Supporting Information of "Recycling of Vat and Reactive Dyed Textile Waste to New Colored Man-Made Cellulose Fibers"

Simone Haslinger,[a] Yingfeng Wang,[a] Marja Rissanen,[a] Miriam Beatrice Lossa,[b] Marjaana Tanttu,[c] Elina Ilen,[c] Marjo Määttänen,[d] Ali Harlin,[d] Michael Hummel,[a] Herbert Sixta[a]*

[a]Department of Bioproducts and Biosystems, Aalto University, Espoo, P. O. Box 16300, FI-00076, Aalto, Finland, simone.haslinger@aalto.fi, yingfeng.wang@aalto.fi, marja.rissanen@aalto.fi, michael.hummel@aalto.fi, herbert.sixta@aalto.fi

[b.]Department of Chemistry and Biology, Hochschule Fresenius, University of Applied Science, Limburger Str. 2, 65510 Idstein, Germany

[c] Department of Design, Aalto University, 02150 Espoo, Otaniementie 13, marjaana.tanttu@aalto.fi, elina.ilen@aalto.fi

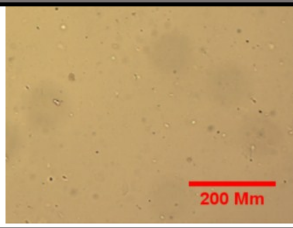
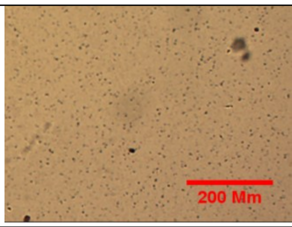
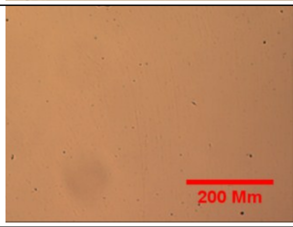
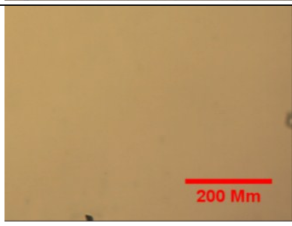
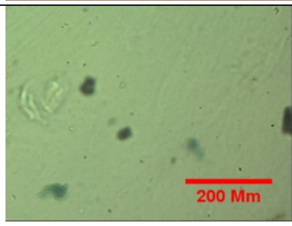
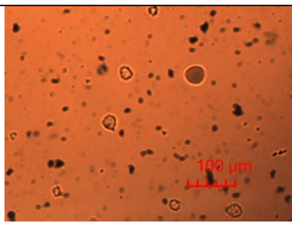
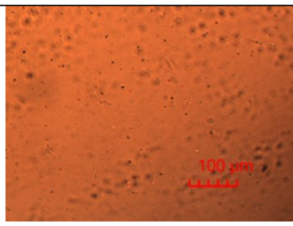
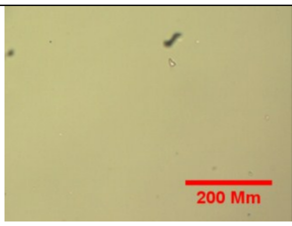
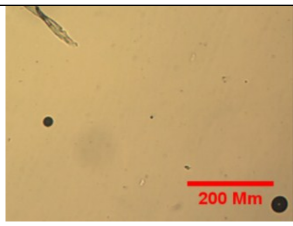
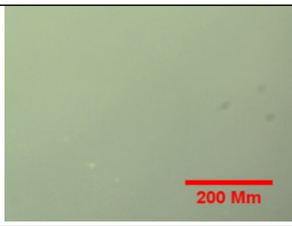
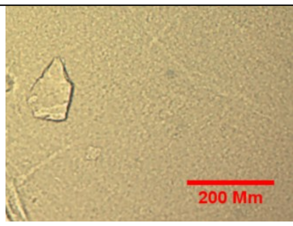
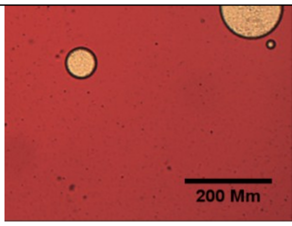
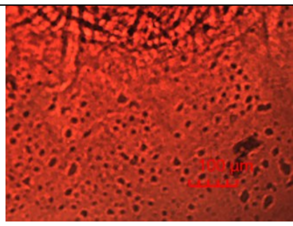
[d] VTT Technical Research Centre of Finland Ltd, Espoo, P.O. Box 1000, FI-02044 VTT, Finland, marjo.maattanen@vtt.fi, ali.harlin@vvt.fi

