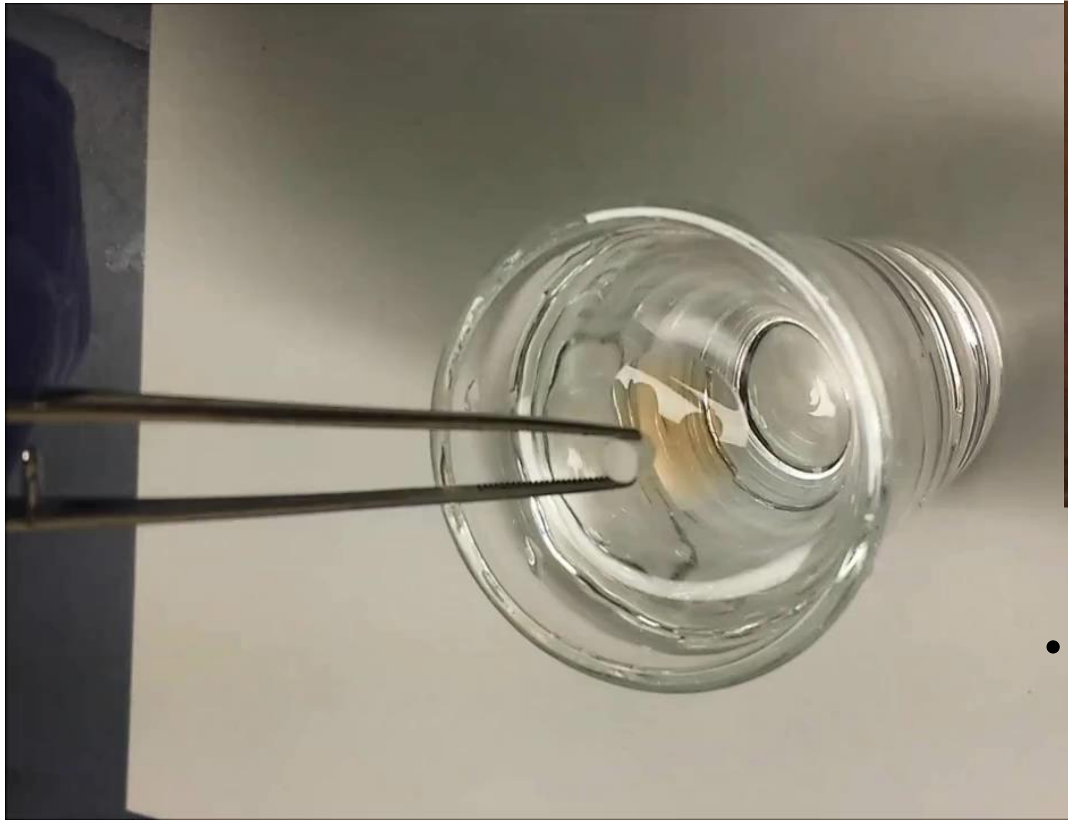
A. Rizvi, A. Tabatabaei, R. Barzegari, H. Mahmood, C.B. Park, *Polymer,* **2013**, 54, 4645-4652

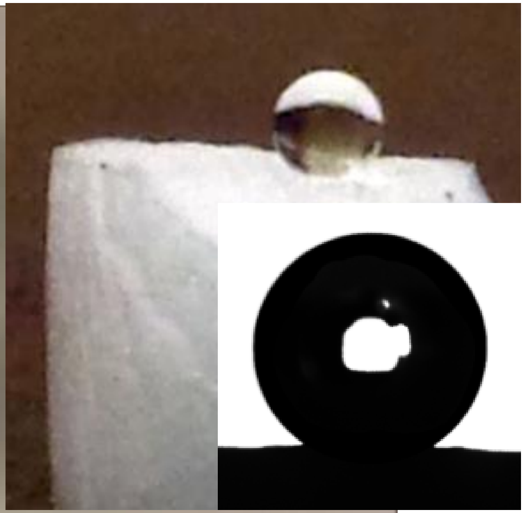
Open-cell foams at 150°C



A. Rizvi, R.K.M. Chu, J.H. Lee, C.B. Park, *ACS Appl. Mater. Interfaces*, 2014, *6*, 21131-21140

Video of gasoline uptake by open-cell foam





- Foam subjected to **120°C** for 1 h.

Superhydrophobicity maintained.

A. Rizvi, R. K.M. Chu, J.H. Lee, C.B. Park, *ACS Appl. Mater. Interf.*, 2014, 6, 21131-21140

Problem:

- Chemically-modified PTFE is expensive!

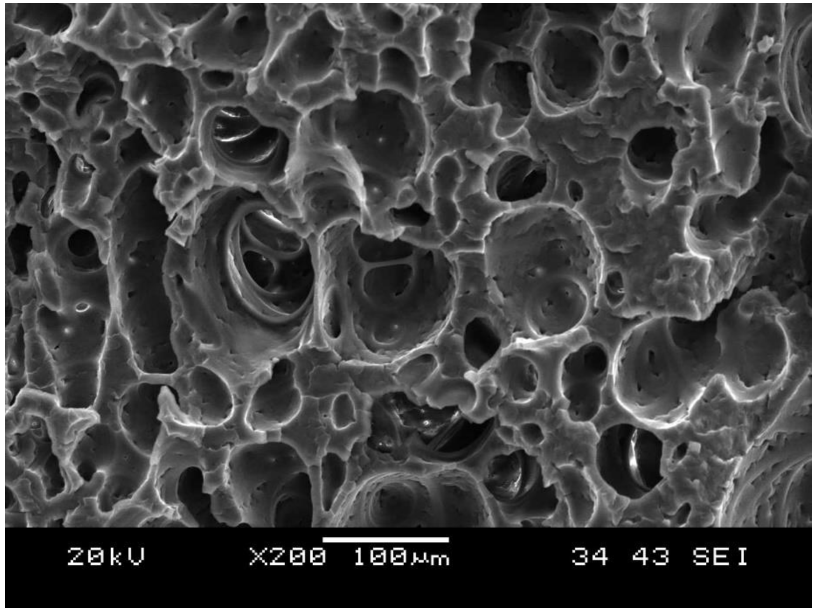
Solution:

- Find an inexpensive alternative to this PTFE.

UNIVERSITY OF TORONTO

Development of polymeric fibrils as foam enhancing additives: PP/PET Case Example

