

Tuning properties of high-consistency enzymatically fibrillated cellulose (HefCel) for various applications

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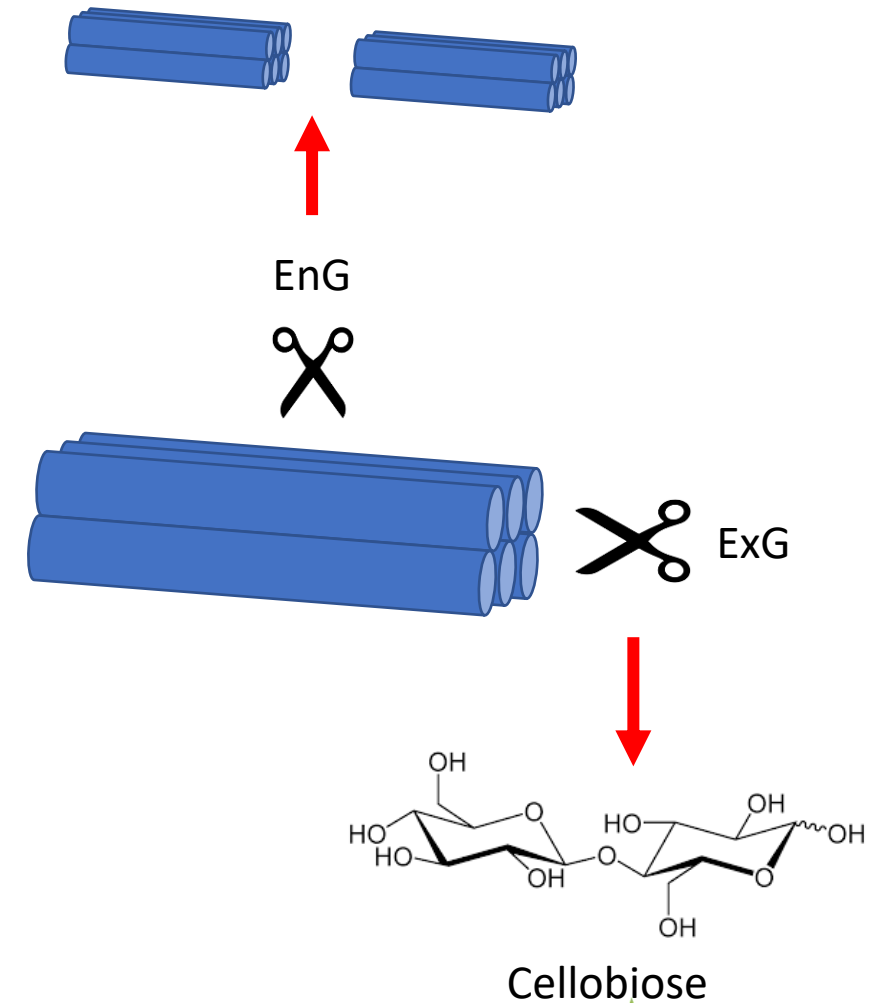


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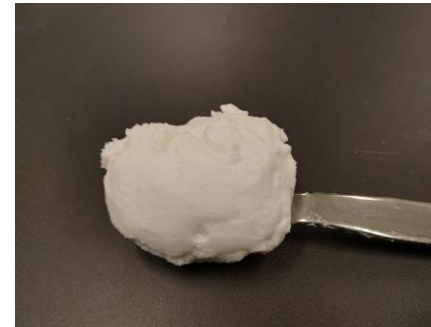
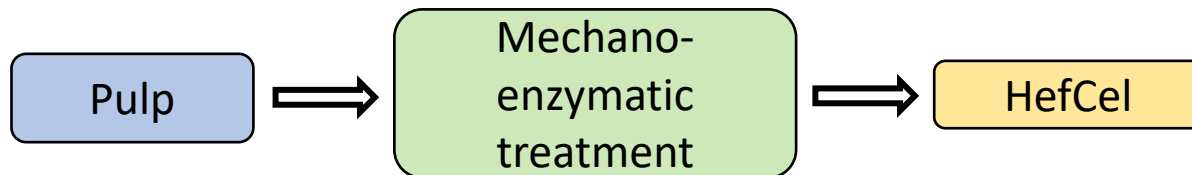
The Enzymatic Route to CNF