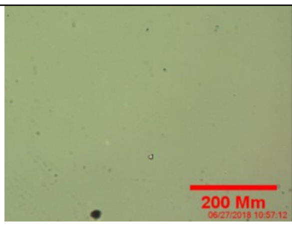
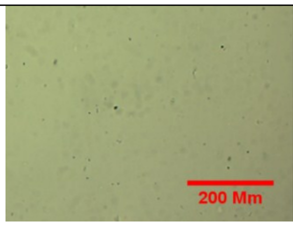
Table of Contents

Dissolution Experiments

Table S1 summarizes the heating stage microscopy experiments conducted for the dyes in pure [DBNH] [OAc] and for the dyed cotton substrates dissolved in the ionic liquid. As displayed below, all dyes apart from Indanthren Blue BC 3% dissolved homogenously. The same also applied for all spinning solutions.

Table S1 Micrograph images of the dyes dissolved in [DBNH] [OAc] and the spinning solutions prepared from dyed cotton fabrics. A reference without dyes was added for comparison.

Sample	Ionic Liquid + Dye	Spinning Solution
Blank	n.a.	
Indanthren Brilliant Red FBB		
Indanthren Brilliant Green FBB Coll		
Indanthren Blue BC 3%		
Remazol Black B gran 133%		
Remazol Brilliant Blue R spec		
Levafix Brilliant Red E-4BA		

Levafix Blue E-GRN gran		

Grey Scales

Figure S1 and Figure S2 depict the grayscales employed to assess color change and staining during wash fastness testing. In both cases, 5 describes no color difference, while the values 4-1 indicate a color change with increasing intensity.

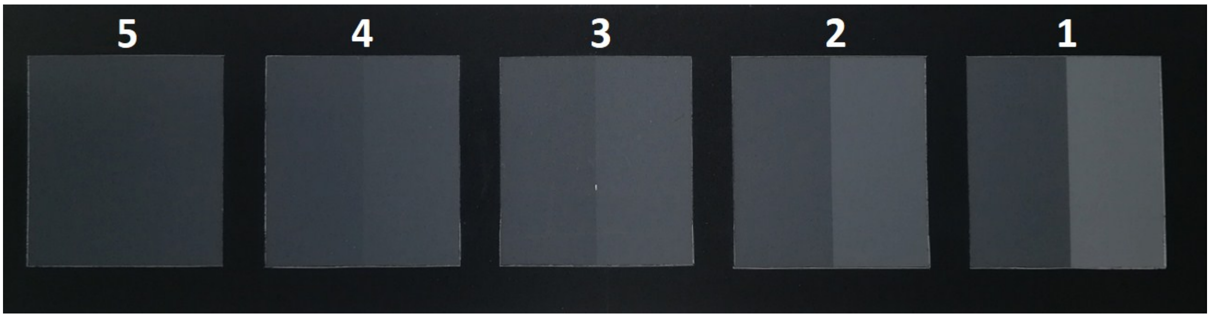


Figure S1 Greyscale for assessing color changing in wash fastness testing. 5 represents no change of color, while 1 denotes the largest color difference

