# High performance man-made cellulosic fibres from recycled newsprint

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List of terms related to spinning and fiber properties

Dry – jet wet spinning	The spinning dope is extruded via an air gap (where the filament remains in liquid form) into the coagulation bath. The filaments are allowed to be stretched in the air gap which results in an orientation of cellulose polymer chains along the spinning axis.
Extrusion velocity (V <sub>e</sub> )	The speed of dope extruded from the spinneret. The velocity is expressed as ml/min.
Take-up velocity (V <sub>tu</sub> )	The rotation speed of the take-up godet where the fibre is collected. The velocity is expressed as m/min.
Draw ratio (DR)	A measurement of the stretching during the orientation of a filament. The ratio between take-up velocity and extrusion velocity. DR = $V_{tu}/V_e$ .
Titer	In textile industry, titer expresses as the ratio of the weight of a fibre to the length. The unit used is dtex which stands for weight in gram per 10000 meters.
Tenacity	The measure of strength of a fibre. Unit in cN/tex
Elongation	The fibre deformation caused by a force. It is expressed as a percentage of the original fibre length.

#### 1. Experimental methods

Acid organosolv pulping of deinked newsprint. To simulate the propylene glycol (PG) pulping of deinked newsprint (which consist of mainly softwood), we utilized softwood thermo-mechanical pulp (TMP) as a raw material in the PG pulping. The fractionation of TMP was done in pure propylene glycol with a liquor-to-solid ratio of 10:1 at 170 °C and a sulfuric acid charge of 0.3 wt% as catalyst. The fractionation was done in 5 different durations: 30, 60, 90, 120 and 150 min. The PG pulps were then washed thoroughly and air-dried prior to dissolution. To compare with the PG pulping of TMP, the SO<sub>2</sub>-ethanol-water (SEW) pulping of TMP was carried out at 135 °C (80 and 120 min) and 150 °C (60 and 100 min) with a liquor-to-solid ratio of 6. The weight fraction SO<sub>2</sub>:ethanol:water is 12:44:44. In addition to TMP, the deinked newsprint was also treated in a SEW process at 150 °C from 20, 40, 60 and 80 min. The SEW pulps were washed thoroughly afterwards and air-dried prior to use.

**Rheology measurement.** The rheological properties of the spinning dopes were analysed by means of an Anton Paar MCR 300 rheometer with a parallel plate geometry (25 mm plate diameter, 1 mm measuring gap). The complex viscosity and the dynamic moduli (storage modulus G' and loss modulus G'') were determined by means of a dynamic frequency sweep over an angular frequency range of 0.1 -100 s<sup>-1</sup> at temperatures ranging from 50 to 100 °C. The zero shear viscosity was determined by fitting the complex viscosity data with the Cross model.<sup>27</sup>

**Molecular weight distribution.** The molar mass distribution (MMD) of the raw materials and fibres was determined by gel permeation chromatography (GPC). Before the analysis, the samples were ground and delignified for better solubility. The pulps and fibres were pre-activated by a water/acetone/*N*,*N*-dimethylacetamide (DMAc) solvent exchange sequence. The samples were then dissolved in a 90 g/l lithium chloride (LiCl)/DMAc mixture at room temperature. Finally, the solution was diluted to 9 g/l LiCl/DMAc and filtered through a 0.2 µm syringe filter and analyzed by using a Dionex Ultimate 3000 system with a precolumn (PLgel Mixed-A, 7.5 × 50 mm), four analytical columns (4 × PLgel Mixed-A, 7.5 × 300 mm) and a refractive index (RI) detection (Shodex RI-101).

**Chemical composition.** The chemical composition (carbohydrate, Klason lignin and acid soluble lignin) of the raw materials and fibres were analysed according to NREL/TP-510-42618. Carbohydrates were identified and quantified by means of high-performance anion exchange chromatography with pulse amperometric detection (HPAEC-PAD) using a Dionex ICS-300 system. The cellulose and hemicellulose contents were calculated according to the amount of monosaccharides following the Janson formula<sup>28</sup> based on pinewood (exact wood species mix of DNP is unknown). According to the chromatography data, the newsprint consists mainly of softwood, thus, factors from pinewood were used. Acid-soluble lignin (ASL) was determined with a Shimadzu UV 2550 spectrophotometer at a wavelength of 205 nm using an absorption coefficient of 110 L g<sup>-1</sup> cm<sup>-1</sup>.

