A Comparison of Films from High Lignin Content Wood Fibers and Microfibrils

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High-density hot-pressed fibers

Masoinite HDF

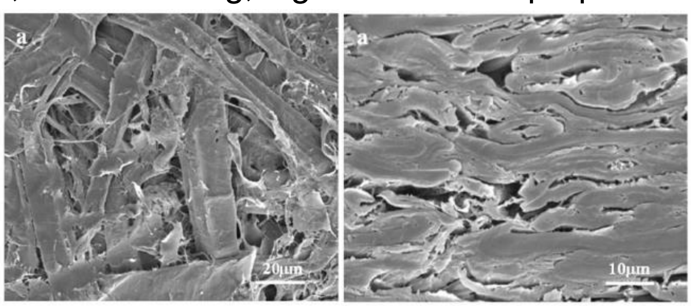
"Without commitment to a particular theory I believe that the **lignins**, which are plastic under conditions of <u>heat</u>, <u>moisture</u> and <u>pressure</u> hereinafter described, serve for producing a welding or coalescing of the cellulose fibers in the surface portion of my product solidly together…"

Mason W. H., US Patent, 1931, [US1812969A]

A light-delignification of wood fibers:

- diameter enlargement & cell wall thickness reduction
- Increase in lignin coverage (reduction in total lignin)

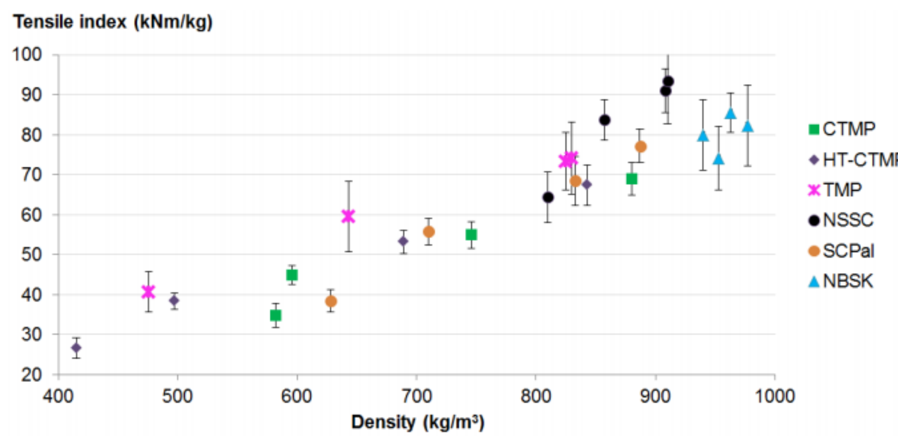
Facile compaction, better binding, high mechanical properties



Wang Q, et al. (2018) Scientific Reports. 8: 955.

High yield pulps

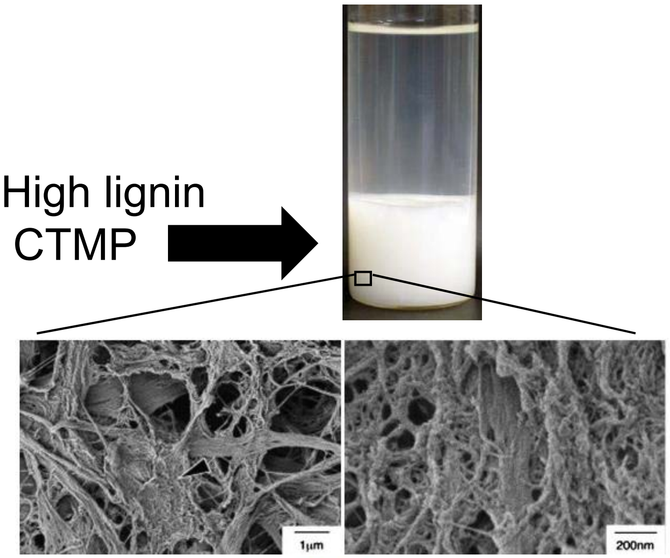
- Process condition (temperature, pressure, moisture, time)
- Mechanism (density, lignin,…)
- Type of pulp



Joelsson T (2020) Licentiate thesis, Mid Sweden University, Sundsvall, 2020

Microfibrillated Lignocellulose (MFLC) and hot-pressed films

High lignin
CTMP



E ~ 10 Gpa
Bend σ ~ 220 MPa

Abe K, Nakatsubo F, Yano H (2009) Composites Science and Technology. 69: 2434–2437

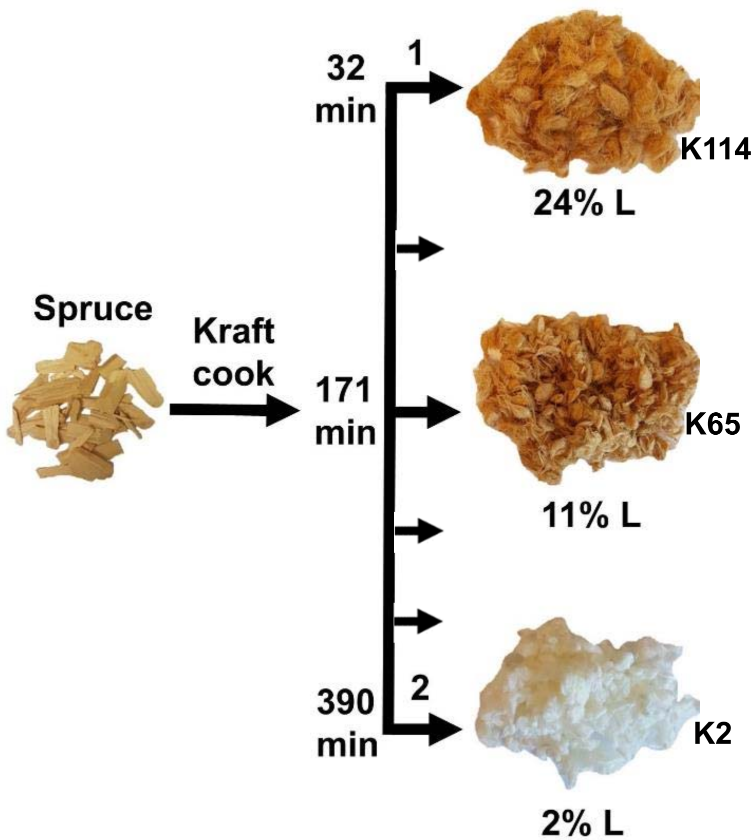
Sulfur dioxide-ethanol-water treated high lignin fibers