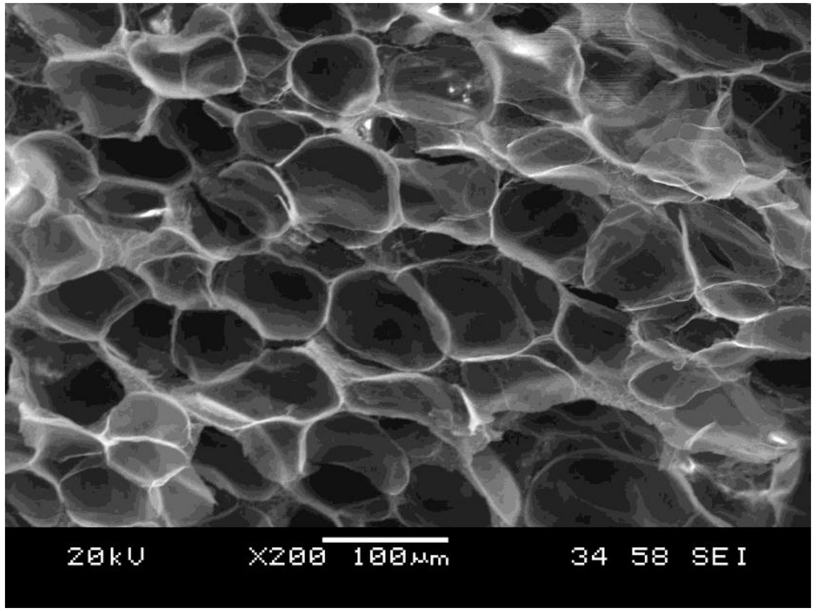
PP



0.1 wt%

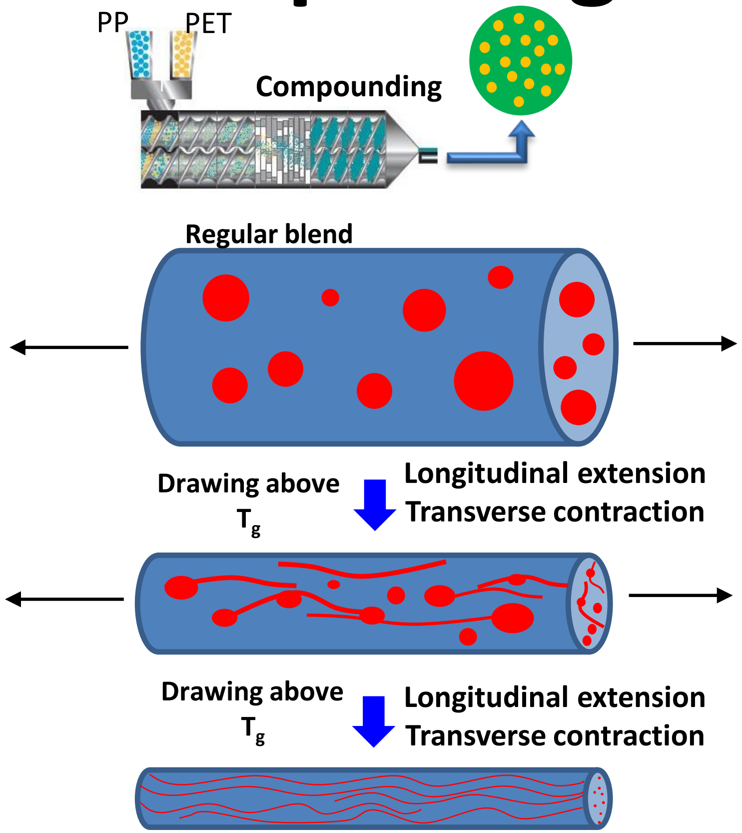
PET fibrils

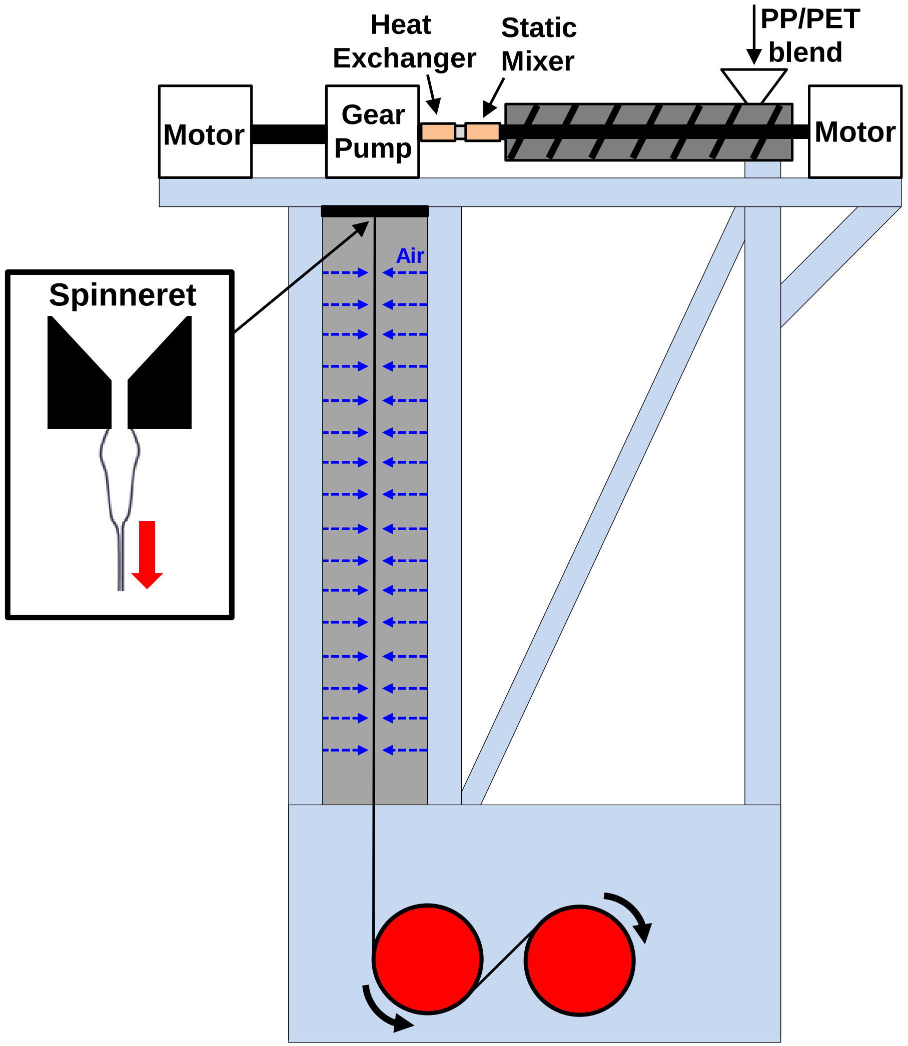
PP/fibrillated-PET



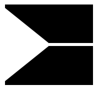
A. Rizvi, C. B. Park, B.D. Favis, Polymer, 68, 83-91, 2015

Mechanism of fibrillation during fiber spinning of blend (by decoupling!)





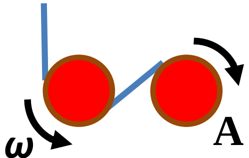
Extension occurs in **2 stages**:



1. **Die exit**

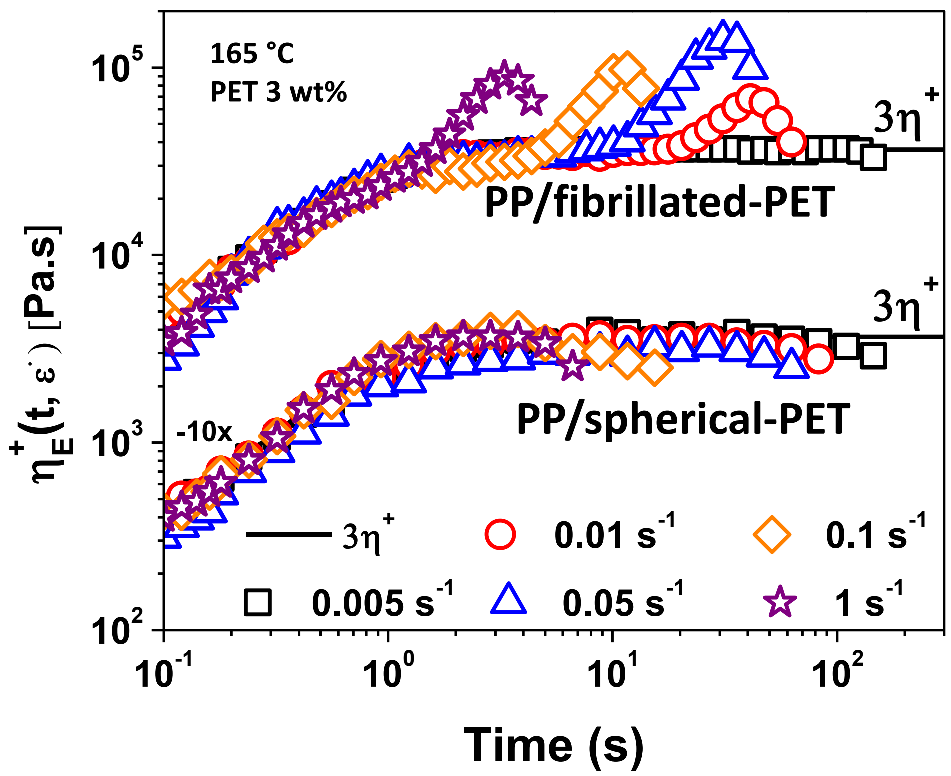
Contraction in transverse direction, extension in longitudinal direction