**Mechanical properties.** Linear density (titer), conditioned and wet tenacity were measured at 20 °C and 65% RH using a Vibroskop 400 and Vibrodyn 400 (Lenzing Instruments GmbH & Co KG, Austria). The settings for the Vibrodyn 400 were as follows: gauge length 20 mm, strain rate 20 mm/min and pre-tension (5.9±1.2) mN/tex. Ten fibres of each sample were measured. The birefringence of the fibres was determined using a Zeiss Axio Scope A1 polarised light microscope with a Leica B 5 $\lambda$ -Berek tilting compensator. Three filaments of each sample were measured. The linear density was determined three times for each filament by using the Vibroskop, and the diameter was calculated by using a density value of 1.5 g cm<sup>-3</sup>.<sup>29</sup> The retardation of the polarised light was determined three times from a selected spot on the fibre. The birefringence  $\Delta$ n was calculated by dividing the retardation of polarised light by the diameter of the filament. The total orientation f<sub>\_tot</sub> was obtained by dividing  $\Delta$ n by 0.062, which is the maximum birefringence of cellulose.<sup>30</sup> Lyocell and viscose fibres from Lenzing AG (Austria) were used as reference fibres for the comparison of the mechanical properties.

**X-ray diffraction (XRD).** The samples were cut into pieces and gently pressed into the sample holder (thickness 1 mm). X-rays were generated with a conventional sealed X-ray tube with a copper anode. The radiation was focused and monochromatized ( $\lambda = 1.541$  Å) with Montel optics (Incoatec, Geesthacht, Germany) and detected with a Pilatus 1M (Dectris, Baden-Daettwil, Switzerland). The samples were measured in perpendicular transmission geometry; the sample-to-detector distance

was 8.5 cm. The scattering angle was calibrated with silver behenate and lanthanum hexaboride standards. Measurement times were 30 min. The scattering intensity was corrected for the geometry of the detector, absorption, polarisation and air scattering.

The crystallite size was calculated with the Scherrer formula:

$$s = \frac{0.9\lambda}{\sqrt{FWHM_{peak} - FWHM_{inst}}\cos\theta}$$

where  $\lambda$  is the used wavelength,  $\theta$  half of the scattering angle, FWHM<sub>peak</sub> and FWHM<sub>inst</sub> the full width at half maximum of the diffraction peak and the instrumental broadening, respectively. The instrumental broadening was determined from the width of the diffraction peak of lanthanum hexaboride.

The crystallinity was calculated with the amorphous fitting method adapted for cellulose II.<sup>31</sup> The diffraction pattern was modelled with an amorphous background (sulfate lignin) and 19 Gaussian functions in positions based on the diffraction pattern of cellulose II.

**Dynamic vapour sorption.** A dynamic vapour sorption (DVS) intrinsic apparatus (Surface Measurement system, London, UK) with a measuring accuracy of 0.1 µg was used for water vapour sorption analysis. Approximately 10 mg of a pre-dried fibre bundle was placed in the sample pan and preconditioned at a relative humidity (RH) of 0% at 23.8 °C until the equilibrium was reached using nitrogen (flow rate 100 cm<sup>3</sup> s<sup>-1</sup>). The adsorption cycle was performed in 10% RH steps to a maximum of 90% RH, and vice versa for the desorption cycle. In both cases, the RH was kept constant until a defined equilibrium condition was reached, *i.e.* dm/dt was less than 0.001% per minute over a 10 minutes period. The hysteresis of the sorption and desorption isotherms is calculated as:

 $Hysteresis = (M_{desorption} - M_{sorption})/M_{sorption}$ 

**Yarn Spinning.** The yarn formation, which consists of carding, drawing, roving and ring spinning, and it was performed at Tampere University of Technology, Finland. The AlkaPoIP DNP fibres were carded (using Laboratory carding machine, Mesdan 337A) in 25 g batches twice. The carded webs were

pleated into slivers. A blend sliver was formed by pleating different fibre type webs together. The sliver was then drafted and two drafted slivers were combined together to form a roving (with Stiroroving lab, Mesdan 3371). Subsequently, the roving was ring spun by Mesdan ring lab 3108A. The spinning was done by blending AlkaPoIP DNP fibres and commercial viscose fibres (from Kelheim Fibres GmbH, carded and roved in the same procedure as AlkaPoIP DNP fibres) with equal amount. The total draft in ring spinning was 22. The yarn had 700 twist/meter.