- Commonly used cocktails include **endoglucanases (EnG)**, **exoglucanases (ExG)**, hemicellulases
- EnG activity selective to β -1,4-glucosidic bonds. Along dislocations on fibre surface
- ExG activity on ends of cellulose chains
- Enzyme access to fibres must be ensured:
 - Bleaching, Refining
- Hemicellulases allow better access to EnG for attacking fibres
- Enzyme cocktail should be tailored for raw materials



HefCel process

- Mechano-enzymatic treatment
- Enzyme cocktail tailored for wood-pulp as a raw material
- EnG + ExG ratio optimized for best results:
 - Low fibre cutting
 - Low amount of liberated soluble sugars
 - High degree of fibrillation
- HefCel processing consistency: 20-30%

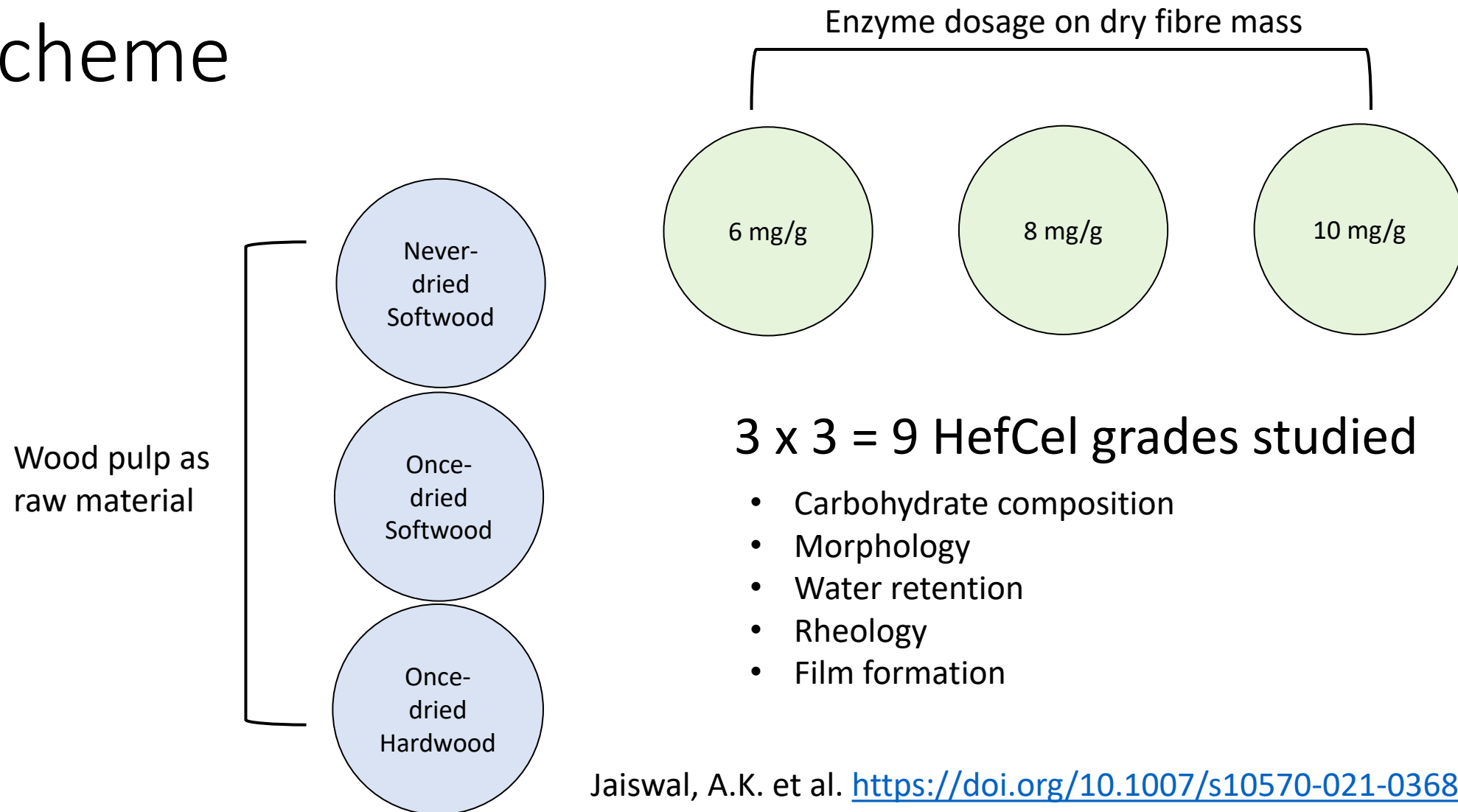


HefCel at 20% consistency



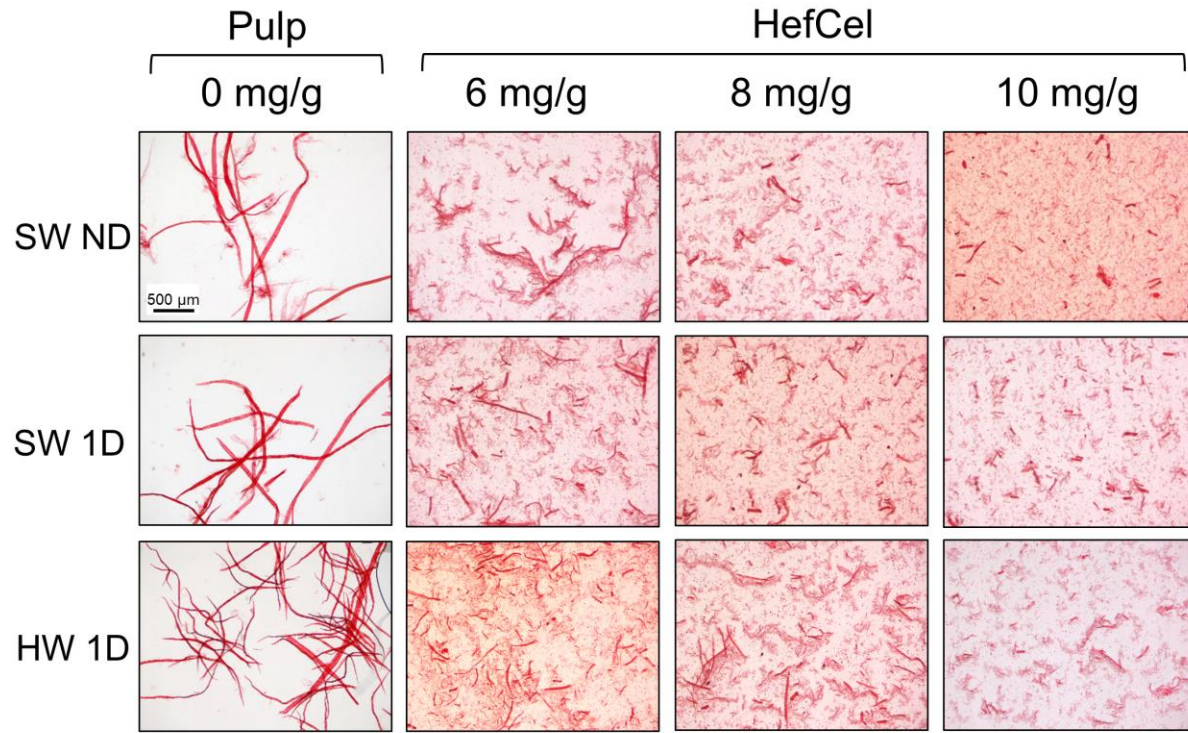
HefCel processing

Scheme

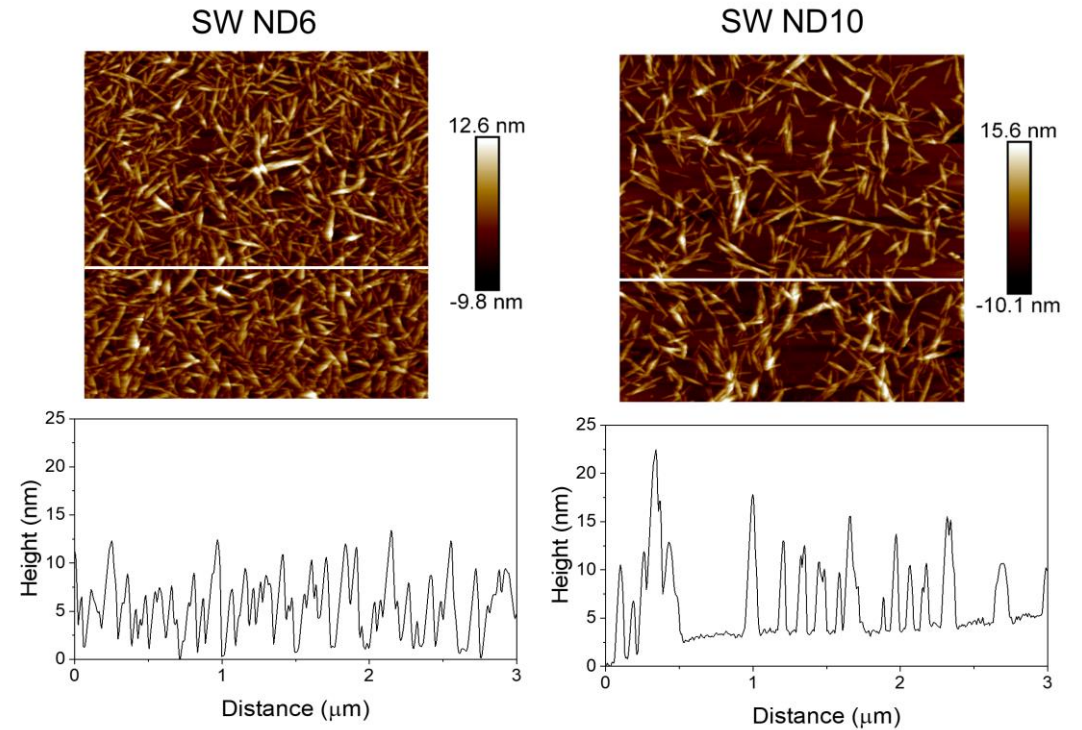


Jaiswal, A.K. et al. <https://doi.org/10.1007/s10570-021-03688-y>

Morphology



Optical Microscopy



AFM

Carbohydrate composition

- No hemicellulases used in the dosed cocktail
- More soluble sugars liberated as enzyme dosage increased --> Minor yield loss
- Molar mass reduced from ~700 kDa for the source pulps to 200-300 kDa for HefCel grades

Sample	Enzyme dosage (mg/g)	Xylan (%)	Cellulose (%)	Liberated reducing sugars (%)
SW ND Pulp	0	7.8 ± 0.2	71.3 ± 1.1	-
SW ND6	6	7.7 ± 0.2	69.6 ± 0.5	9.7
SW ND8	8	7.7 ± 0.2	69.8 ± 1.7	10.3
SW ND10	10	7.3 ± 0.3	66.3 ± 3.3	14.0
SW 1D Pulp	0	8.9 ± 0.2	71.5 ± 1.1	-
SW 1D6	6	9.3 ± 0.1	70.6 ± 0.4	9.4
SW 1D8	8	9.3 ± 0.1	69.9 ± 0.8	11.5
SW 1D10	10	9.3 ± 0.1	70.0 ± 0.3	13.5
HW 1D Pulp	0	19.6 ± 0.7	63.6 ± 1.9	-
HW 1D6	6	19.6 ± 0.1	63.1 ± 0.4	9.7
HW 1D8	8	19.7 ± 0.2	63.7 ± 0.3	12.6
HW 1D10	10	19.7 ± 0.2	63.4 ± 0.3	13.9