2. **Blowing & Cold drawing**



A Rizvi, ZKM Andalib, CB Park, *Polymer* ,110, 139-148, 2017

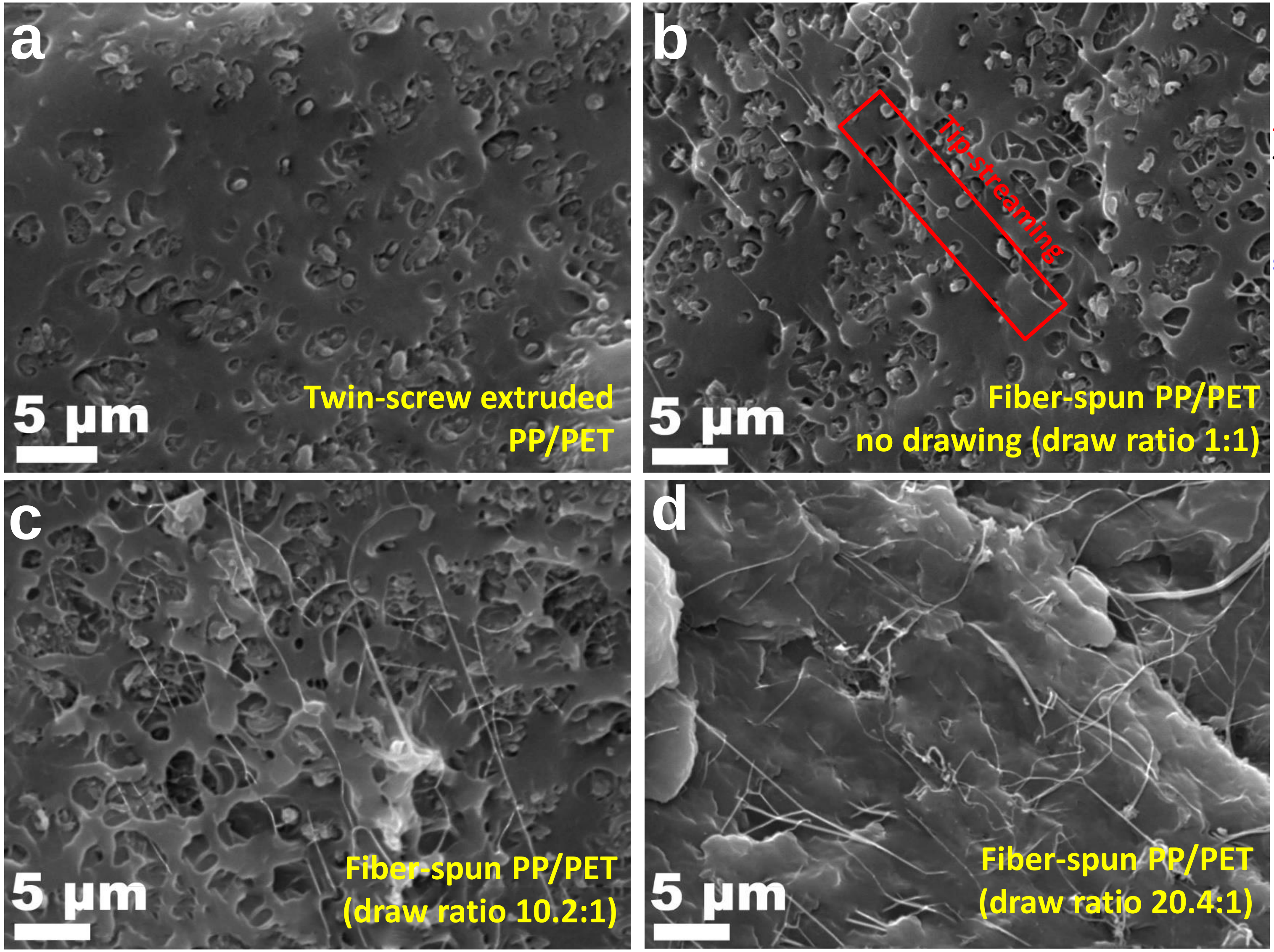
Small-scale: Uniaxial extensional flow behavior of PP/PET



Strain-induced hardening in uniaxial extensional flow observed at **strain rates ≥ 0.01 s^{-1}**

A. Rizvi, C. B. Park, B.D. Favis, Polymer, 68, 83-91, 2015

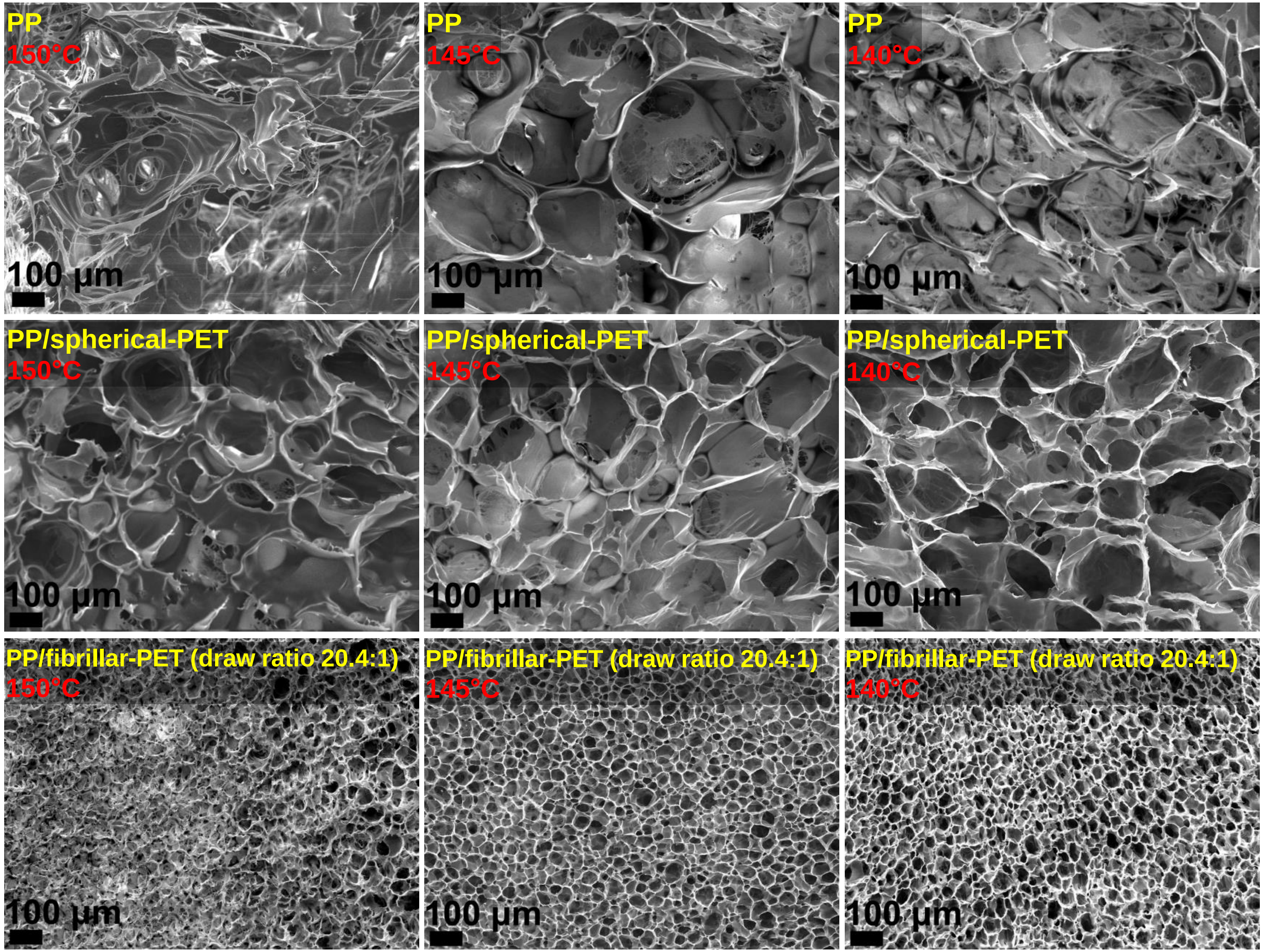
Effect of draw ratio on morphology of PP/PET (95/5 wt%)



tip streaming:
Transition morphology between **spherical** and completely **fibrillated structure**

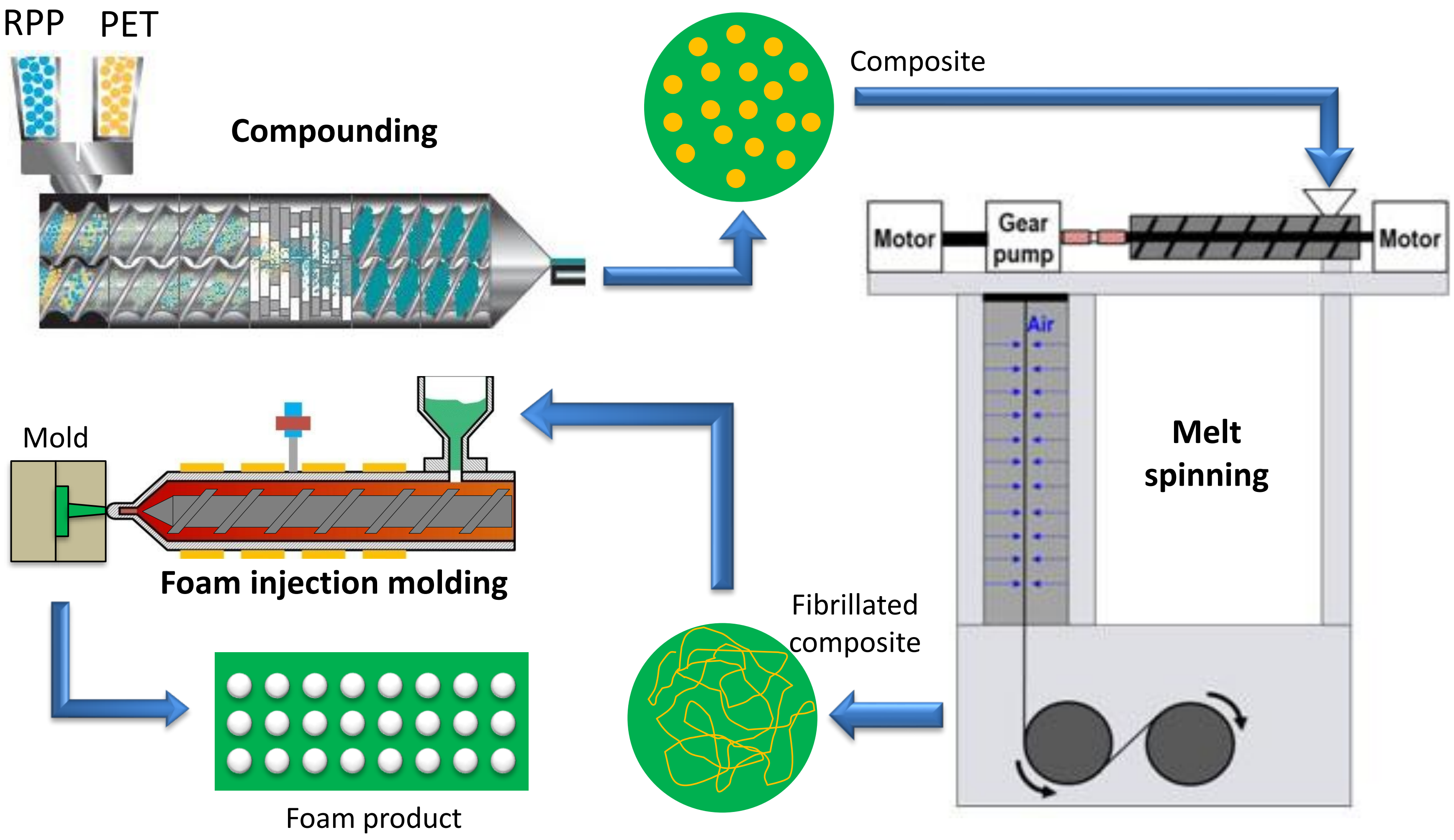
Length~38 μm
Diamater~210 nm
Aspect Ratio~ 181