## 2. Kraft pulping parameters

	H25	H50	H500	H1000	H1500
Sulphidity, %	40	40	40	40	40
Alkali charge, % EA	20	20	20	20	20
Liquor to solid ratio	10	10	10	10	10
Cooking temperature,°C	130	130	170	170	170
H-factor	25	50	500	1000	1200
Cooking time, min	92	116	98	131	162

 Table S1. Kraft cooking parameters and conditions.

## 3. Molar mass distribution of Kraft DNP and fibres



Figure S1. The molar mass distribution of kraft DNPs and spun fibres.

	Mn kg/mol	Mw kg/mol	Mz kg/mol	Mz+1 kg/mol	< DP50	< DP100	> DP2000	PDI
DNP	82.37	473.95	1716.12	3334.97	0.0%	1.7%	38.4%	5.75
H500 DNP	76.02	463.98	1626.61	3354.84	0.9%	3.3%	38.2%	6.10
H1000 DNP	79.85	450.29	1573.95	3264.65	0.6%	2.9%	37.6%	5.64
H1500 DNP	103.26	608.58	1915.78	3614.80	0.3%	2.0%	46.3%	5.89
H500 DNP 10 kGy	73.28	330.60	1317.10	3940.23	0.9%	3.2%	27.7%	4.51
H500 DNP 10 kGy	73.79	321.73	1053.66	2317.73	0.8%	3.1%	28.2%	4.36
H500 DNP 10 kGy	75.53	334.71	1101.78	2436.33	0.8%	3.2%	29.7%	4.43
H1000 DNP 10 kGy fibre	75.48	321.87	1173.80	2329.04	0.6 %	2.6 %	24.4 %	4.26
H1500 DNP 10 kGy fibre	65.25	342.09	1295.13	2563.32	1.1 %	3.6 %	26.1 %	5.24

**Table S2**. The average molar mass of kraft DNPs and spun fibres.

4. Characterization of propylene glycol (PG) treated TMP pulps and SO<sub>2</sub>-Ethanol-Water (SEW) treated TMP and DNP pulps



Figure S2. The molar mass distribution of PG treated TMPs at 170 °C.

Table S3. The average	molar mass of	PG treated	TMPs at 170 °C.
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	Mn kg/mol	Mw kg/mol	Mz kg/mol	Mz+1 kg/mol	< DP50	< DP100	> DP2000	PDI
30 min	50.385	127.100	442.877	1165.960	0.6%	3.9%	7.6%	2.52
60 min	44.654	114.276	387.494	963.607	1.3%	5.3%	6.6%	2.56
90 min	47.703	102.306	233.226	484.481	0.9%	4.5%	4.3%	2.14
120 min	37.005	73.721	182.915	468.490	1.9%	6.9%	2.1%	1.99
150 min	33.954	63.458	192.351	2122.466	2.3%	8.1%	1.1%	1.87

Table S4. Characterization of PG treated TMPs

	Yield %	Viscosity ml/g	Cellulose %	Hemicellulose %	Lignin %
ТМР	100		42.6	27.0	30.4
30 min	76.4	145	49.4	26.7	23.9
60 min	72.8	125	56.2	25.1	18.7
90 min	67.9	111	62.3	23.1	14.6
120 min	62.0	106	69.8	18.9	11.3
150 min	56.5	90	80.3	10.1	9.6



Figure S3. The molar mass distribution of SEW treated TMPs and DNPs at 135 and 150 °C.

	Temp. °C	Time min	Mn g/mol	Mw g/mol	Mz g/mol	Mz+1 g/mol	< DP50	< DP100	> DP2000	PDI
ТМР	150	60	43.41	211.4329	1132.80	3001.66	2.1%	7.1%	16.4%	4.87
ТМР	150	100	30.98	138.18	1904.10	5588.86	4.1%	10.5%	5.7%	4.46
TMP	135	80	41.204	230.630	1043.11	2341.88	2.7%	8.1%	19.1%	5.60
TMP	135	120	45.81	151.32	472.75	980.81	1.8%	6.9%	11.7%	3.30
DNP	150	20	29.12	69.18	249.24	1150.07	4.2%	11.1%	1.3%	2.38
DNP	150	40	33.15	92.34	397.92	1365.59	3.4%	9.5%	3.6%	2.79
DNP	150	60	30.20	79.19	326.48	1359.00	4.2%	10.9%	2.3%	2.62
DNP	150	100	30.28	62.01	117.85	243.78	3.8%	10.7%	0.8%	2.05

Table S5. The average molar mass of SEW treated TMPs AND DNPs at 135 and 150 °C.