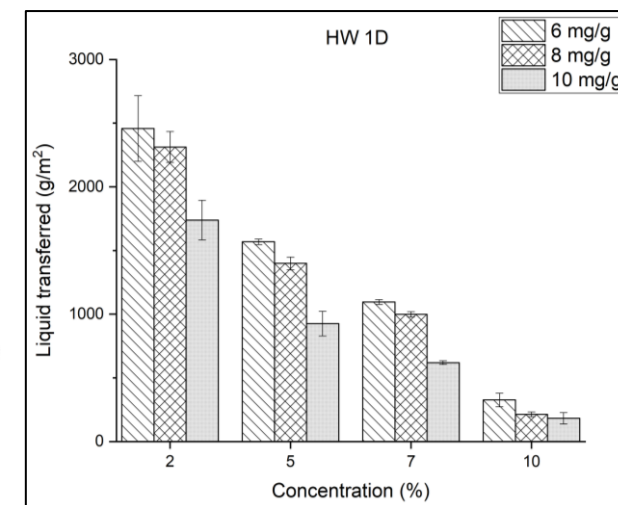
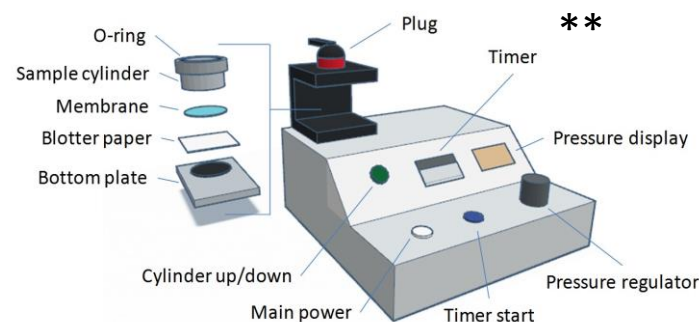
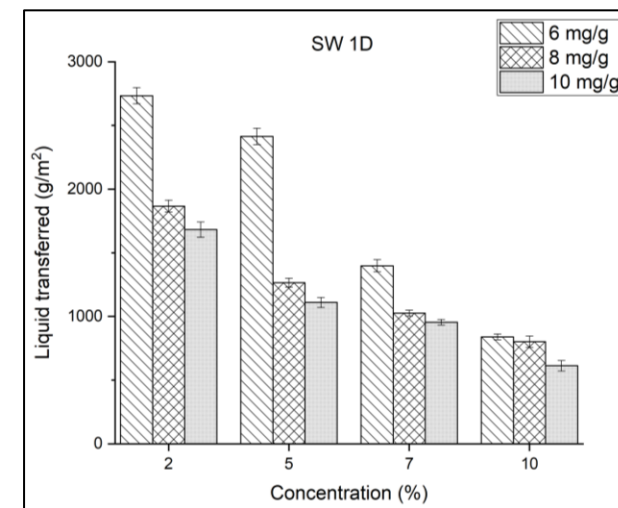
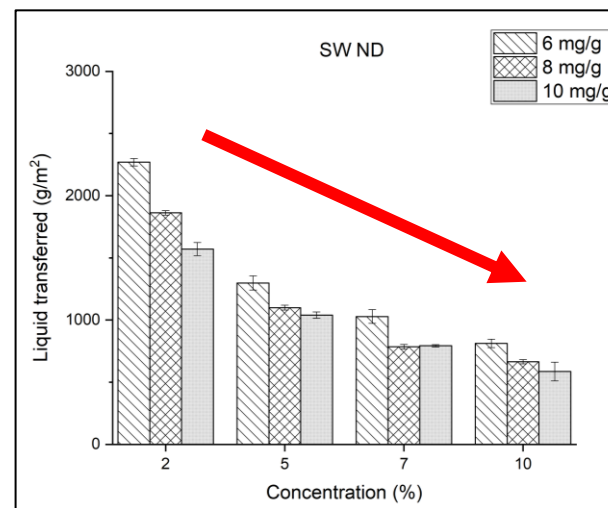
SW: Softwood; HW: Hardwood; ND: Never-dried; 1D: Once-dried

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Water retention

- Important parameter for paper and board coating applications
- Measured using the ÅA-GWR* method
- Overpressure: 50 kPa; Dewatering time: 120 s
- 3000 g/m² corresponds to 20% dewatering
- Higher water retention at higher enzyme dosage

