# Analysis of the properties of anisotropic foams as a tool for characterizing the fibrillation degree of cellulose nanofibrils

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TAPPI

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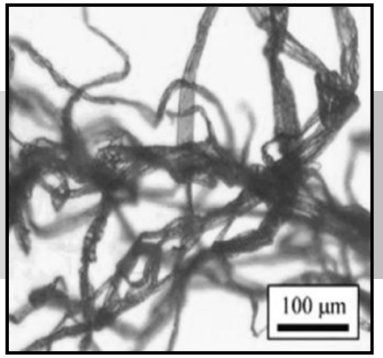
# Challenges in production of CNFs

## Cost-efficient production is challenging

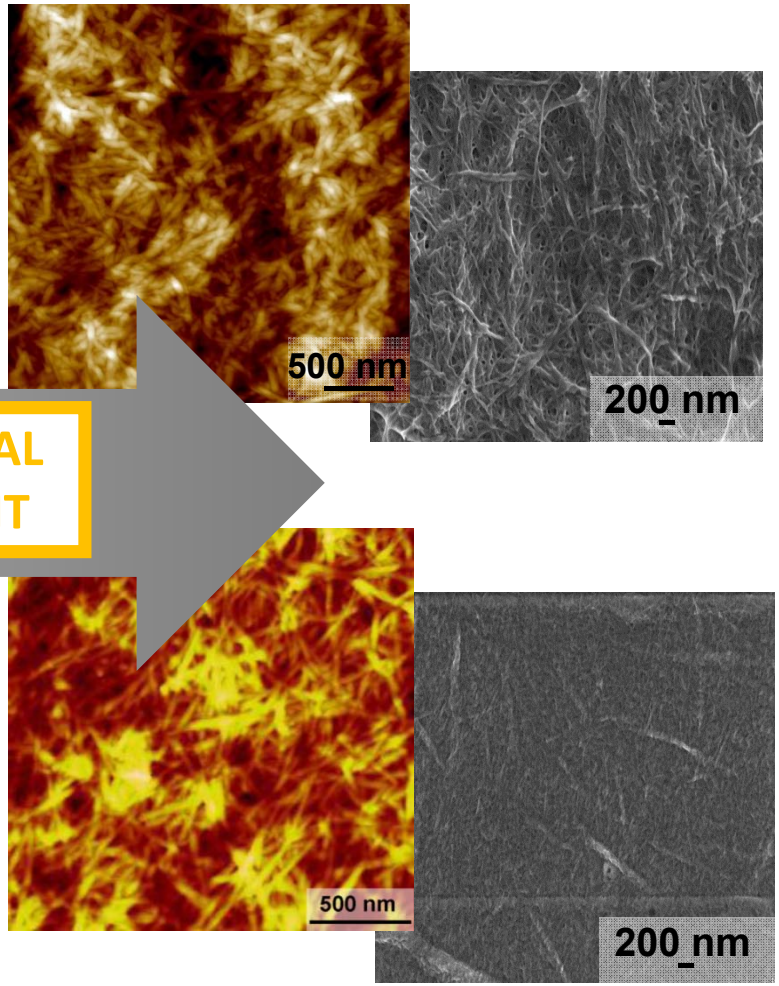
Cellulose Fibers (Wood Pulp)




ENZYMATIC PRETREATMENT

CHEMICAL PRETREATMENT

MECHANICAL TREATMENT




**Chemical/Enzymatic pretreatments**

High environmental impact (LCA)

Modify surface chemistry of cellulose

Numerous washing steps

*Spence, KL et al. Cellulose **2011**, 18 (4), 1097–1111. Henriksson, M. et al. Eur. Polym. J. **2007**, 43 (8), 3434–3441. Saito, T. et al. Biomacromolecules **2007**, 8 (8), 2485–2491. Li, Q. et al. ACS Sustain. Chem. Eng. **2013**, 1 (8), 919–928. Arvidsson, R. et al. Environ. Sci. Technol. **2015**, 49 (11), 6881–6890.*