Substrate	Temp. °C	Time min	Yield %	Viscosity ml/g	Cellulose %	Hemicellulose %	Lignin %
TMP			100		42.6	27.0	30.4
TMP	150	60	58.8	99	65.9	25.1	9.0
TMP	150	100	47.6	94	78.8	16.9	4.3
TMP	135	80	74.9	130	54.4	25.6	20.0
TMP	135	120	63	110	63.0	26.1	10.9
DNP			100		45.0	27.0	28.0
DNP	150	20	68.9	129	65.1	21.9	13.0
DNP	150	40	57.9	118	72.4	20.9	6.7
DNP	150	60	50.4	102	79.2	17.0	3.8
DNP	150	100	47.1	103	83.8	14.3	1.9

Table S6. Characterization of SEW treated TMPs and DNPs.

#### 5. Molar mass distribution of AlkaPolP DNPs



Figure S4. The molar mass distribution of AlkaPolP DNPs at 170 °C



Figure S5. The molar mass distribution of AlkaPolP DNPs at 180 °C.

 Table S7. The average molar mass of AlkaPolP DNPs.

Temp. °C	Time h	Mn kg/mol	Mw kg/mol	Mz kg/mol	Mz+1 kg/mol	< DP50	< DP100	> DP2000	PDI
170	1	88.79	519.34	1808.47	3464.66	0.3%	2.3%	39.8%	5.85
170	2	69.60	513.13	2472.93	5320.85	1.1%	3.9%	33.2%	7.37
170	3	78.05	621.78	2958.62	6428.71	0.8%	3.3%	38.4%	7.97
180	1	70.26	396.37	1426.52	2815.86	1.0%	3.7%	31.6%	5.64
180	2	58.50	329.70	1323.92	2623.46	1.5%	5.0%	24.5%	5.64
180	3	54.86	311.92	1738.55	3838.16	1.4%	5.5%	19.9%	5.69

#### 6. Tensile properties of the fibres spun from AlkaPolP DNPs

Fibres	Draw ratio	Titer (dtex)	Dry tenacity (cN/tex)	Dry elongation %	Wet tenacity (cN/tex)	Wet elongation %	Young's modulus (MPa)
170 °C 3 h	12	1.31	37.82	9.73	32.13	11.12	17.40
170 °C 3 h	18	0.87	37.03	8.69	36.9	9.59	16.00
180 °C 1 h	12	1.18	40.95	8.92	34.95	9.02	16.74
180 °C 1 h	18	0.76	43.89	8.04	37.5	8.69	14.15

Table S8. Tensile properties of spun fibres from AlkaPolP at DR=12 and maximum DR=18.

### 7. X-ray diffraction (XRD) of AlkaPolP DNP pulps



Figure S6. The normalized X-ray diffraction patterns of selected raw materials and fibres.

# 8. Monolayer (ML) hydration

Table S9. The ML hydration (sorption and desorption) of the fibres at selected draw ration and its
main governing factors.

Samples	Draw		ML hydratio	n	Lignin	Hemicellulose	Degree of
	Draw	Sorption	Desorption	Hysteresis		nemicellulose	Degree Of
	ratio	g/g	g/g	%	70	70	orientation
AlkaPoPI 180 C 60min	1	0.0695	0.0886	27	4.76	21.56	0.605
AlkaPoPI 180 C 60min	10	0.0630	0.0853	35			0.675
AlkaPoPI 180 C 60min	18	0.0641	0.0821	28			0.719
AlkaPoPI 170 C 180min	1	0.0696	0.0871	25			0.623
AlkaPoPI 170 C 180min	10	0.0651	0.0861	32	3.63	20.95	0.682
AlkaPoPI 170 C 180min	18	0.0672	0.0833	24	]		0.675