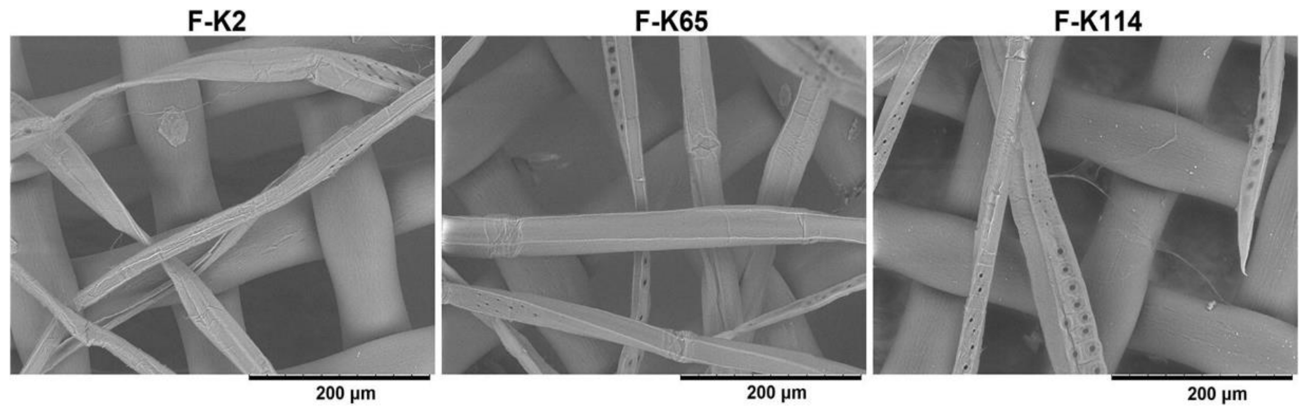
- Softening & flow of lignin
(pores/voids filling, smoother surface, barrier properties)
- Binding function

E ~ 13 Gpa
σ ~ 160 MPa

Rojo, E et al. (2015) Green Chemistry 17 (3): 1853-1866.

Production of pulp fibers





	Cellulose (%)	Lignin (%)	Hemicellulose (%)		Length (mm)	Width (mm)	Kink index
			Glucomannan (%)	Xylan (%)			
K2	79.6	**1.8**	10.0	8.6	2.51 (0.1)	33.2 (0.3)	1.68 (0.01)
K27	76.5	**5.1**	9.8	8.6	2.45 (0.0)	34.8 (0.5)	0.77 (0.03)
K34	75.4	**6.2**	9.8	8.6	2.47 (0.0)	33.8 (0.1)	0.63 (0.02)
K65	69.7	**11.0**	9.9	8.0	2.48 (0.0)	35.7 (0.1)	0.49 (0.02)
K96	64.1	**16.9**	9.6	7.7	2.46 (0.0)	39.1 (0.6)	0.45 (0.01)
K114	57.2	**23.6**	9.7	7.5	2.48 (0.0)	39.1 (0.1)	0.42 (0.01)

Liquor / wood = 4, Effective alkali 18 %, Sulfidity 20 %, 160 °C

$$\text{Kink index} = \frac{2N_{20°-50°} + 3N_{50°-90°} + 4N_{90°-180°}}{L_{tot}}$$

Sample	Lignin (%)	Pulping time (min)	Total pulping yield (%)	Mechanical defibration	Bleaching
F-K114	23.6	32	70.4	Yes	-
F-K96	16.9	90	62.1	Yes	-
F-K65	11.0	171	56.5	-	-
F-K34	6.2	312	53.0	-	-
F-K27	5.1	390	51.4	-	-
F-K2	1.8	390	48.8	-	Yes

Mechanical defibration:

Sprout-Waldron refiner

Bleaching:

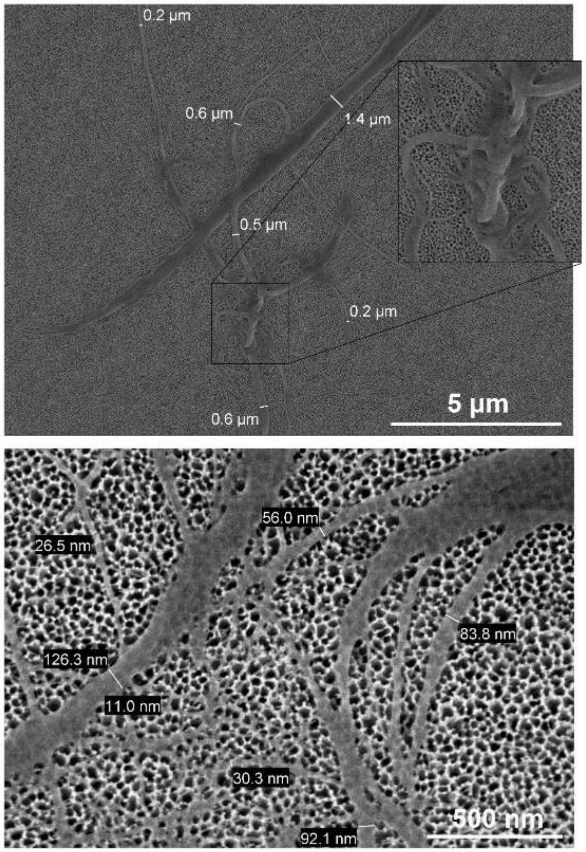
Steps	Active chemical charge (w%)	T (°C)	P (bar)	t (min)	pH
EO	-	100	8	30	Alkali charge = 2.5 w%
D0	4	80	-	120	4
D1	2.8	80	-	120	4
D2	1	80	-	120	4
D3	0.5	80	-	120	4

*pulp consistency = 10%

- Cooking temperature 160 °C
- Liquid to wood ratio 4:1
- Effective alkali $\left(\frac{(n_{NaOH} + n_{Na_2S}) \times 40}{m_{wood}} \times 100\right)$ 18 %
- Sulfidity $\left(\frac{2n_{Na_2S}}{n_{NaOH} + 2n_{Na_2S}} \times 100\right)$ 20 %