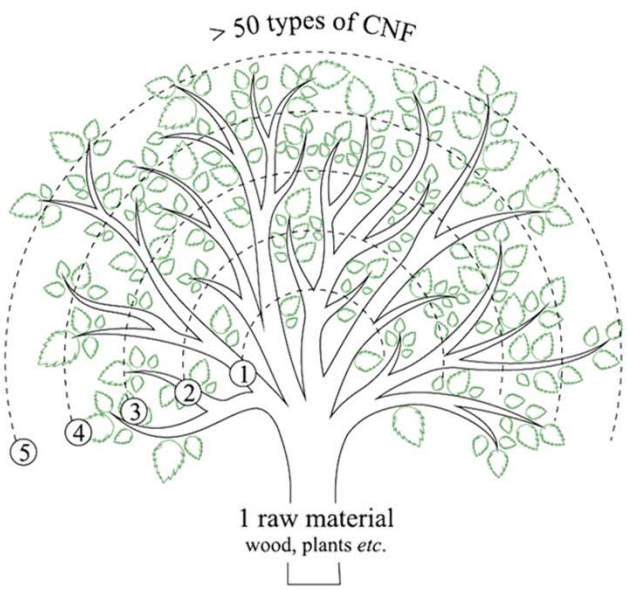
# Challenges in production of CNFs

## No 'unique' material
## Challenges in characterization and benchmarking

① Purification
cooking and bleaching

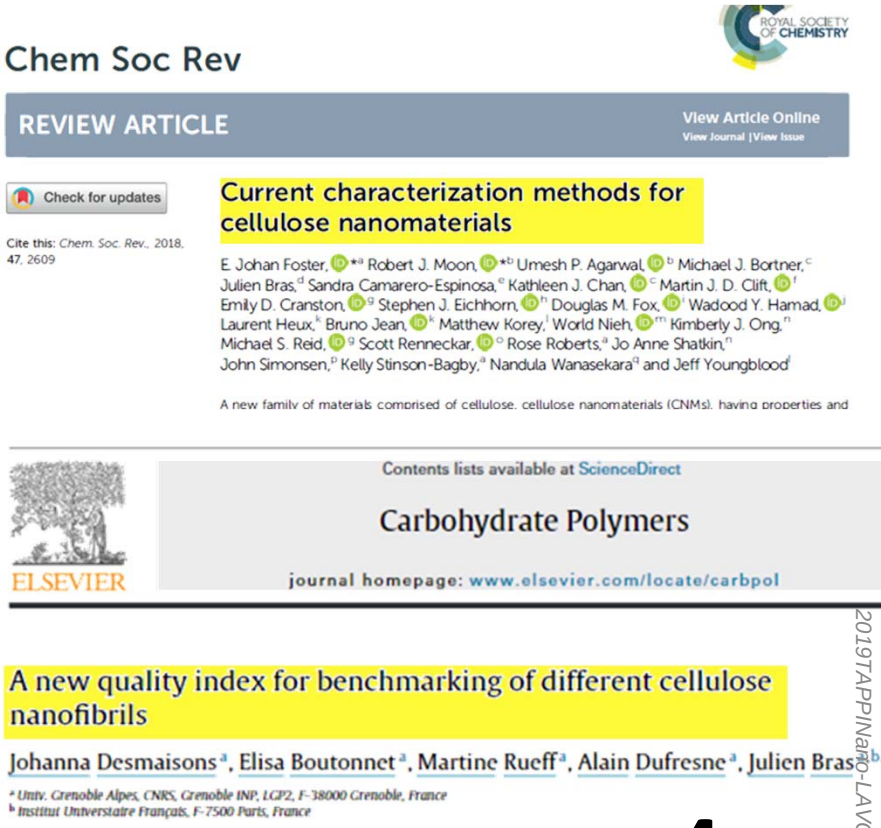
② Mechanical pretreatment
– blending;
– refining;
– grinding.

③ Biological/chemical pretreatment
– enzymatic hydrolysis;
– carboxylation;
– carboxymethylation;
– quaternization;
– sulfonation;
– solvent-assisted pretreatment.




④ Principal mechanical treatment
– homogenization;
– grinding;
– refining;
– extrusion;
– blending;
– ultrasonication;
– cryocrushing;
– steam explosion;
– ball milling;
– aqueous counter collision.

⑤ Post-treatment
– chemical modification;
– fractionation.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**Current characterization methods for cellulose nanomaterials**

E. Johan Foster,[a] Robert J. Moon,[b] Umesh P. Agarwal,[b] Michael J. Bortner,[c] Julien Bras,[d] Sandra Camarero-Espinosa,[e] Kathleen J. Chan,[c] Martin J. D. Clift,[f] Emily D. Cranston,[g] Stephen J. Eichhorn,[h] Douglas M. Fox,[i] Wadood Y. Hamad,[j] Laurent Heux,[k] Bruno Jean,[k] Matthew Korey,[l] World Nieh,[m] Kimberly J. Ong,[n] Michael S. Reid,[g] Scott Renneckar,[o] Rose Roberts,[a] Jo Anne Shatkin,[n] John Simonsen,[p] Kelly Stinson-Bagby,[a] Nandula Wanasekara[q] and Jeff Youngblood[l]

A new family of materials comprised of cellulose, cellulose nanomaterials (CNMs), having properties and

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

**A new quality index for benchmarking of different cellulose nanofibrils**

Johanna Desmaisons[a], Elisa Boutonnet[a], Martine Rueff[a], Alain Dufresne[a], Julien Bras[a,b]

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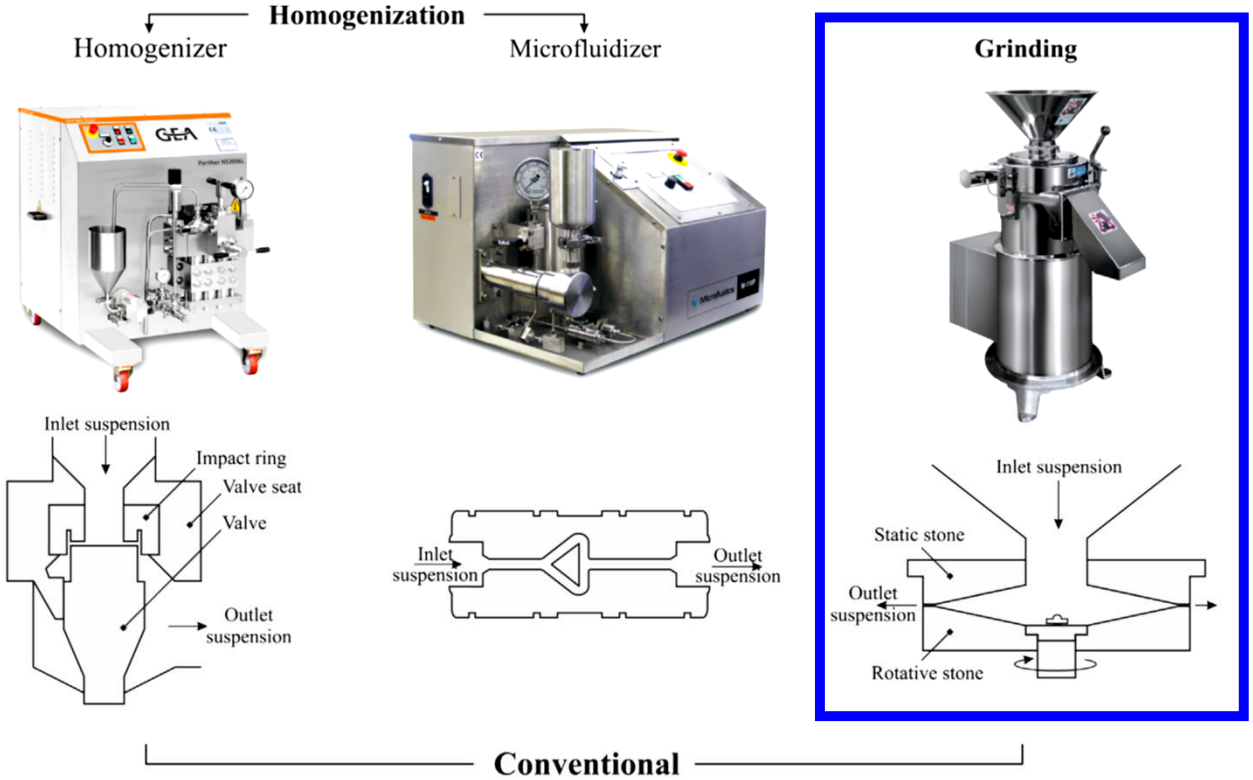
*Nechyporchuk et al. Indus Crops Prod. 2016, 93:2-25. Desmaisons, J. et al. Carbohydr. Polym. 2017, 174, 318–329. Foster et al. Chem. Soc. Rev. 2018, 47, 2609.*