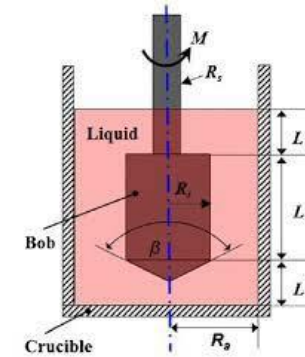


*Åbo Akademi Gravimetric Water Retention

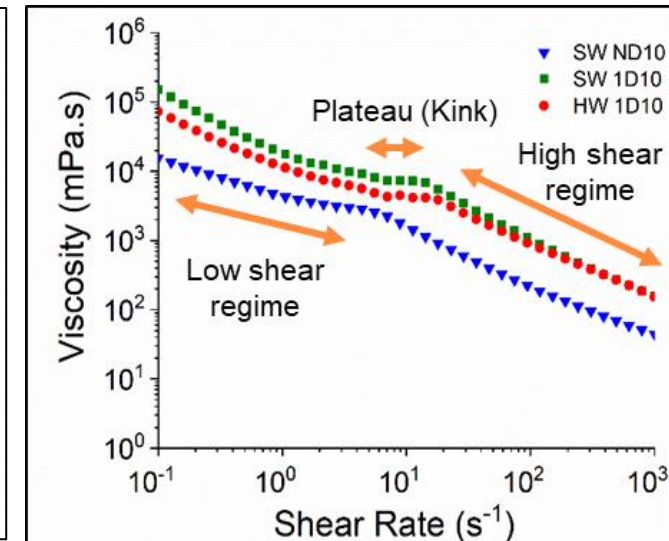
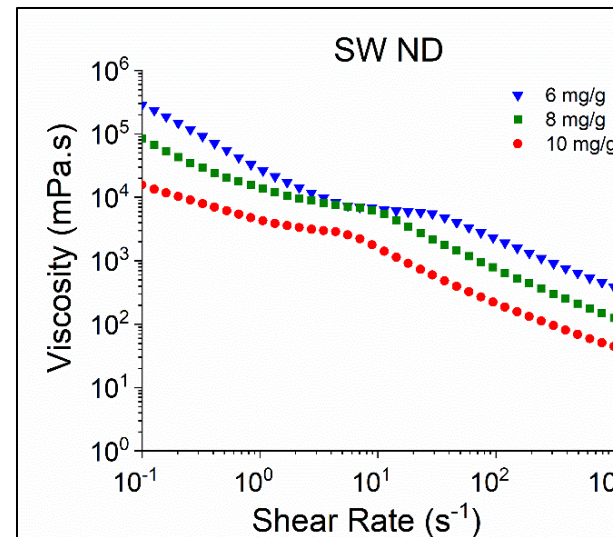
**Kumar, V. (2018). *Roll-to-roll processing of nanocellulose into coatings*

Forward shear ramps

- Concentric cylinder geometry (MCR 301, Anton Paar GmbH)
- Pre-shearing at 100 s^{-1} for 1 min.; 2 min. resting
- Highly shear-thinning nature like conventional CNF grades
- Lower viscosity at higher enzyme dosage
- Appearance of a viscosity plateau at $\sim 10 \text{ s}^{-1}$
- ‘Snowball’ hypothesis probable explanation*