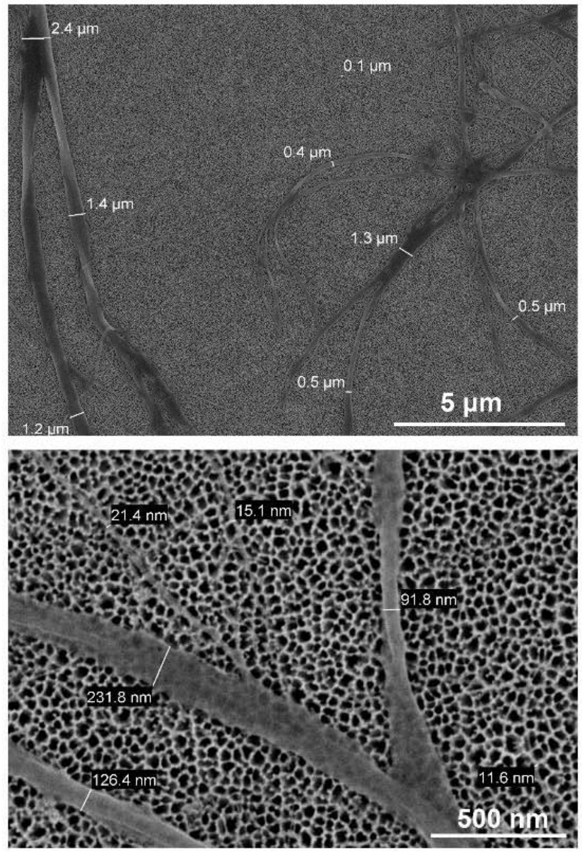
MFLC morphology

MFLC-K2



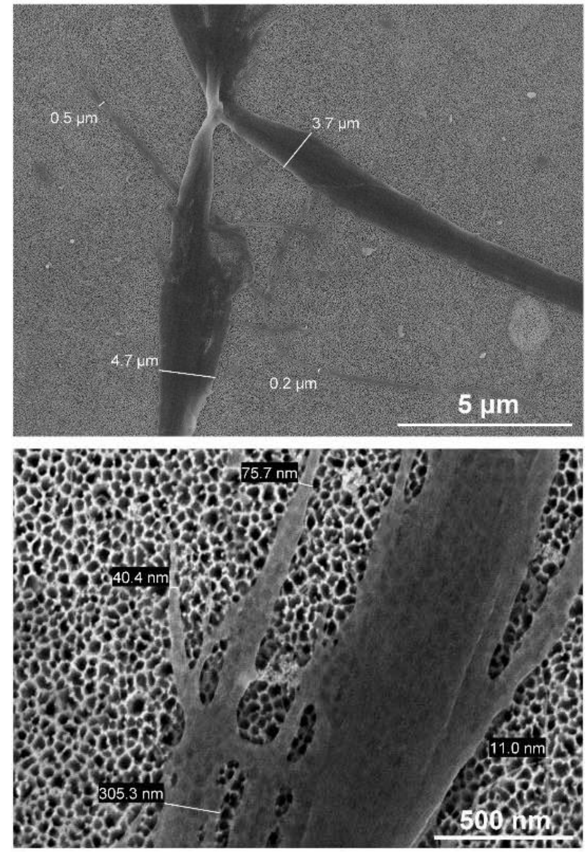
2.5 nm – 0.8 µm Ø

MFLC-K65



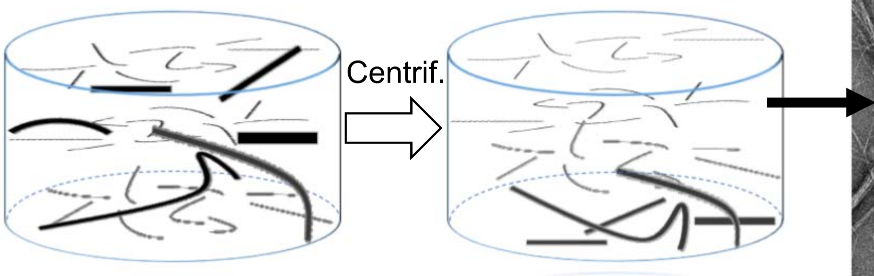
2.5 nm – 0.8 µm Ø

MFLC-K114

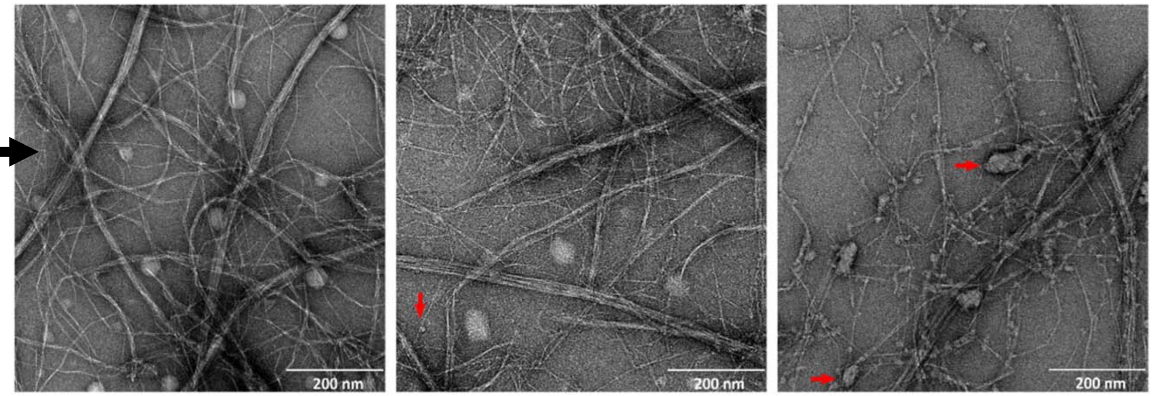


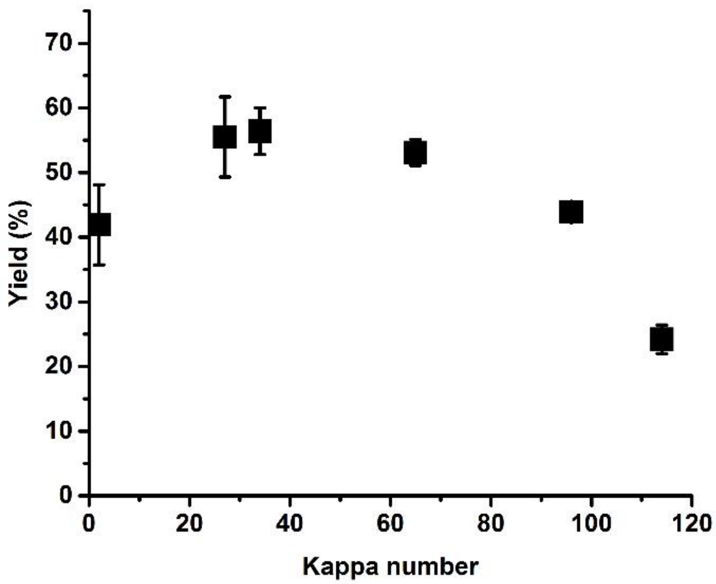
2.5 nm – **2 µm** Ø

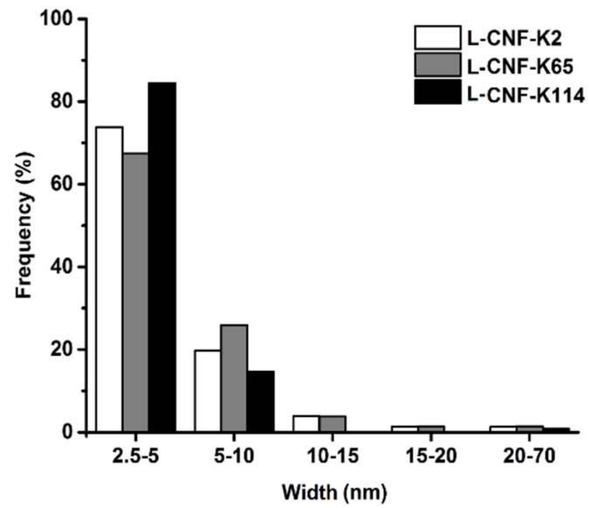
Nano-sized fraction (yield)