# Conventional mechanical treatments




**OBJECTIVE** **Lowering the environmental impact of the no-pretreatment route**

**→ by reducing the electricity usage in selecting the right equipment and running it in a sustainable manner**

*Nechyporchuk et al. Indus Crops Prod. 2016, 93:2-25*

# Selecting the 'right' parameter...

## CHALLENGES

**Comparison** of production efficiency of CNFs → No standard

Many parameters influence **fibrillation outcome**

**Specific Energy Consumption, *E*,** calculated based on the **Operating Power Surplus:**

$$E\ [kWh.kg^{-1}] = \frac{P\ [kW]\ \times t\ [h]}{w\ [kg]}$$

***P*, Operating Power Surplus = Difference between the total and no-load power**

*w,* dry weight of CNFs processed for certain time, *t*

Reported Range for **'good CNF quality'*** at **low energy consumption:**

**1.5 – 5 kWh/kg**

**CNF films with the most improved mechanical properties*

NC STATE UNIVERSITY

# From wood pulps to CNFs to foams

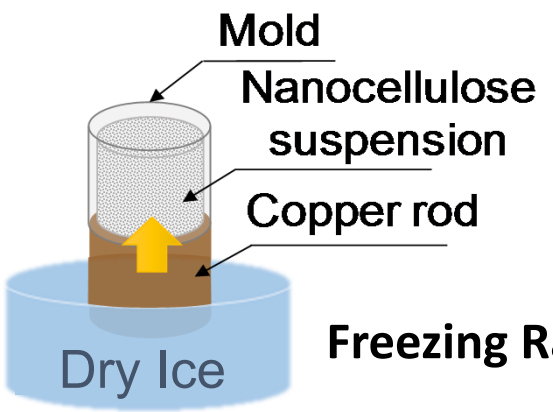
| | KRAFT | SULFITE |
|---|---|---|
| Cellulose | 84% | 96% |
| Hemicelluloses | **16%** | 4% |
| Klason Lignin | <0.5 | <0.5 |