Foam morphology (PET 5 wt%)



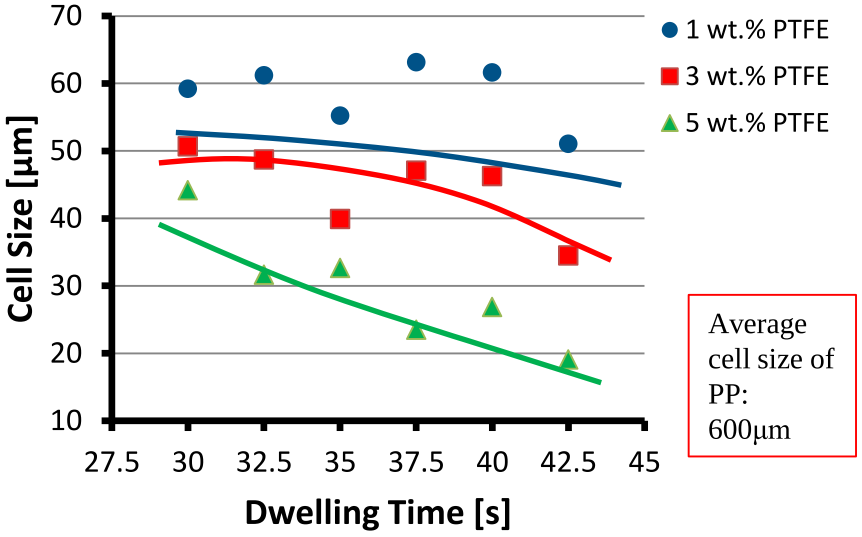
A Rizvi, ZKM Andalib, CB Park, *Polymer,* 110, 139-148, 2017

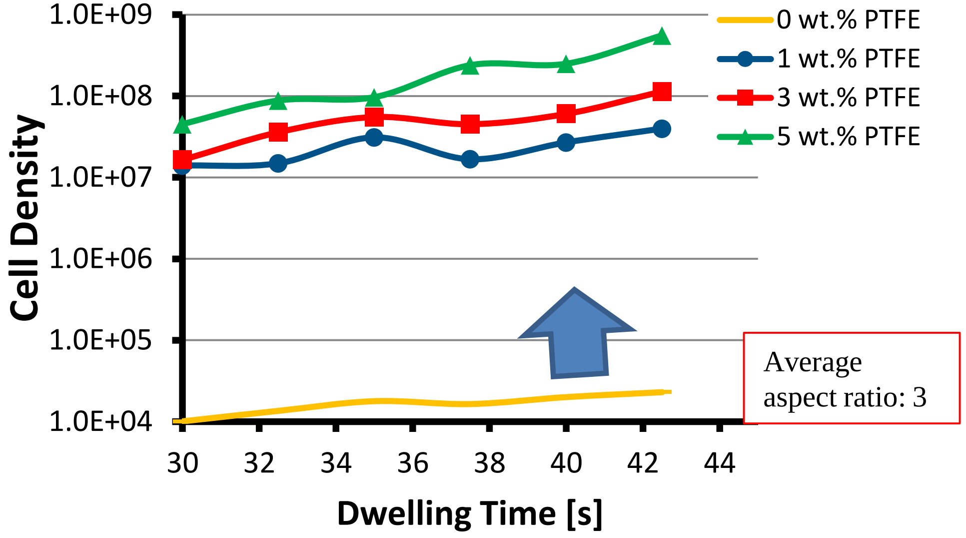
Foam Injection Molding of PP/PTFE Nano-Fibril and PP/PET Nano-Fibril



PP Foam Structure with PTFE Nano-Fibril

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



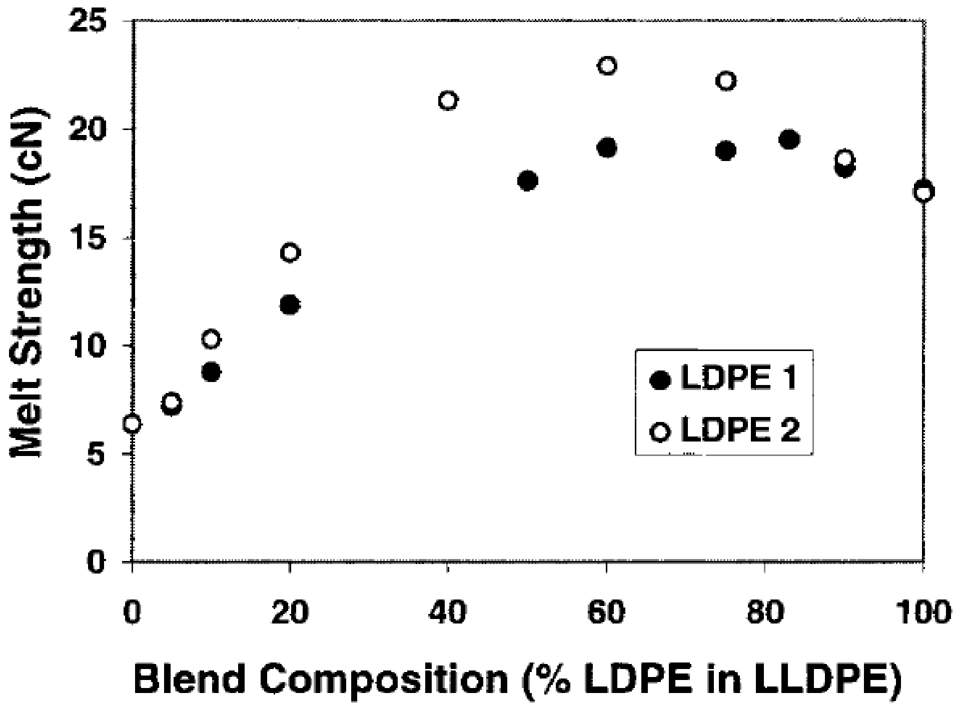


- PTFE improves the cell morphology significantly
  - 3-order increase in cell density;
  - 1-order decrease (~500µm → 50µm) cell size

J Zhao, Q Zhao, C Wang, B Guo, CB Park, G Wang, *Mater Des*, 131, 1-11, 2017.