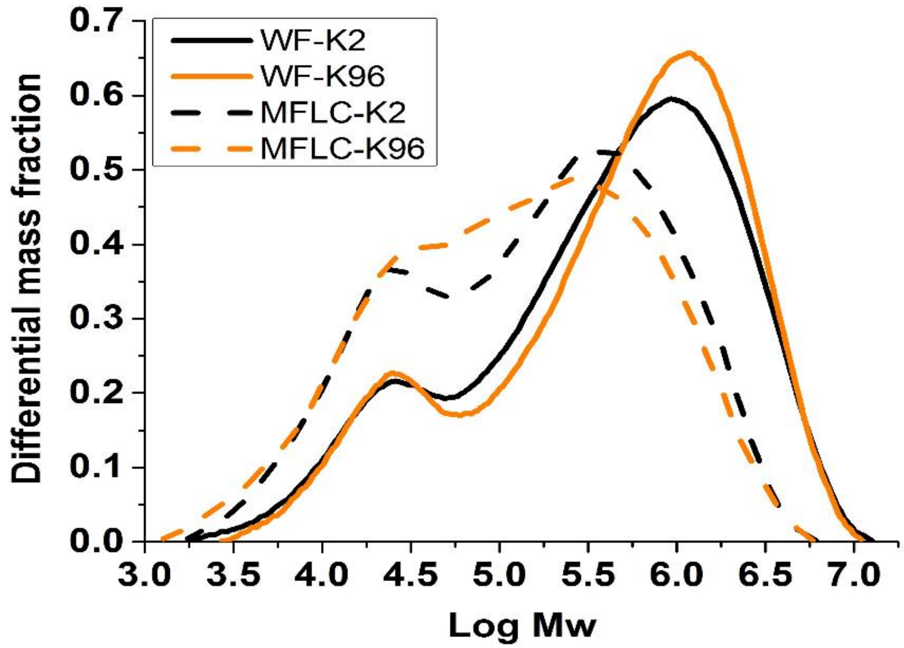
LCNF-K2 | LCNF-K65 | LCNF-K114





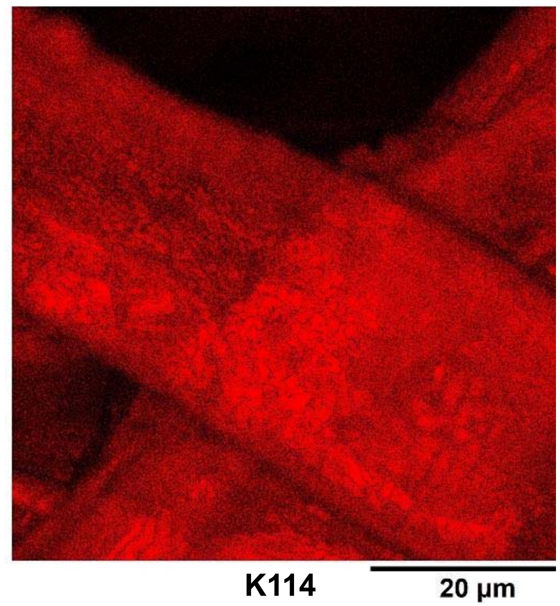


Molar mass and lignin coverage



Sample	$M_W \times 10^6$ (g/mol)	PDI	DP	L (µm)*
WF-K2	1.04	14.3	6420	-
WF-K96	1.10	12.9	6790	-
MFLC-K2	0.45	11.3	2778	2.7
MFLC-K96	0.39	11.7	2407	2.3