**Masuko grinding parameters**

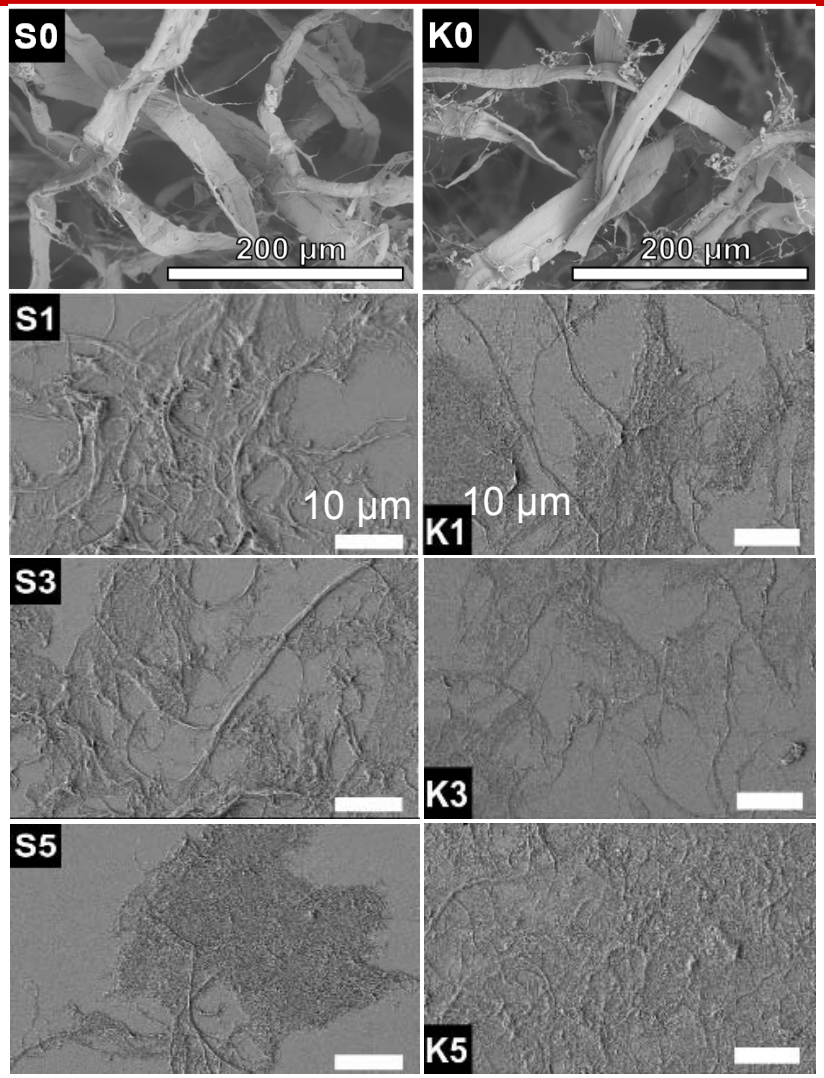
Speed: **750 rpm**

Number of passes: **1 to 5**

Energy consumptions: **0.1, 0.4, and 0.9, 3 and 5 kWh/kg**

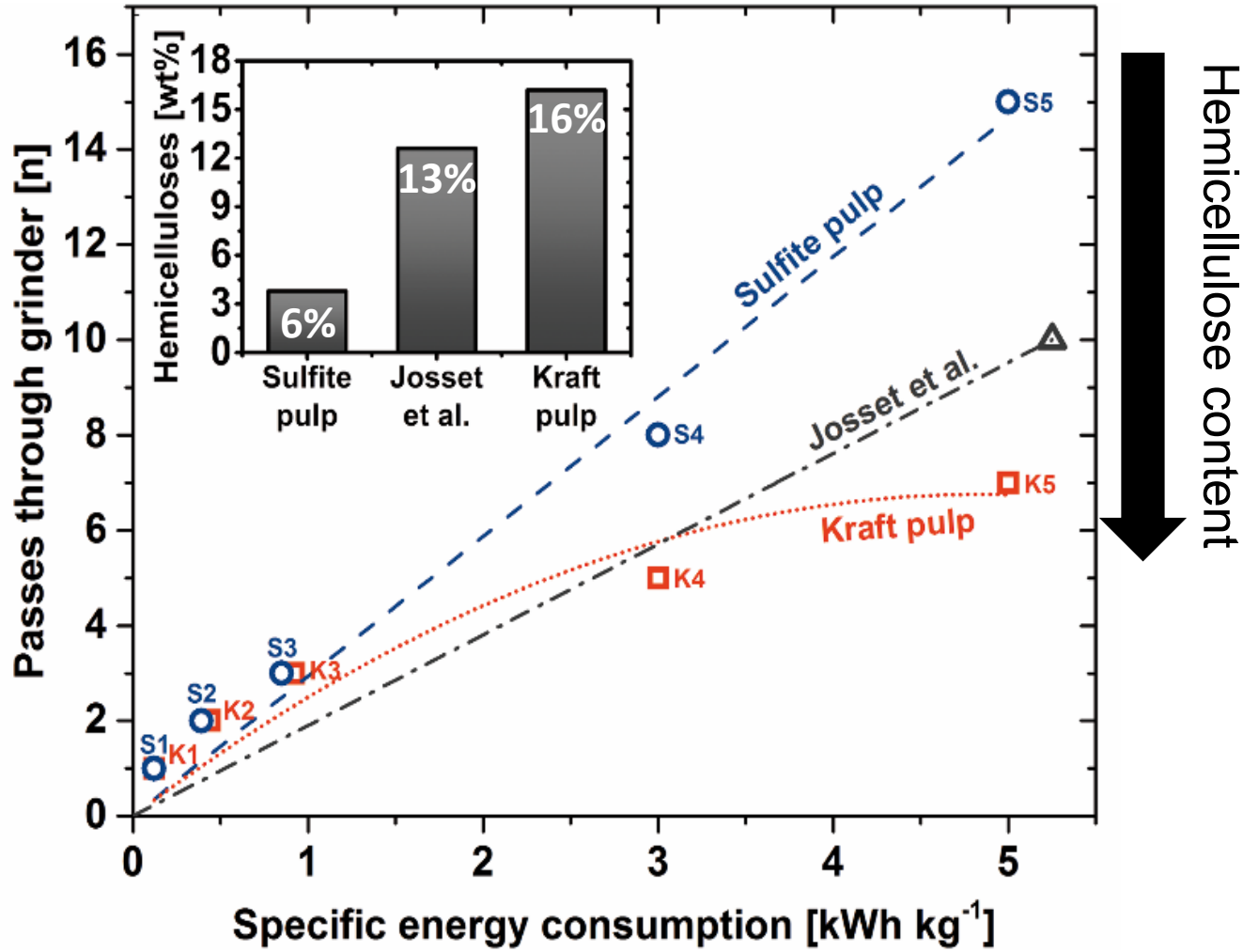



**Freezing Rate: 3 K/min**




*Kriechbaum et al. ACS Sustainable Chem. Eng. 2018, 6, 11959–11967*

# Grinding process





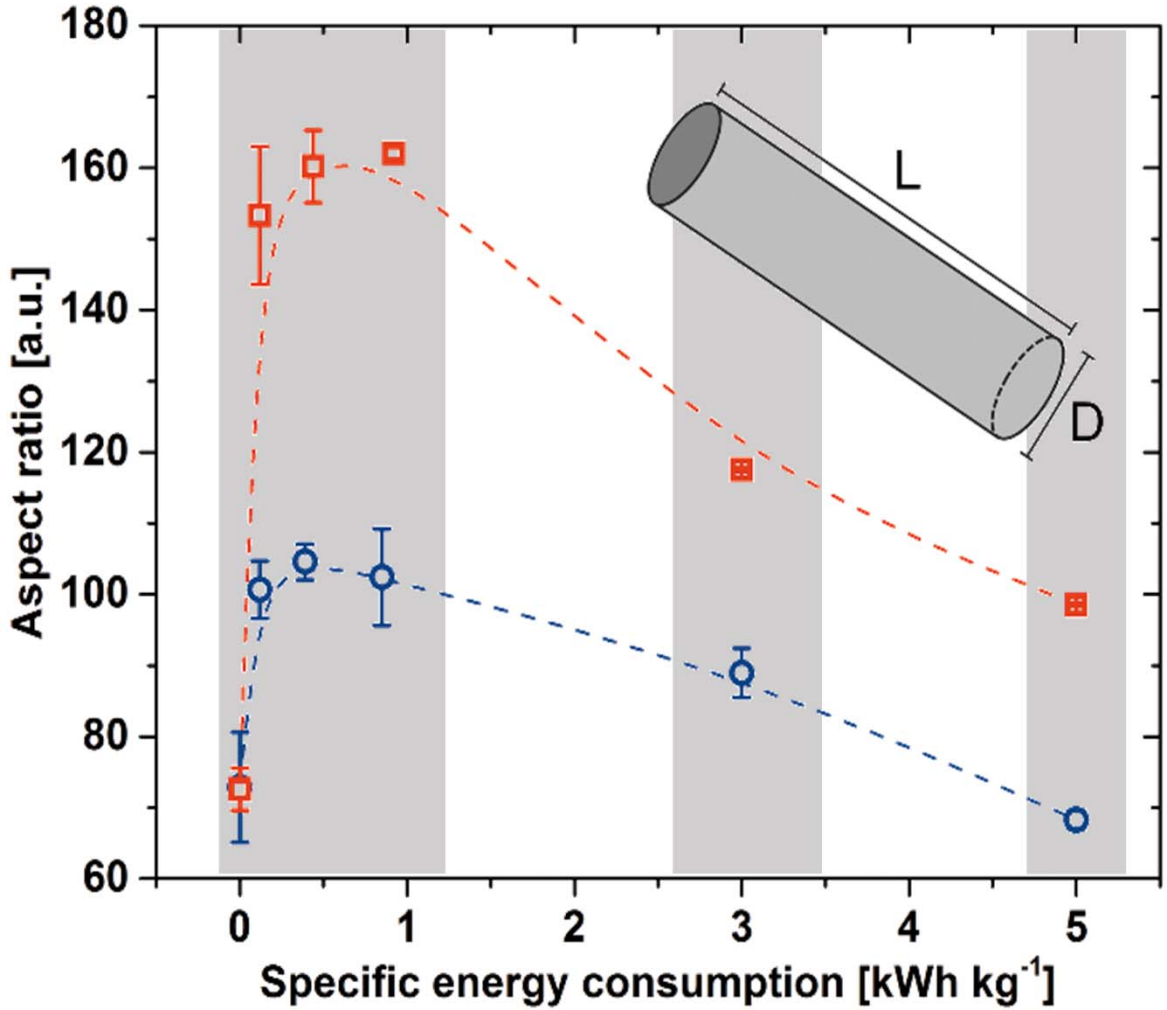