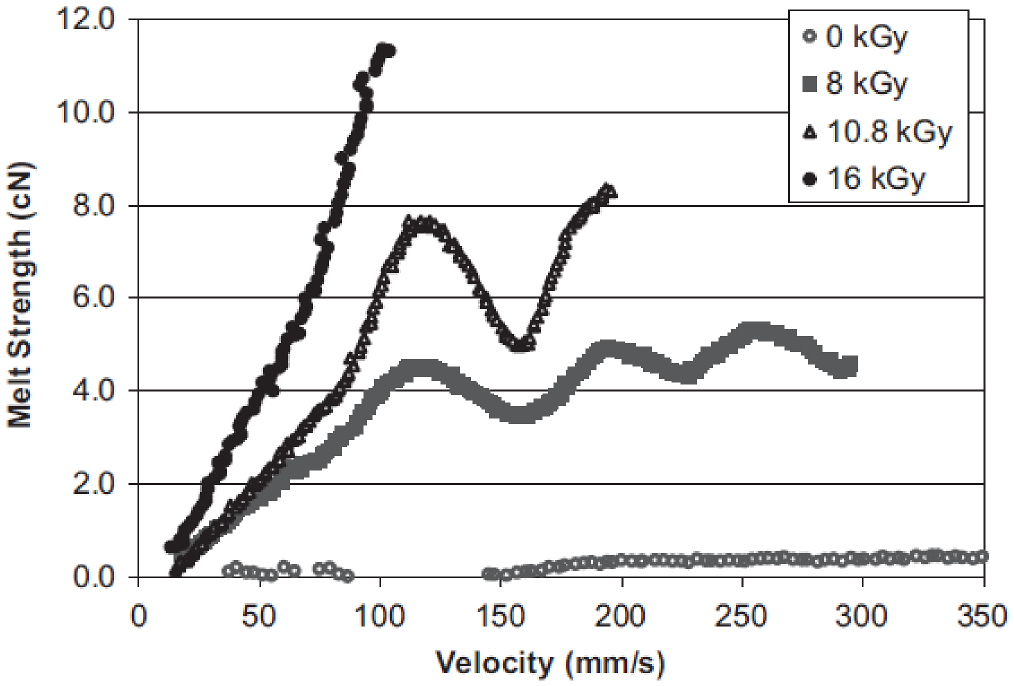
Conventional Melt Strength Enhancement

- Blending LDPE with LLDPE



Moderate efficiency

- Radiation-induced long chain branching



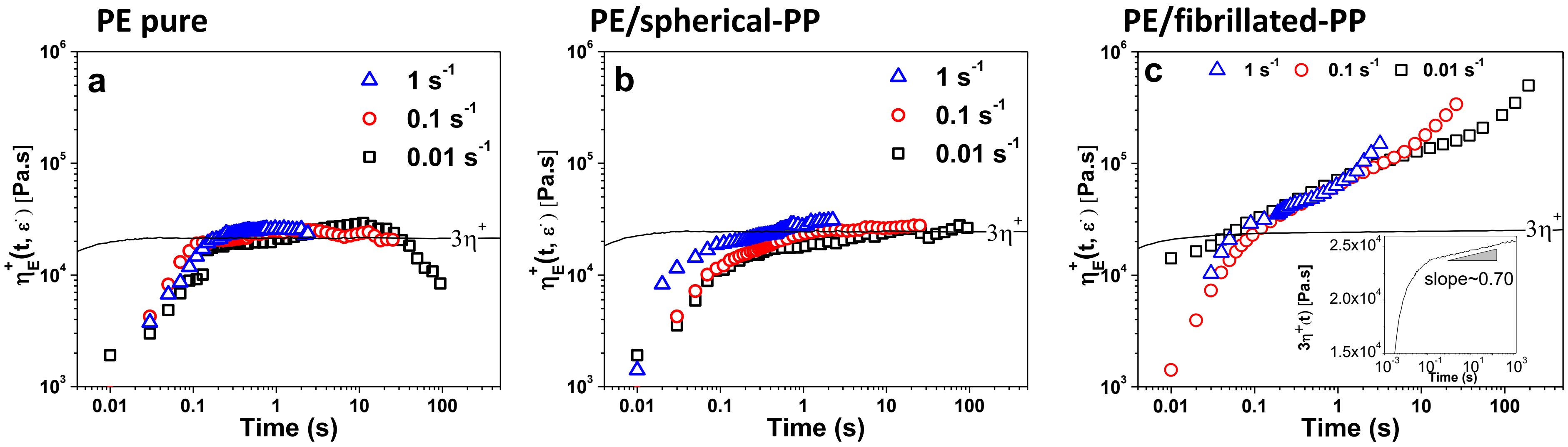
- Undesirable crosslinking;
- Decreasing the recyclability
- Degradation, gelation, oxidation
- Costly

Field et al, Polymer international, 48, 461–466 (1999); Cheng et al., Radiation Physics and chemistry, 79, 329-334 (2010).

Properties of PE/fibrillated-PP (95/5 wt%)

Strain hardening under uniaxial extensional flow

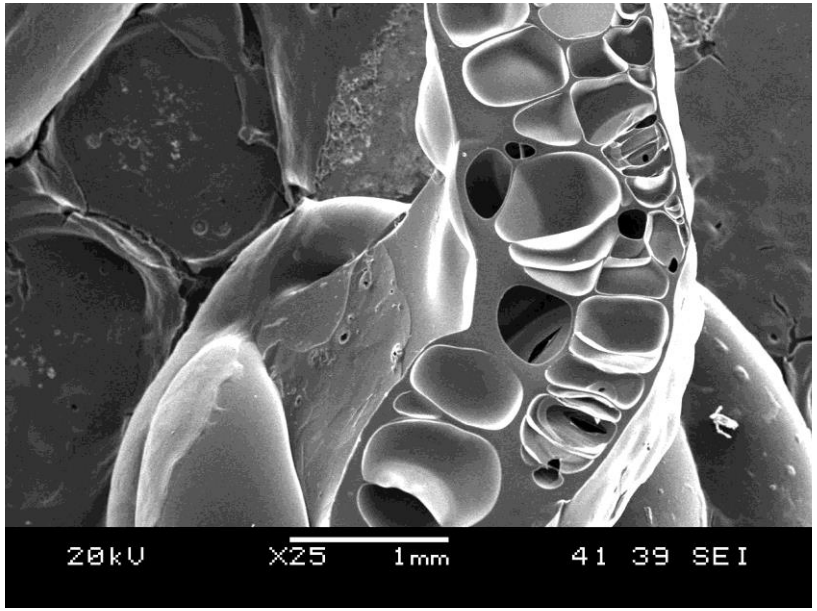
T= 130 °C



A. Rizvi and C. B. Park, *Polymer*, **2014**, *55*, 4199-4205

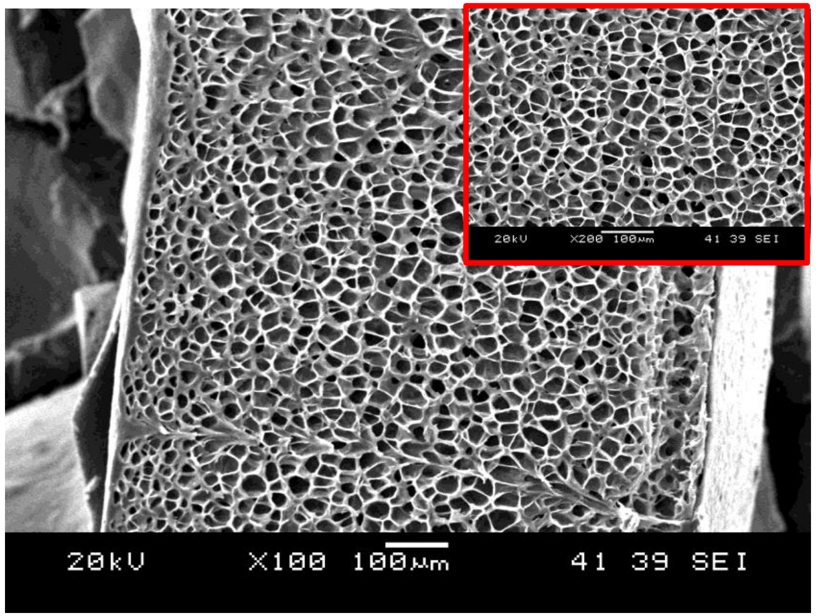
Development of polymeric fibrils as foam enhancing additives: mPE/PP Case Example