**Assuming cellulose Iβ unit cell and full extension along chain axis (c parameter=10.38 Å)*

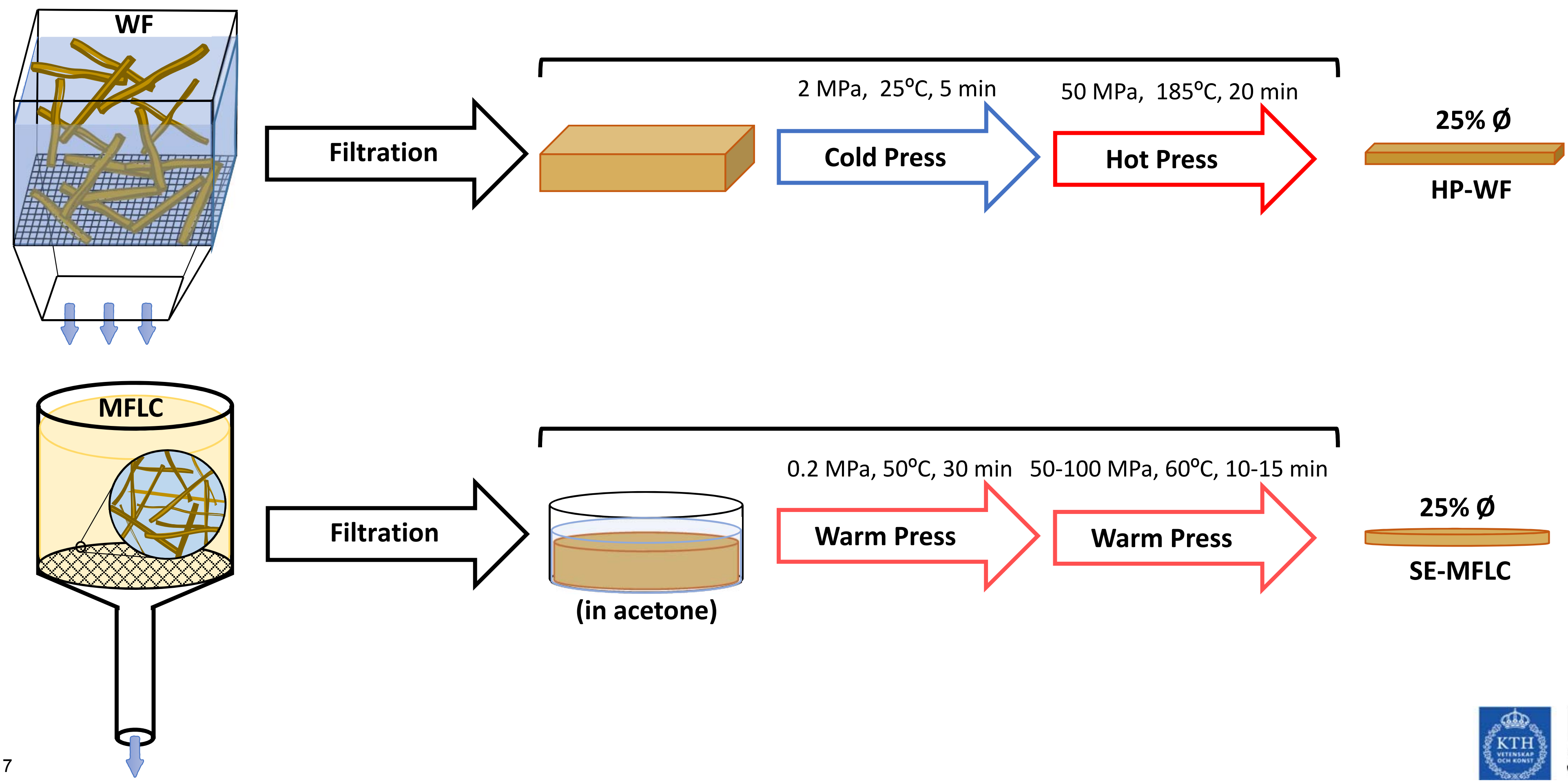


K114

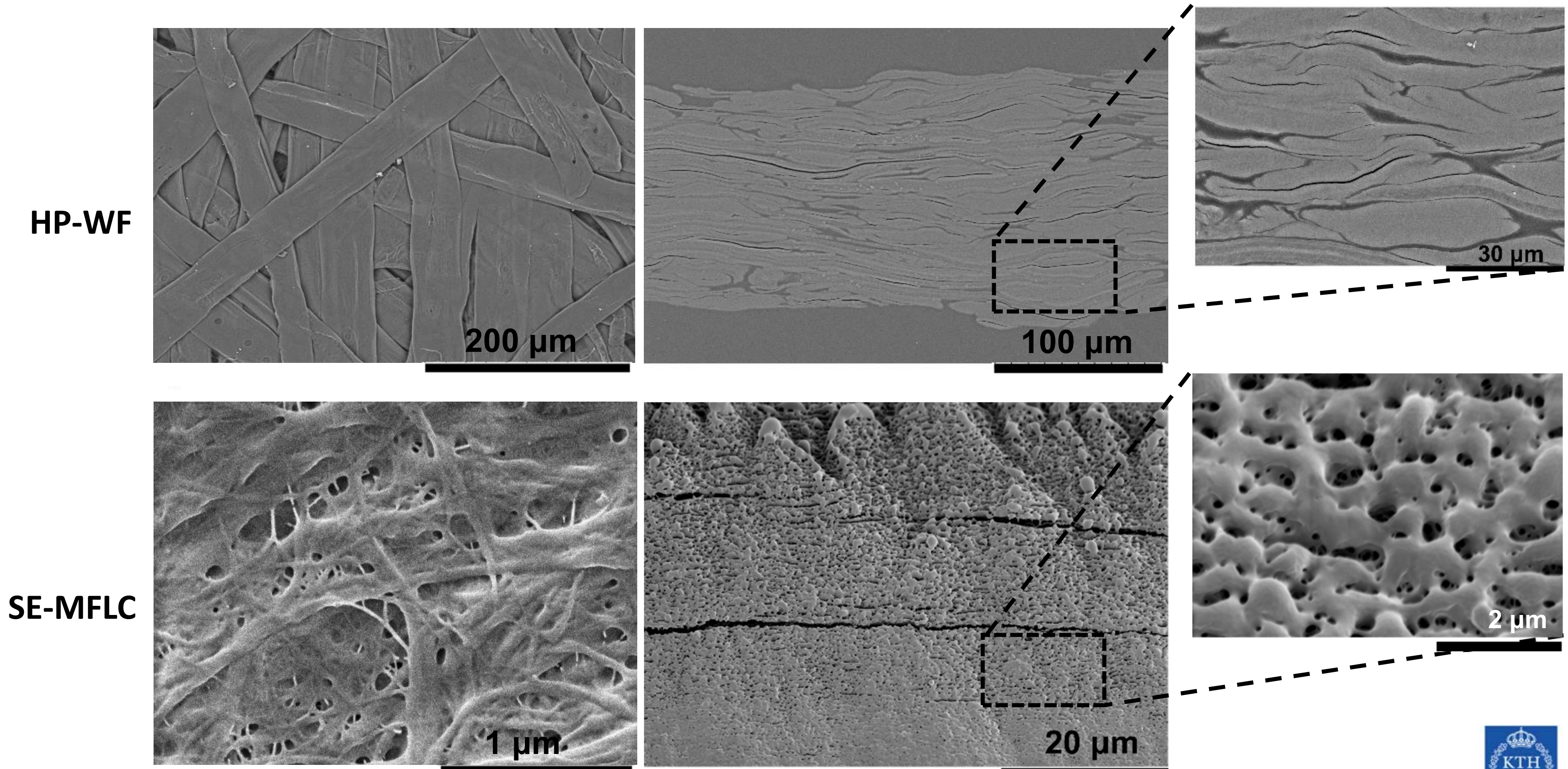
Excitation 543 nm
Emission 633 nm

-

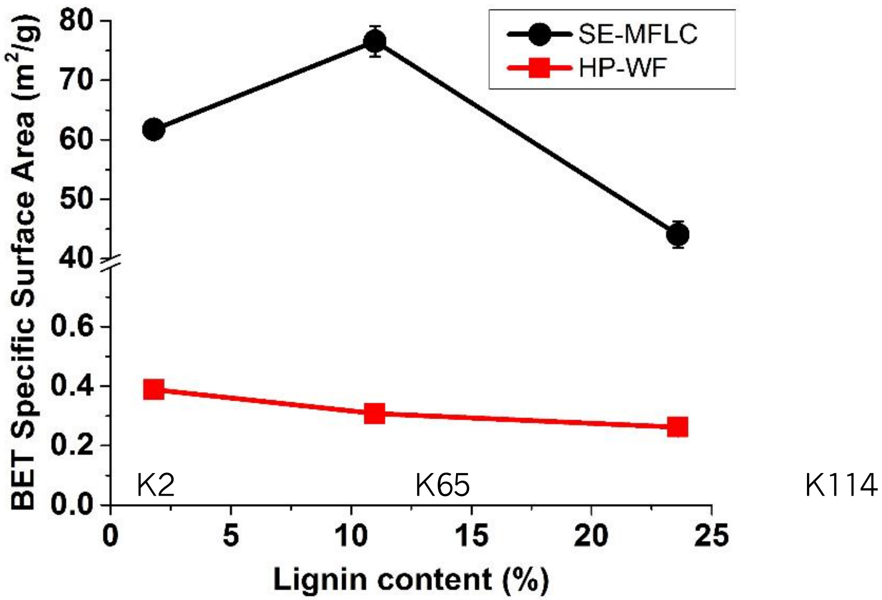
Comparable wood fiber and MFLC films (same density)