*Josset et al. Nord. Pulp Pap. Res. J. 2014, 29 (1), 167–175; Kriechbaum et al. ACS Sustainable Chem. Eng. 2018, 6, 11959–11967*

# Can we estimate the aspect ratio?

**Grinding action:**
Combination of transversal and longitudinal fibrillation of fibers

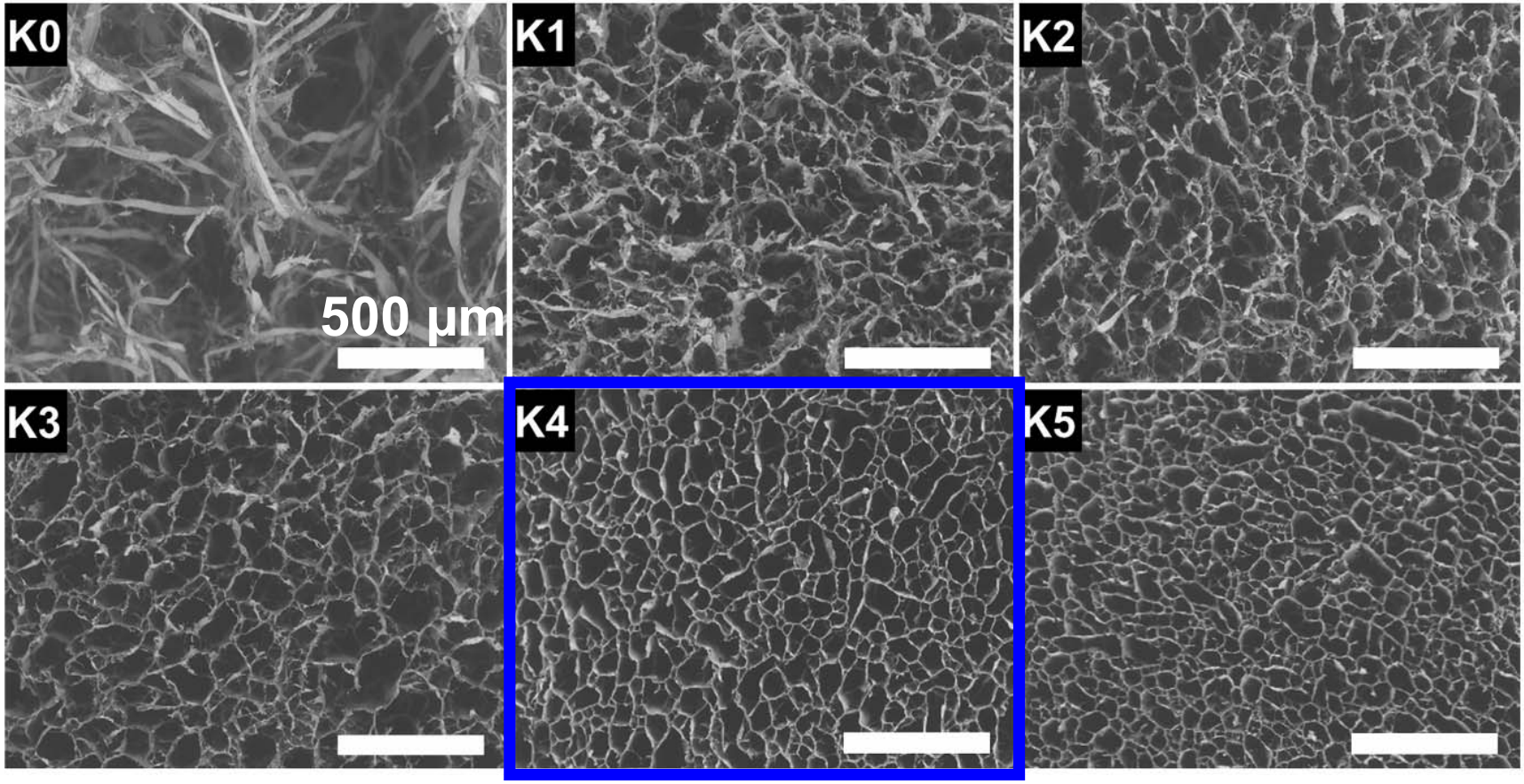
1- Reduction of diameter?
2- Transversal fibrillation?