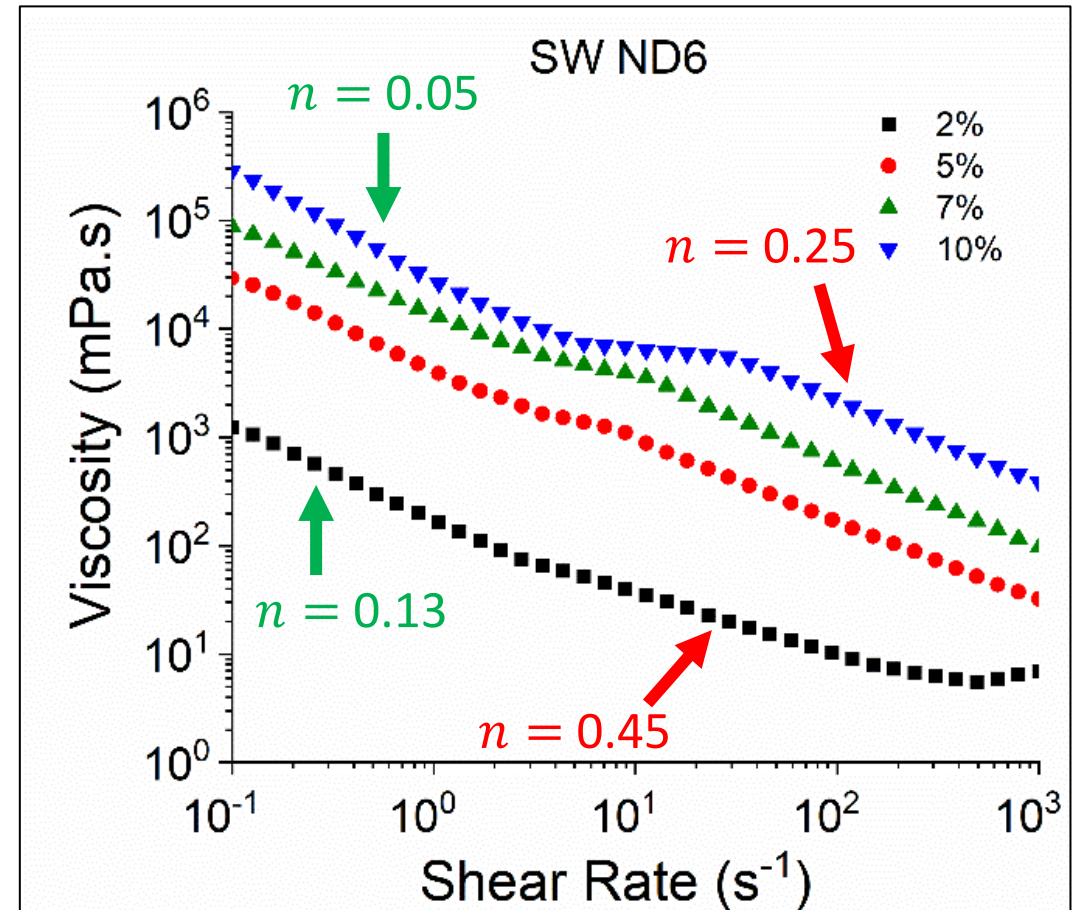
At 10% consistency



*Karppinen et al. <https://doi.org/10.1007/s10570-012-9766-5>

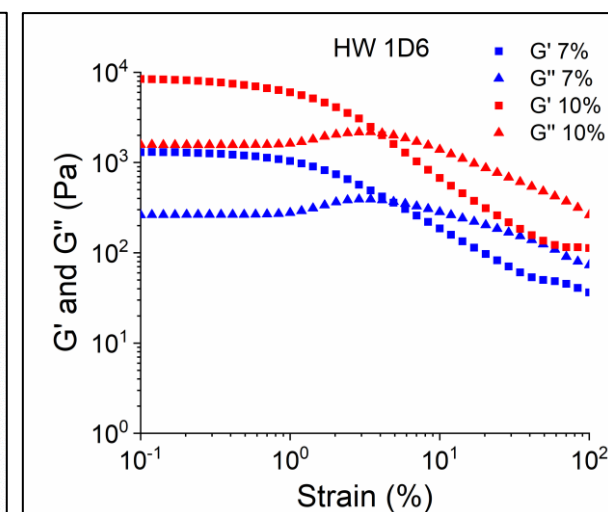
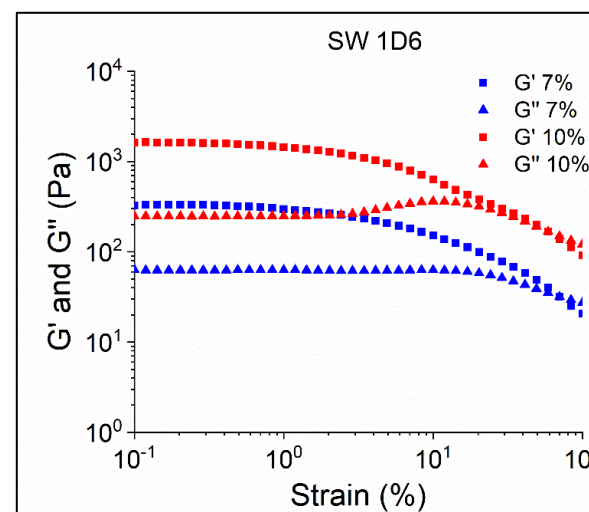
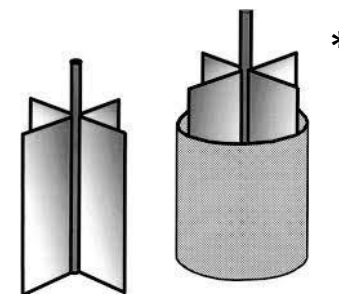
Forward shear ramps

- Power Law fitting: $\tau = K \cdot \dot{\gamma}^n$; $n = 0.11$ to 0.73
- Different slopes of power law fits before and after the plateau
- Viscosity highly dependent on consistency as $\mu \sim c^m$; m ranging from 2.75 to 4.31 (at 1 s^{-1})
- m not unique but a function of shear rate
- More pronounced shear-thinning as consistency increases



Viscoelastic properties

- Vane and cylinder geometry (MCR 301, Anton Paar GmbH) for oscillatory measurements
- Amplitude sweeps and Frequency sweeps (within LVE region <1% strain)
- High gel-point consistency: No gelling up to 5%
- Low yield stress (τ_y) even at 7 and 10% consistencies: **<30 Pa**
- Suitable for 3D/screen printing applications