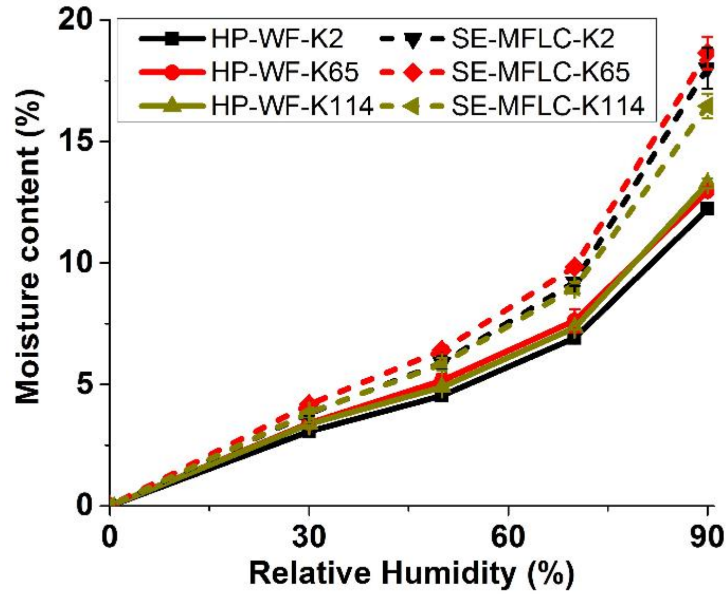


Microstructure of HP-WF vs SE-MFLC

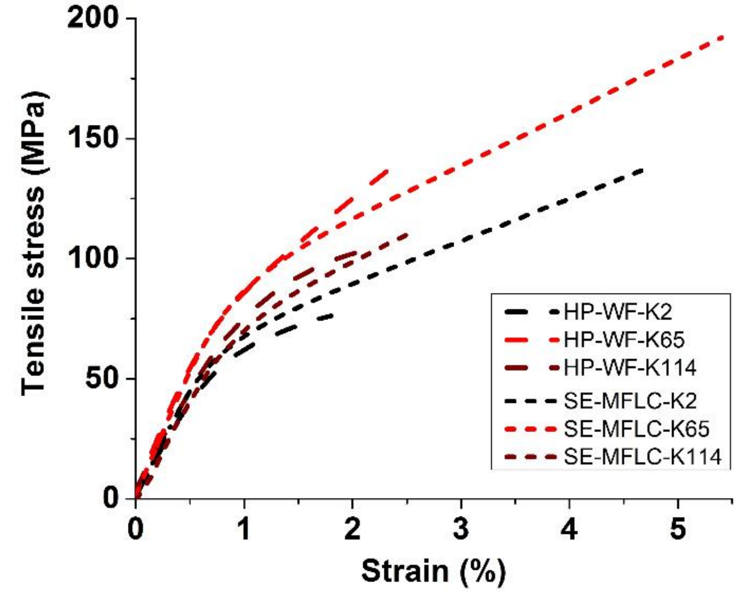


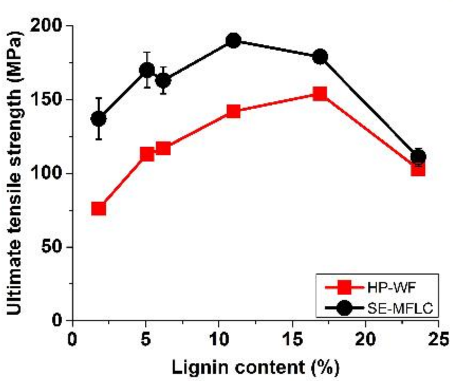
Surface area and moisture absorption

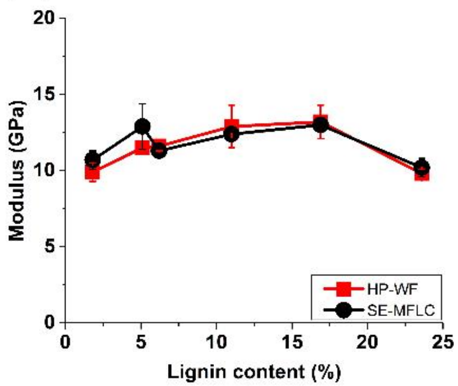


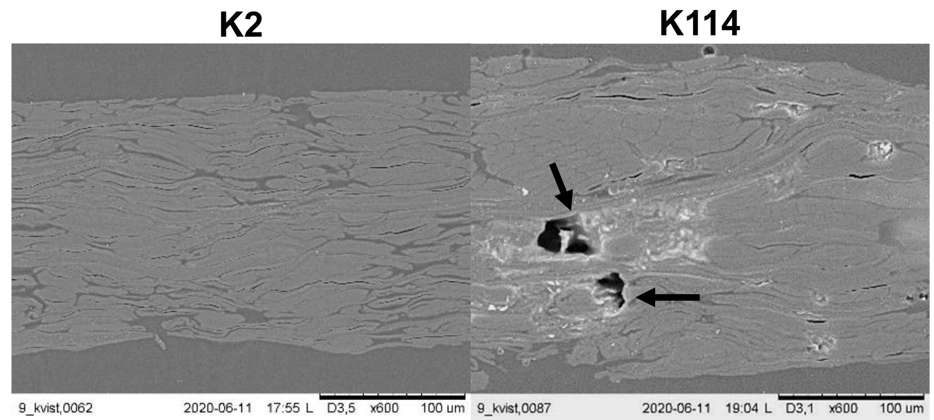


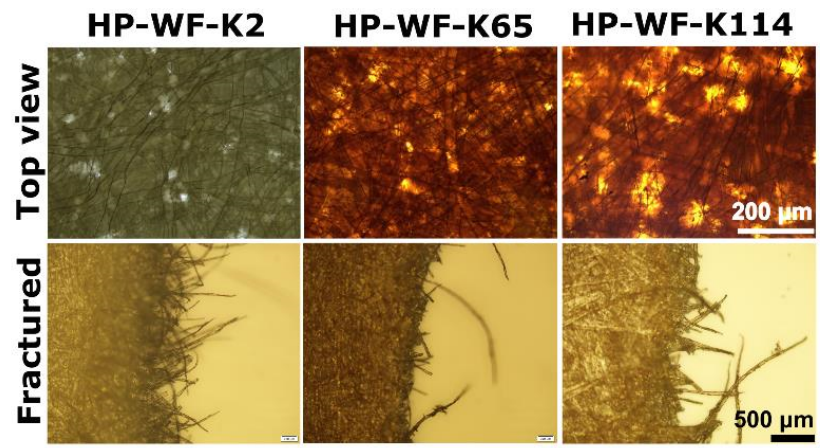
Mechanical properties of WF vs MFLC films