*Martinez et al, 2001, Proceedings 12th Fundamental Research Symposium, Oxford; Varanasi et al. Cellulose, 2013, 20, 1885-1896; Kriechbaum et al. ACS Sustainable Chem. Eng. 2018, 6, 11959–11967*

# Cross-section of CNF foams

**Density: 5.5 kg/m$^3$ - Porosity: 99.6%**




**From 3 kWh/kg**: More homogeneous and regular honeycomb structure with less defected cell walls

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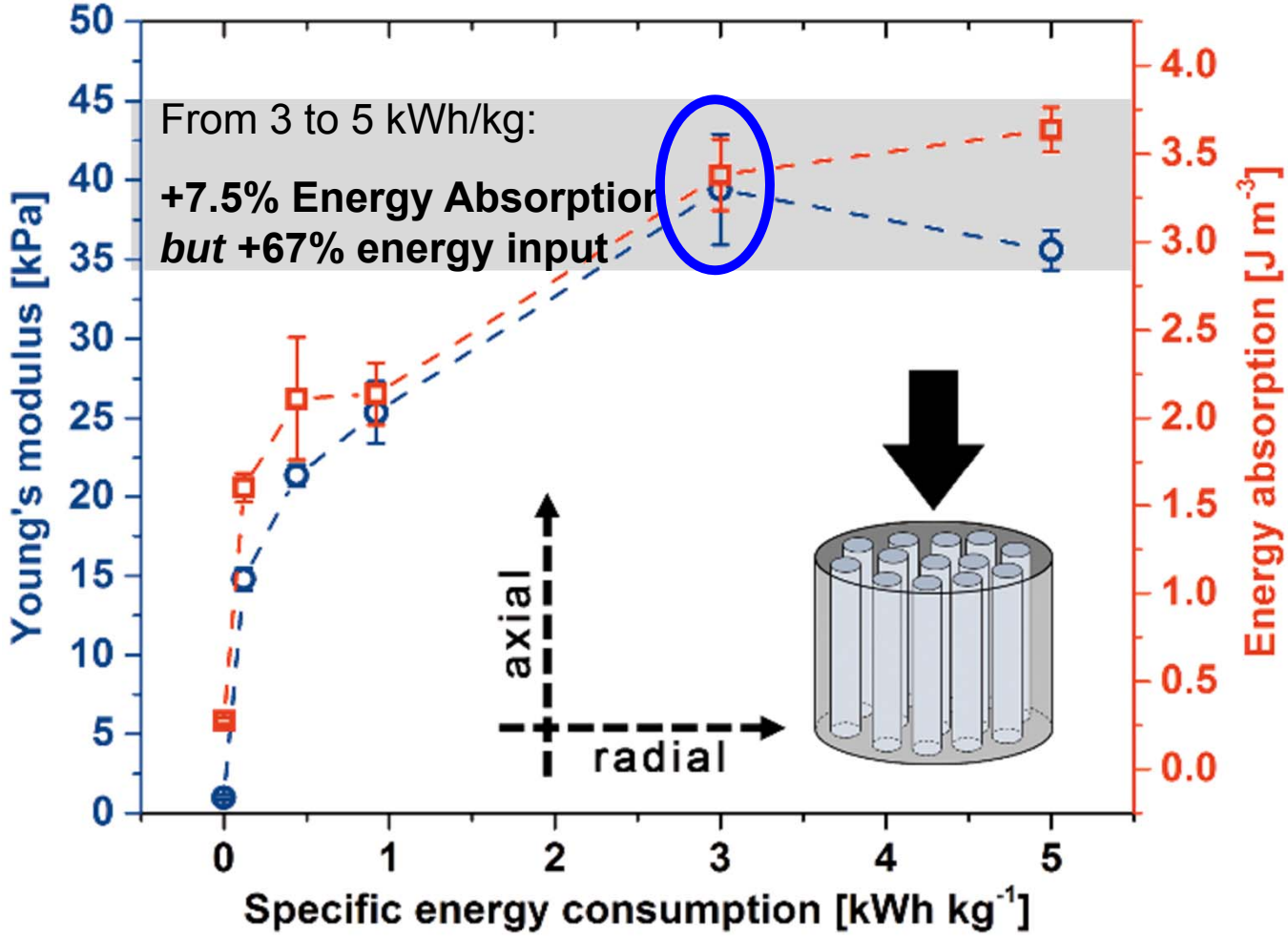
# Compressive strength