mPE



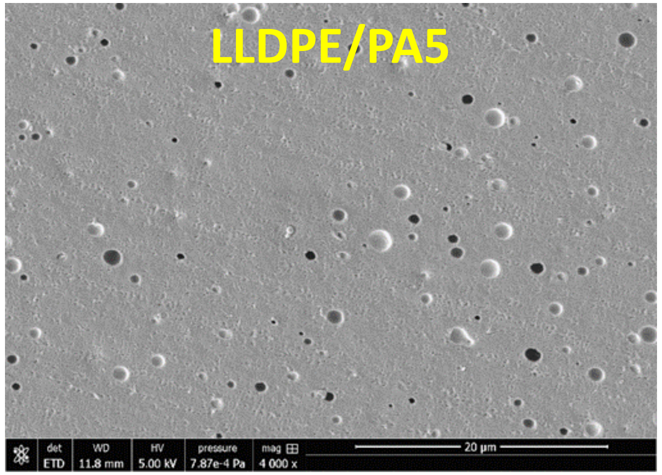
5 wt%
PP fibrils

mPE/fibrillated-PP

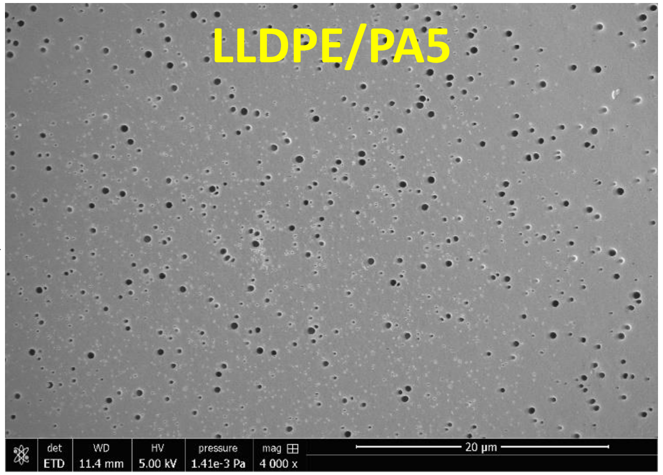


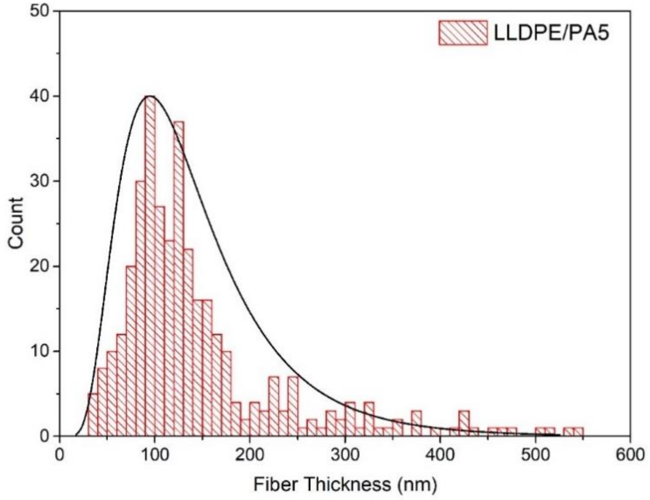
A. Rizvi and C. B. Park, *Polymer*, **2014**, *55*, 16, 4199-4205