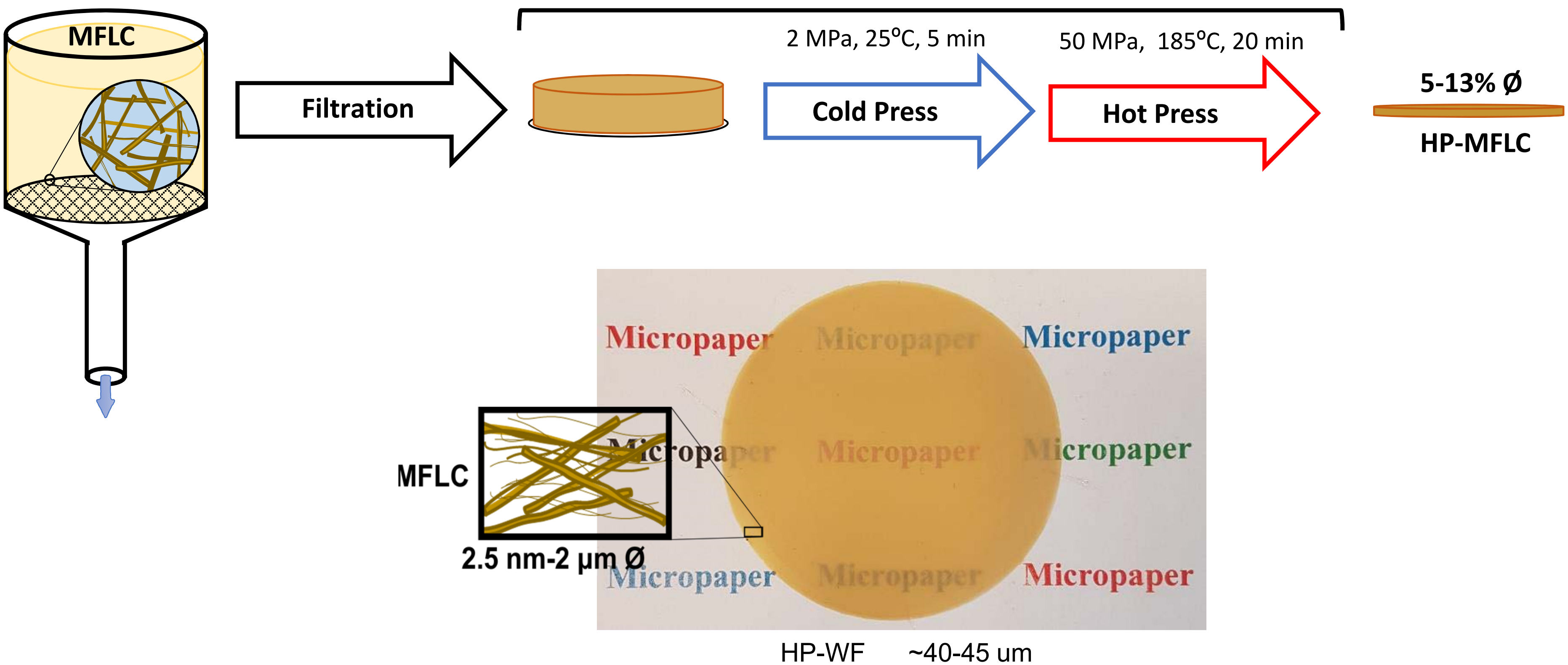




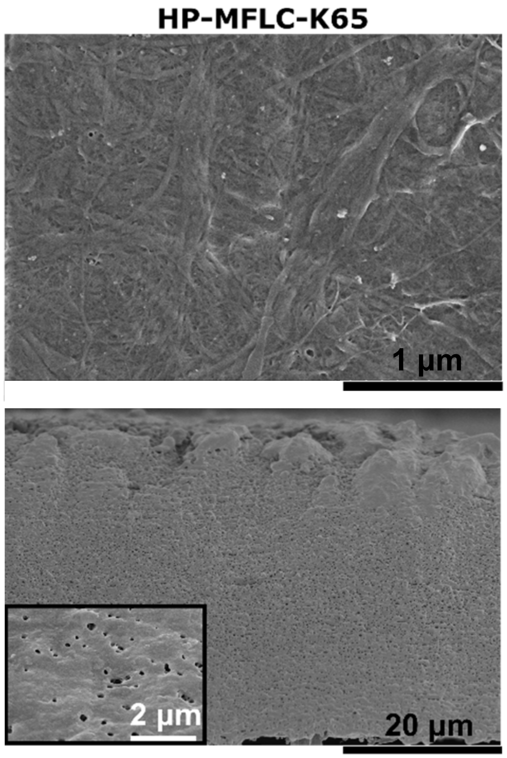


SE-MFLC ~52 um
HP-WF ~170 um

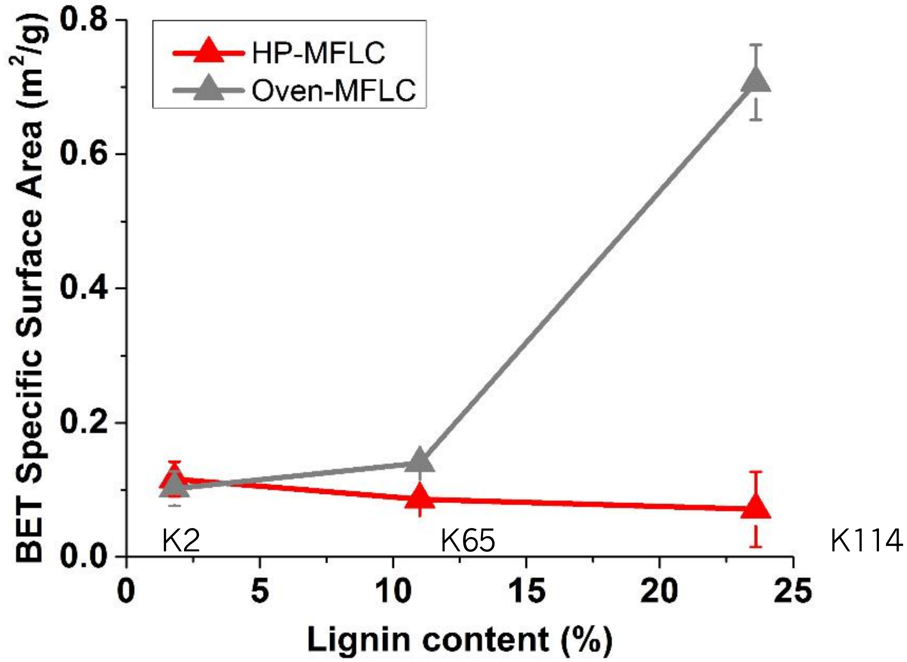
High-density MFLC films



Hot-pressed MFLC

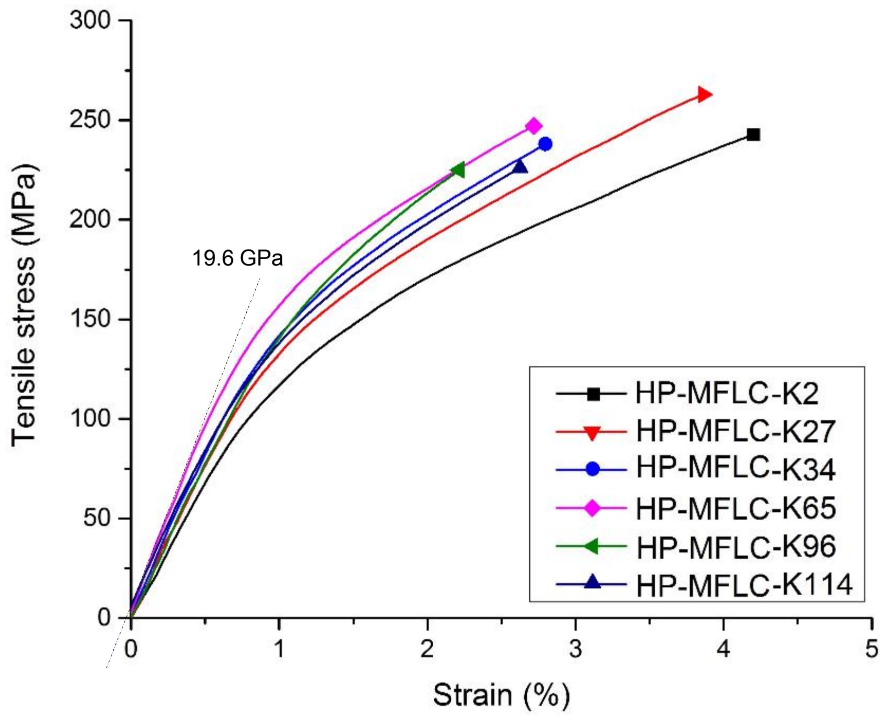


Ø = 6%

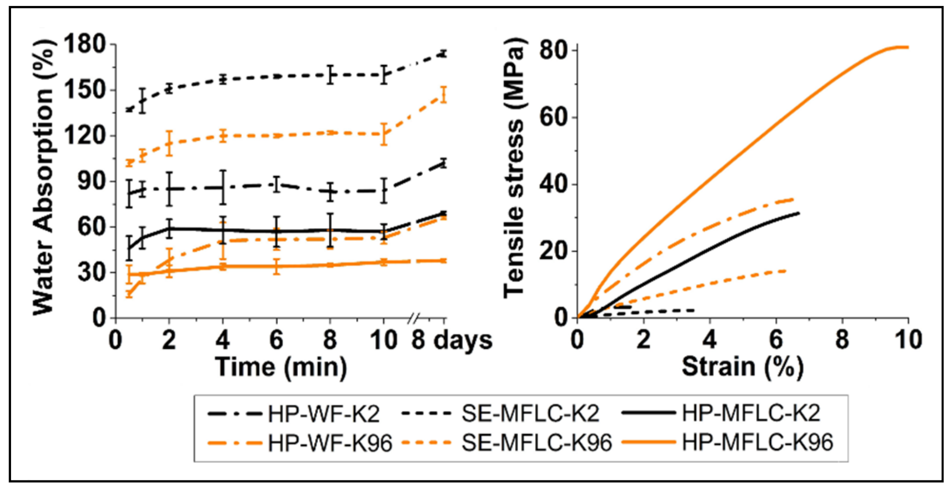


HP-MFLC

- Dry- and wet- mech prop / water absorb



Sample	Density (g/cm^3)	Apparent porosity (%)	Ultimate strength (MPa)	Modulus (GPa)	Elongation at break (%)
HP-MFLC-K2	1.43 (0.06)	5 (0)	242 (4)	17 (1.2)	3.9 (0.4)
HP-MFLC-K27	1.42 (0.02)	5 (0)	263 (17)	18.9 (0.8)	3.9 (0.1)
HP-MFLC-K34	1.41 (0.05)	6 (0)	237 (10)	17.3 (0.5)	2.8 (0.3)
HP-MFLC-K65	1.41 (0.06)	6 (0)	247 (4)	19.6 (1.9)	2.7 (0.2)
HP-MFLC-K96	1.37 (0.04)	9 (0)	225 (4)	16.8 (0.2)	2.2 (0.1)
HP-MFLC-K114	1.30 (0.05)	13 (1)	226 (10)	16.6 (0.7)	2.6 (0.2)



Main findings

Wood fiber and MFLC film (same 25% porosity):

- Hot-pressed wood fibers (HP WF) have similar modulus to the MFLC films (≈13 GPa)
- Ultimate tensile strength of HP WF was as high as 154 MPa, while for strain-hardening SE MFLC as high as 190 MPa. (larger defect/pore size)
- Increased lignin up to ~17% improved interfiber/interfibril bonding & stress transfer (particularly for HP WF)
- At very high lignin content (≈24%), MFLC and fiber films show large defects and inhomogeneity, resulting in reduced mechanical properties.

Hot-pressed MFLC films:

- HP MFLC films show remarkable, yield strength (160-170 MPa), ultimate strength (260 MPa) and modulus (20 GPa), despite presence of coarse fibrils
- Limited water swelling and high wet-strength

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