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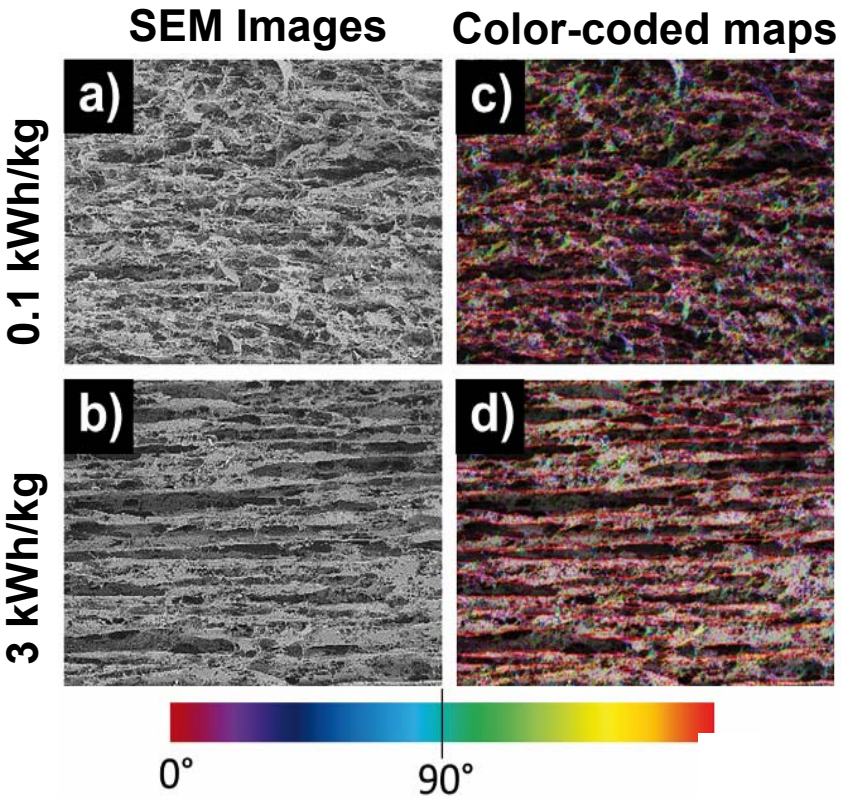
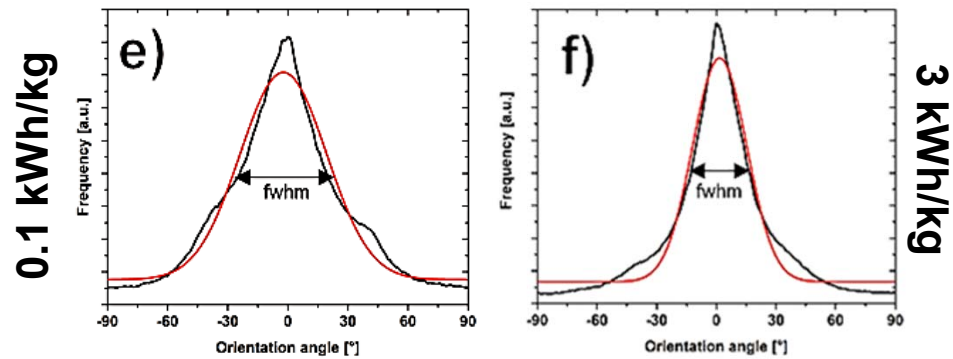
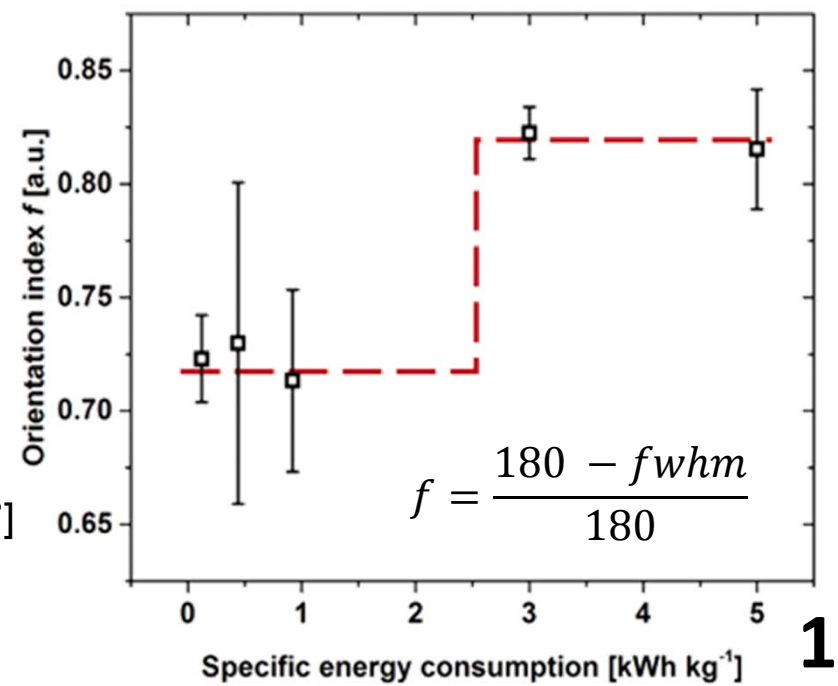
# CNF alignment




A high number of **red pixels**
→ better alignment of the CNFs in the freezing direction [0°]
A greater share of **green** and **blue** color tones
→ CNF orientation deviate from the freezing direction

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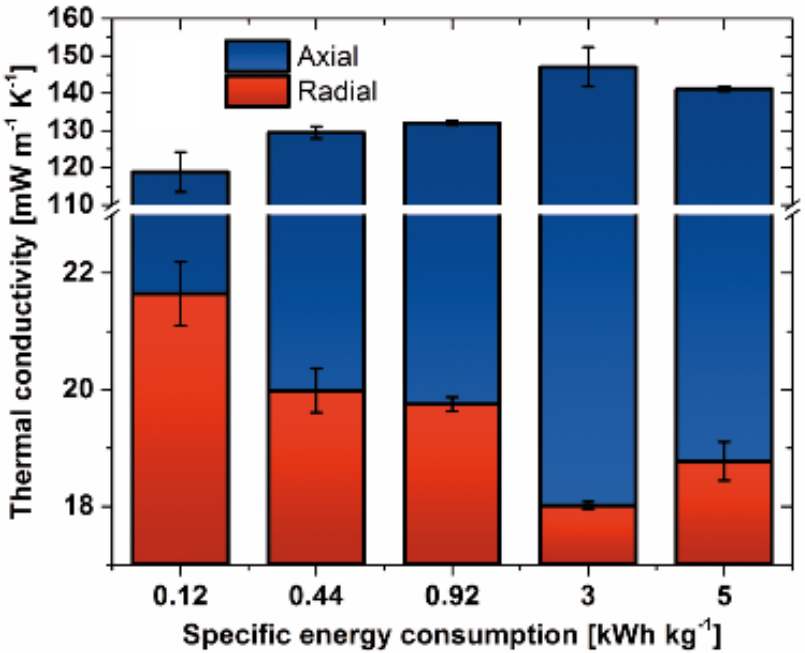
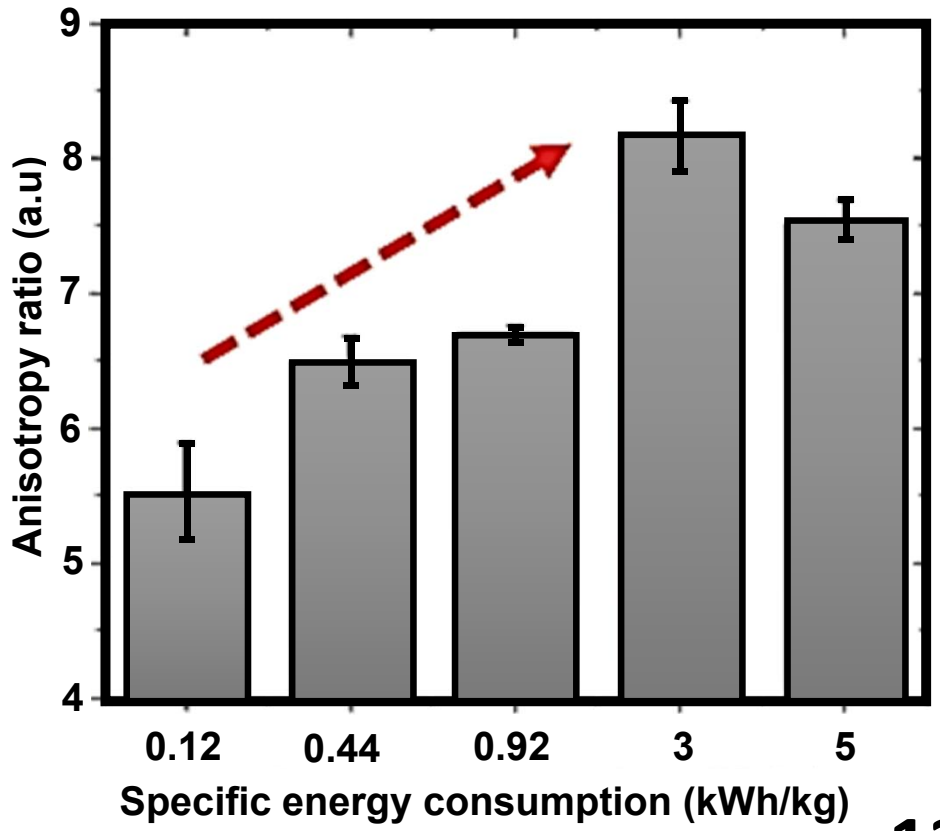
# Thermal Conductivity