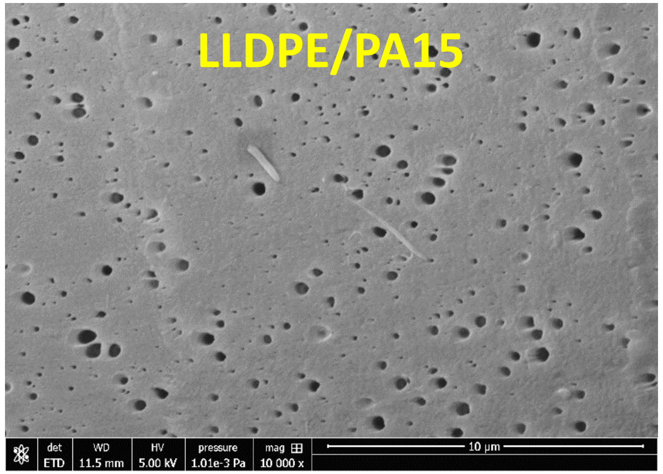
Blends Morphology



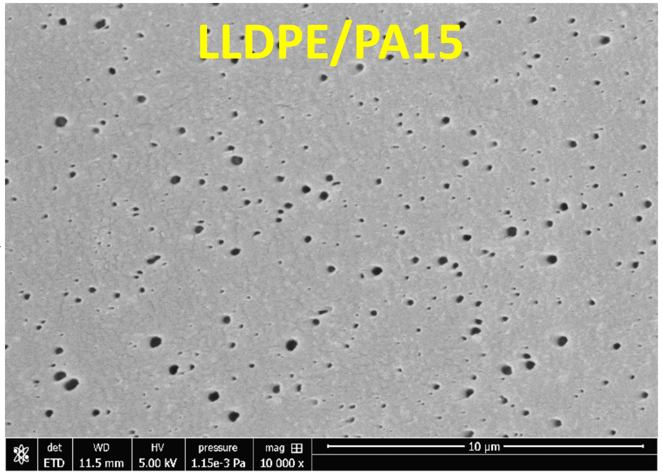
Fibrillation

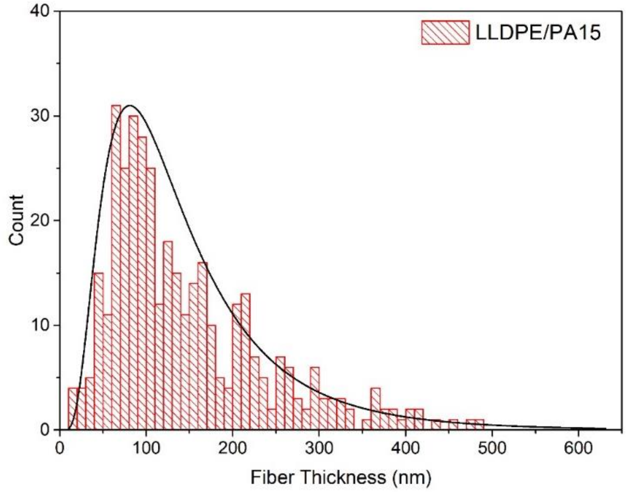






Fibrillation

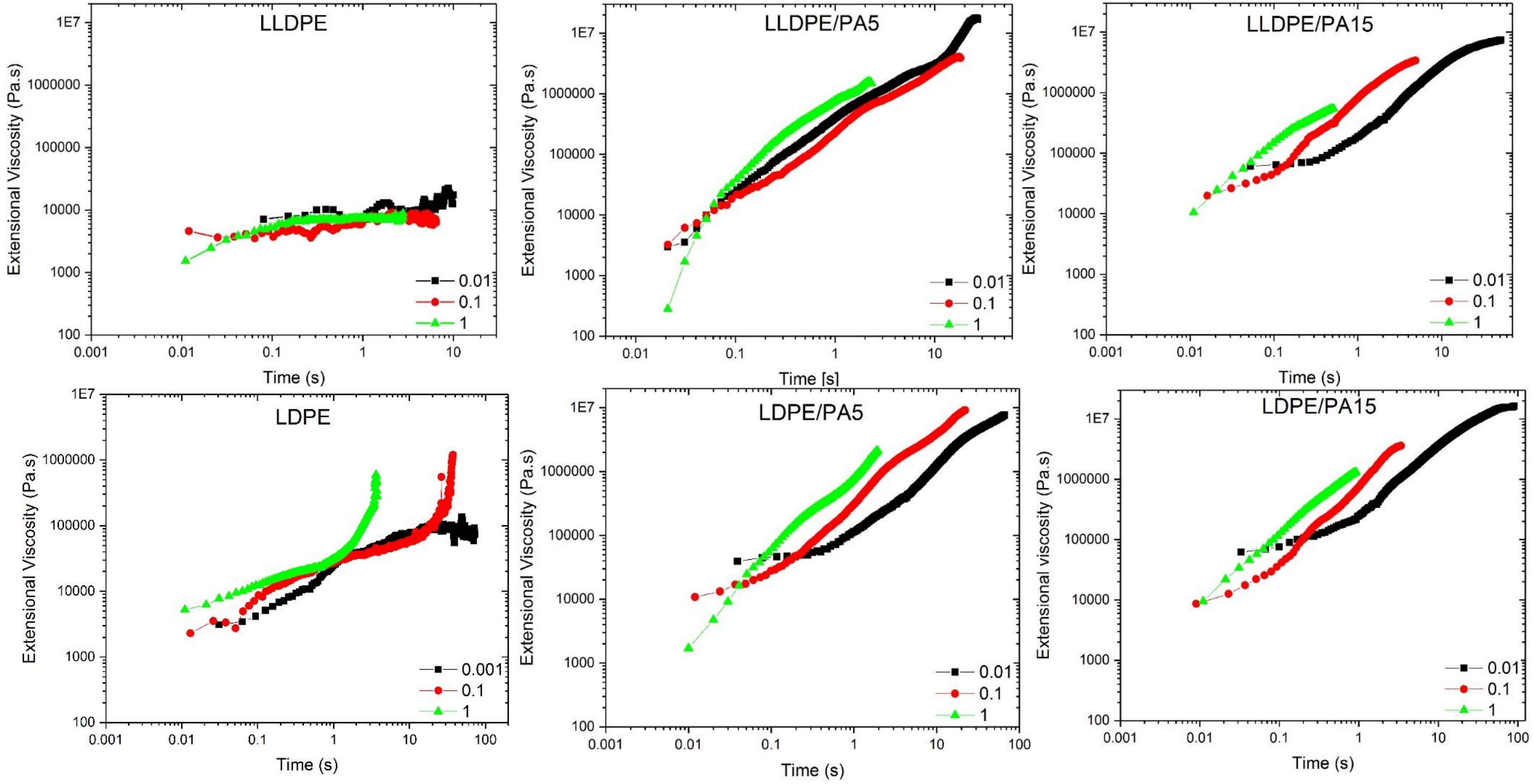




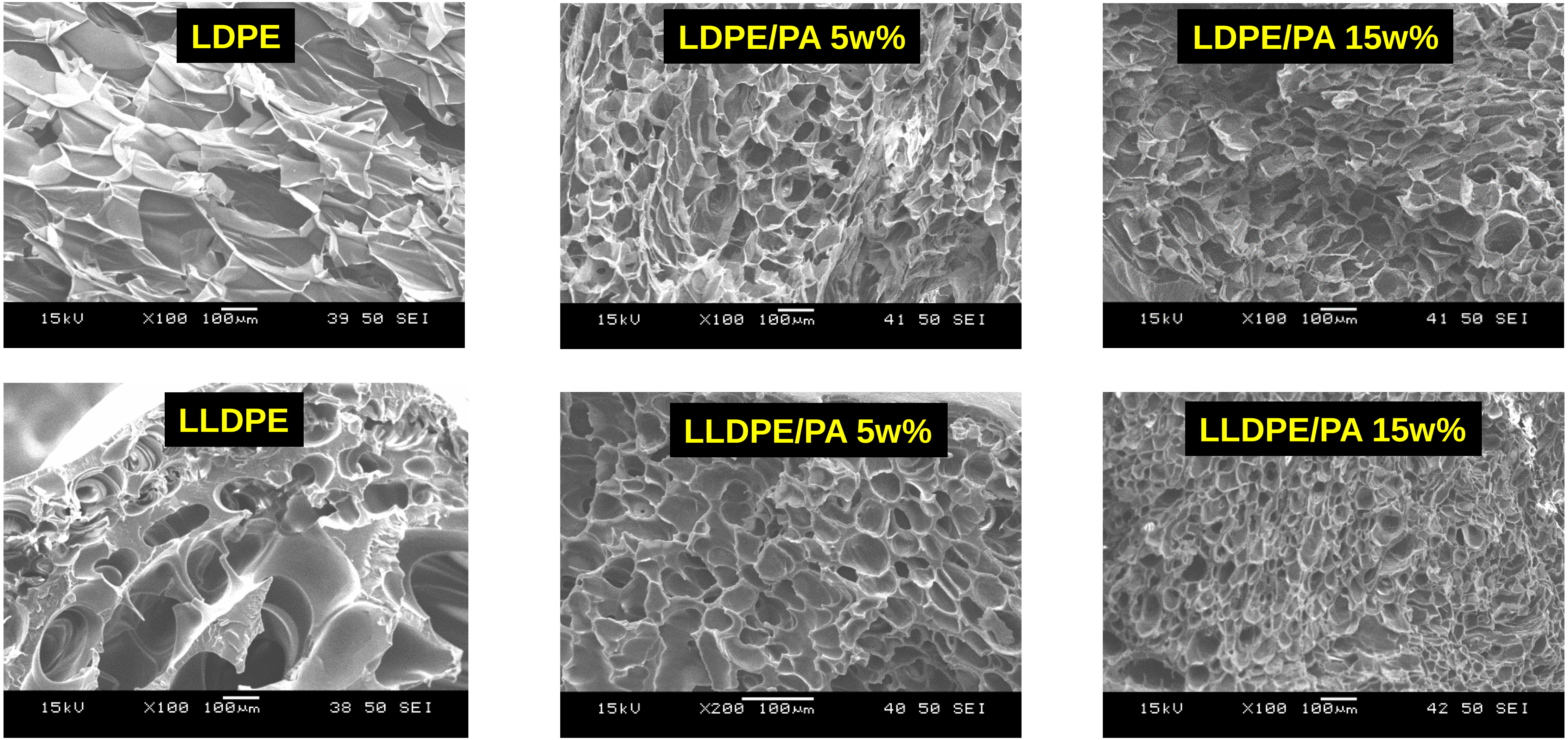
Blends before fibrillation

Cross-section of the fibers

Extensional Viscosity

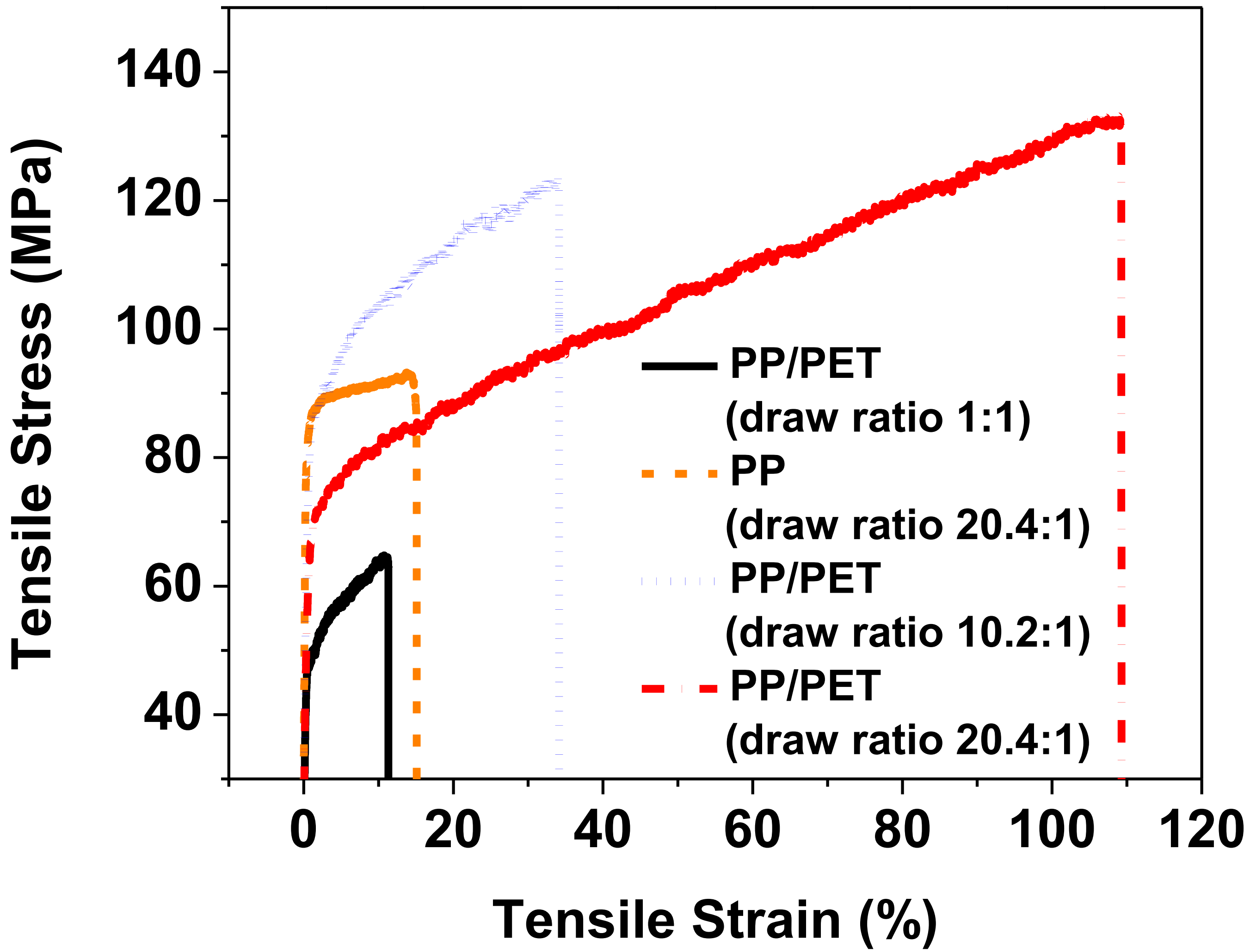


Foaming Ability



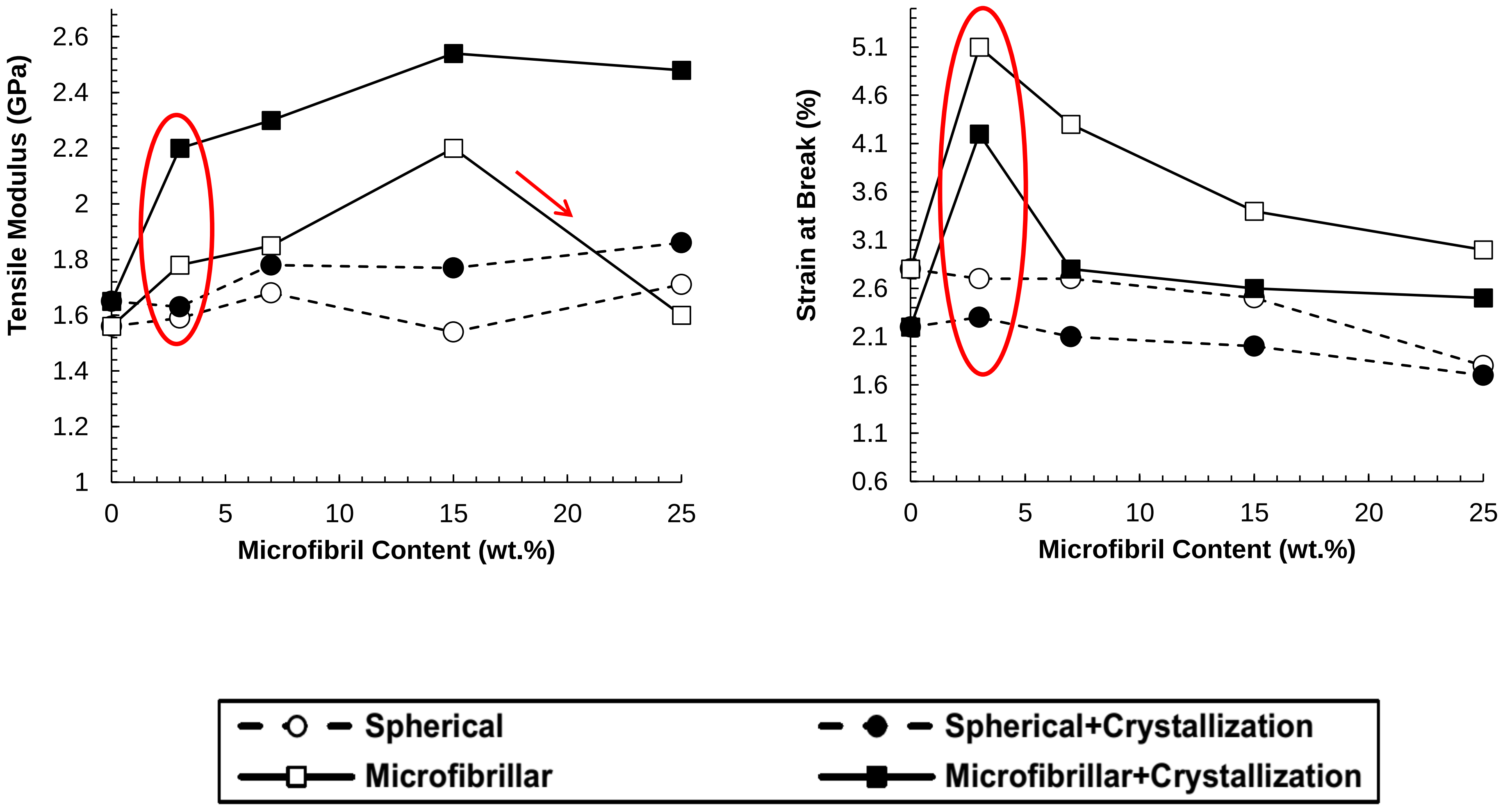
- Foaming Condition: Time: 1 hour; Pressure: 2000 psi; Temperature: 110℃ for LDPE and 115℃ for LLDPE

Tensile Property



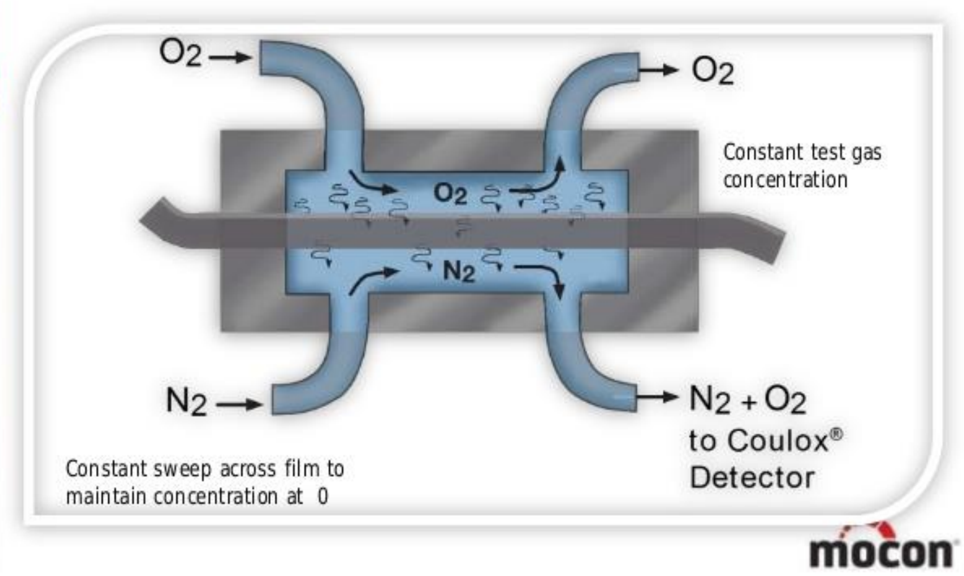
A Rizvi, ZKM Andalib, CB Park, *Polymer,* 110, 139-148, 2017

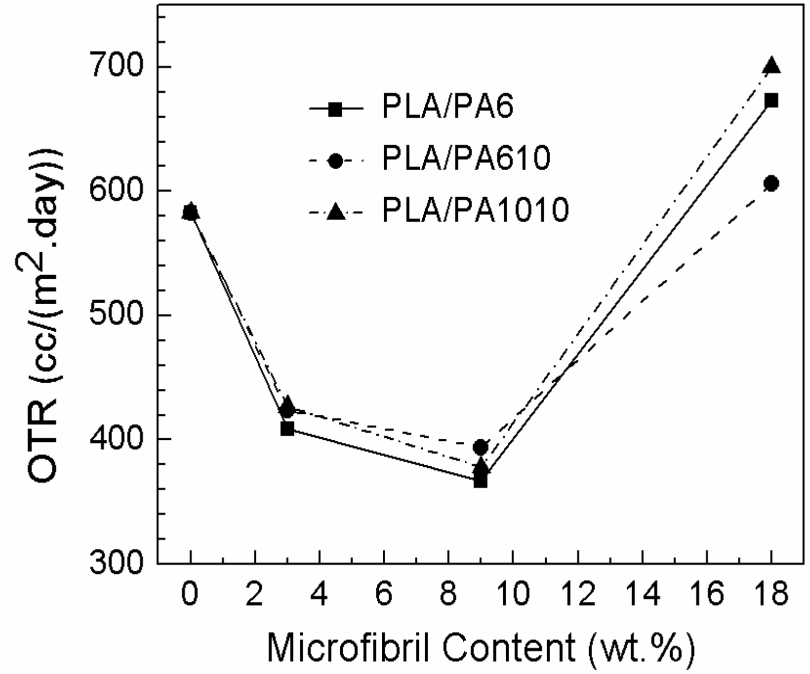
Tensile Properties of PLA/Nano-Fibril PA



A Ramezani Kakroodi, Y Kazemi, WD Ding, A Ameli, CB Park **Biomacromolecules**, 16, 3925-35, 2015.

Oxygen Transmission Rate (OTR)





- **Dramatic reduction in the PLA's OTR** after the inclusion of even a small amount of the PA microfibrils
- The MFCs with **9 wt.%** of the microfibrils showed the lowest OTRs

AR Kakroodi, Y Kazemi, M Nofar, CB Park, **Chem Eng J**, 308, 772-782, 2017

Impact:

- 150-200 nm fibers with 100-200 aspect ratios dramatically Improves the foaming ability of “not foamable” resins.
- The stiffness, tensile strength, and impact strength of the mechanically weakened foams are dramatically increased.
- Barrier property is also improved.

Sustainability of Foam

Foam is preferred because of:

- Use of less material
- Use of less energy (less carbon-foot print)
- Better performance for higher stiffness, elasticity, soft touch, sealing, etc.

Increasing market demand from:

- Automotive (mileage)
- Sports (footware)
- Construction (insulation)
- PP foam food containers over PS foam food containers
- PP foam cups over PS foam cups and paper cups
- Oil spill cleaning
- Chemical blowing agent vs physical blowing agent for footware, etc.

But there are numerous technical challenges in PO foam processing.

Sustainability of Nanofibril Technology

To overcome the numerous technical challenges of PO foam processing, the nanofibril technology can be used:

- **Improved PO foam quality with finer cells and better mechanical properties, by using the nanofibril technology.**
- **Largely expanded Lightweight PO foams using the nanofibril materials. So less material required. Less carbon foot print.**
- **Recyclable open-cell PO foam cushion out of nanofibril PO composites over non-recyclable open-cell PU foam cushion**
- **Nanofibril-containing PO foams over cross-linked PO foams in automotive industry**