*Barnes and Nguyen [https://doi.org/10.1016/S0377-0257\(01\)00095-7](https://doi.org/10.1016/S0377-0257(01)00095-7)

Film formation

- Transparent, hazy, flexible films upon self-assembly
- Target basis weight: 50 gsm; No plasticizers

Sample	Film Density (kg/m ³)	Tensile Strength (MPa)
SW ND6	1083 ± 7	45.7 ± 0.8
SW ND8	1173 ± 68	50.8 ± 4.1
SW ND10	966 ± 17	30.9 ± 4.9
SW 1D6	1067 ± 30	42.9 ± 2.4
SW 1D8	1056 ± 27	37.3 ± 3.4
SW 1D10	1138 ± 28	36.0 ± 3.3
HW 1D6	1062 ± 34	50.2 ± 6.8
HW 1D8	1092 ± 28	42.0 ± 3.6
HW 1D10	992 ± 55	46.6 ± 2.6

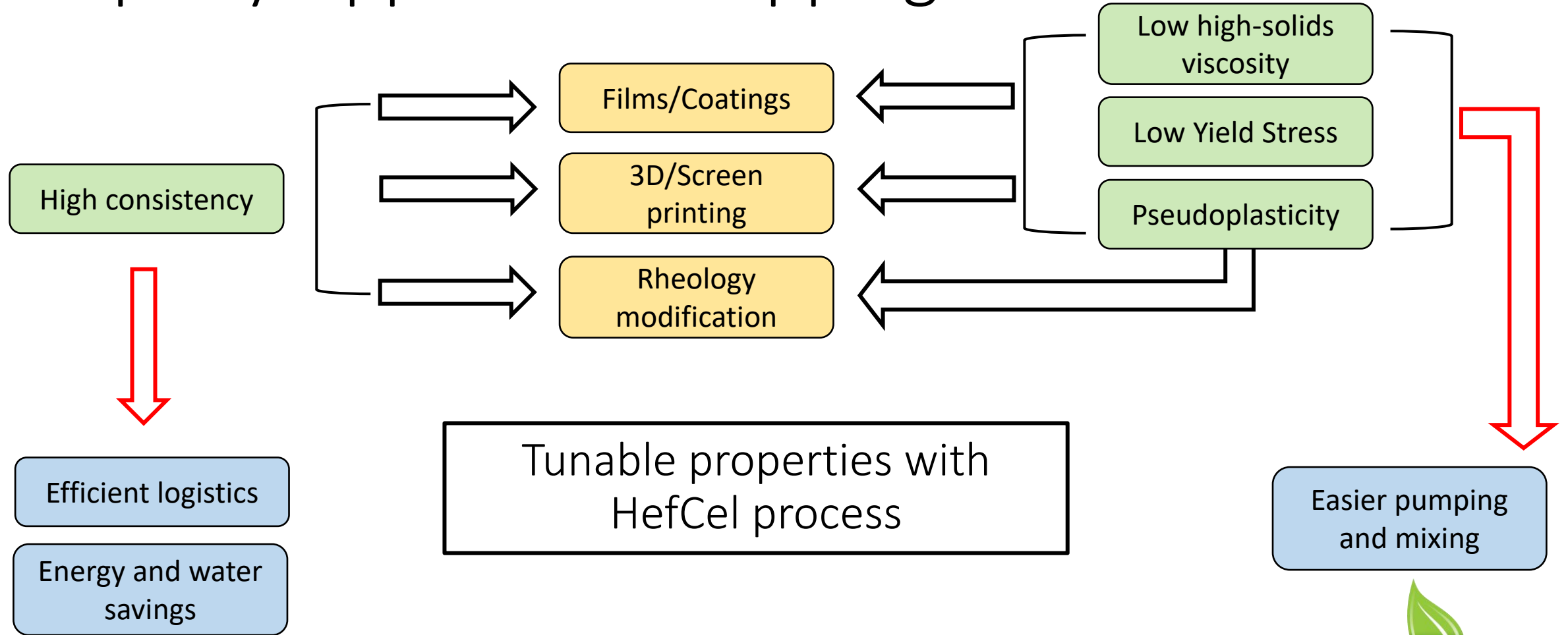
Without film



With 50 gsm film



Property-Application mapping





Questions and Comments

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