$$Anisotropy\ Ratio = \frac{\lambda axial}{\lambda radial}$$



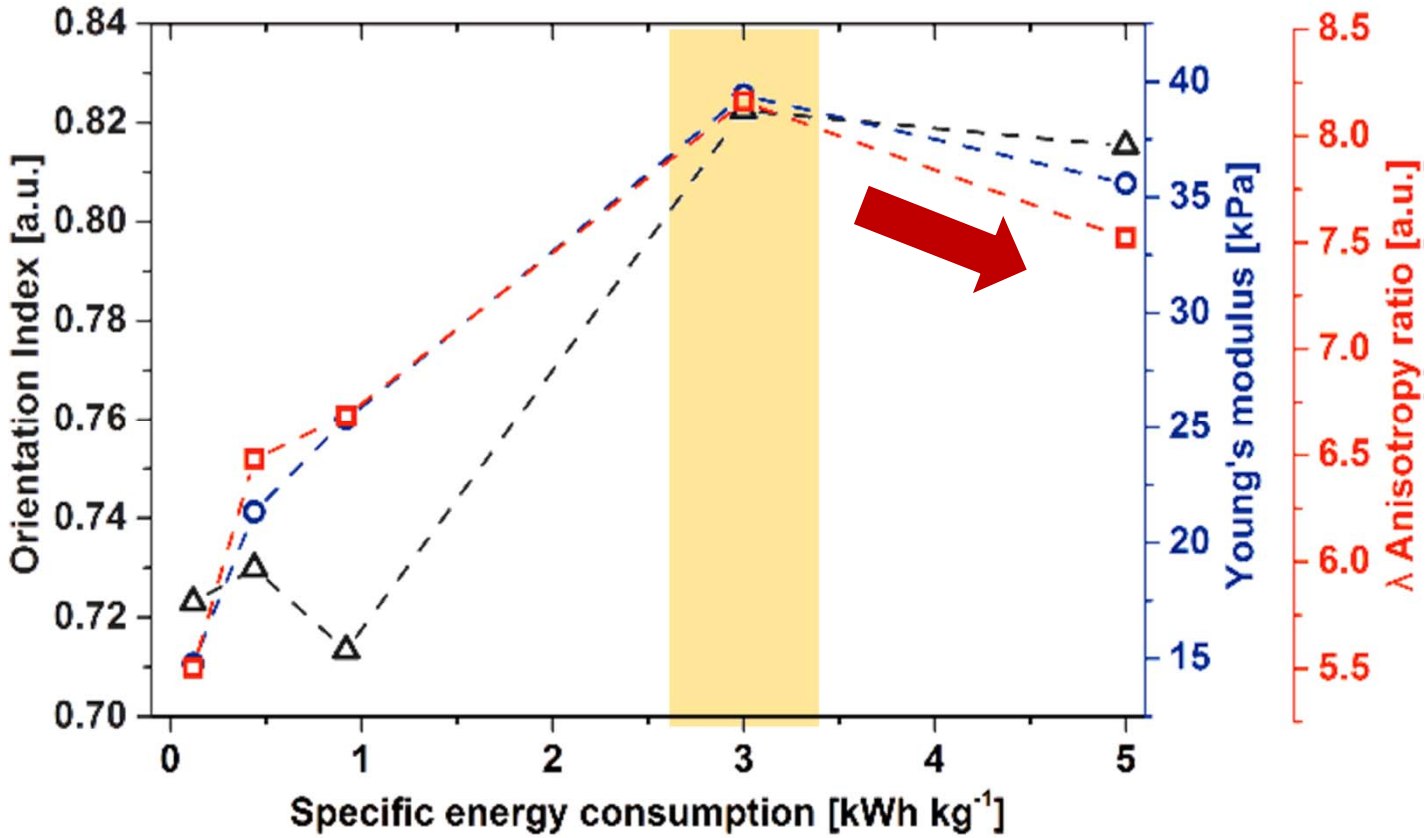

Up to 3 kWh/kg: Increase in anisotropy with increasing energy consumption

**Fibrillation optimum reached for 3 kWh/kg**

*Kriechbaum et al. ACS Sustainable Chem. Eng. 2018, 6, 11959–11967*

# Conclusion

Each properties optimum **converges to a specific energy consumption of 3 kWh/kg**
→ **Optimum value to reach** for achieving high degree of **fibrillation by energy-efficient grinding**




*Kriechbaum et al. ACS Sustainable Chem. Eng. 2018, 6, 11959–11967*

# Thank you!

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