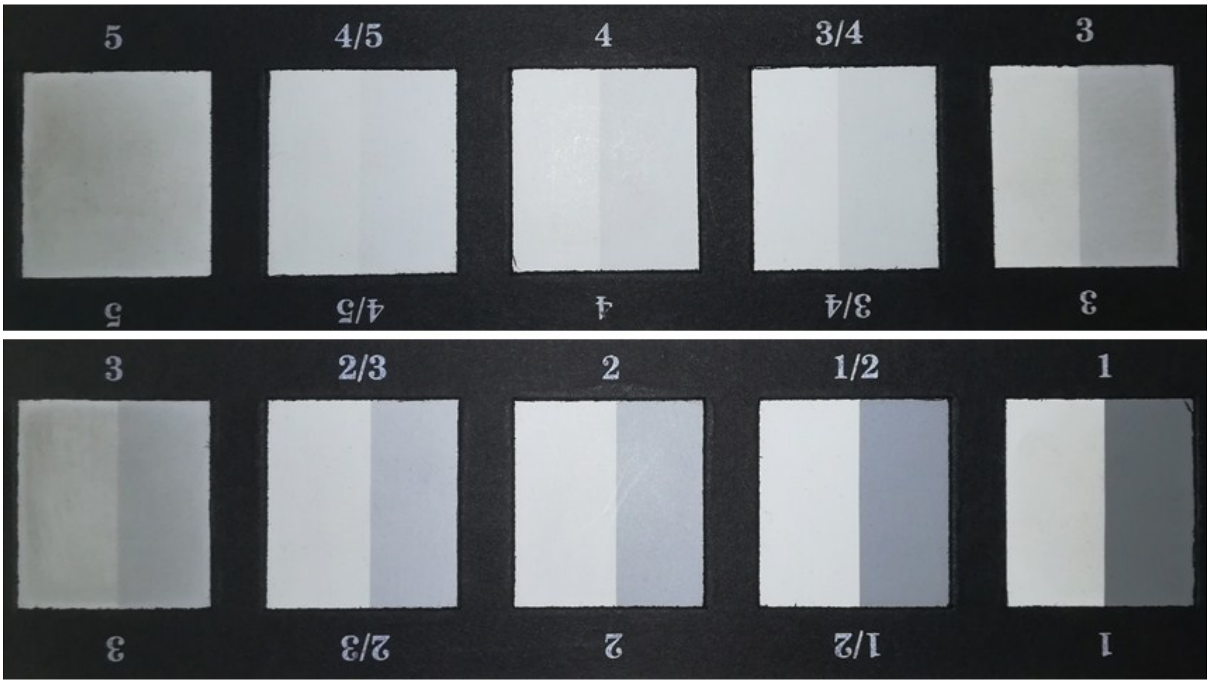
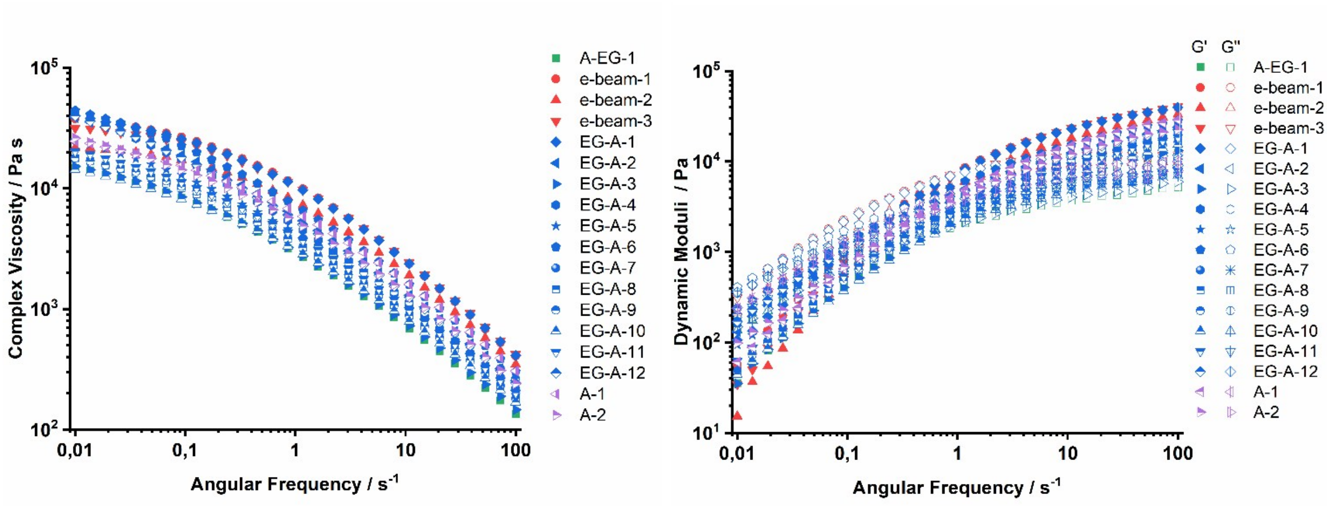


Figure S2 Greyscale for assessing staining during wash fastness testing. 5 describes no staining, while 1 respresents the severest case of staining.

Rheology Data

Figure S3 and Figure S1 illustrate the complex viscosity η* of and of the dynamic moduli (G',G'') as a function of the angular frequency ω of all tested post- and pre-consumer samples. The post-consumer substrates Indanthren Red FBB and Levafix Brilliant Red E-4BA exhibited an evident gel character due a crossover point (COP) at very low angular frequencies, or due to the complete absence of the COP. Besides, their complex viscosities were altered to a rather linear trend as compared to the remaining samples that approached a Newtonian plateau at lower angular



frequencies.

Figure S3 Rheogramms of the dyed pre-consumer samples as a function of the angular frequency ω at 70°C. Left: Complex viscosities η*. Right: Storage and Loss Moduli (G',G'').

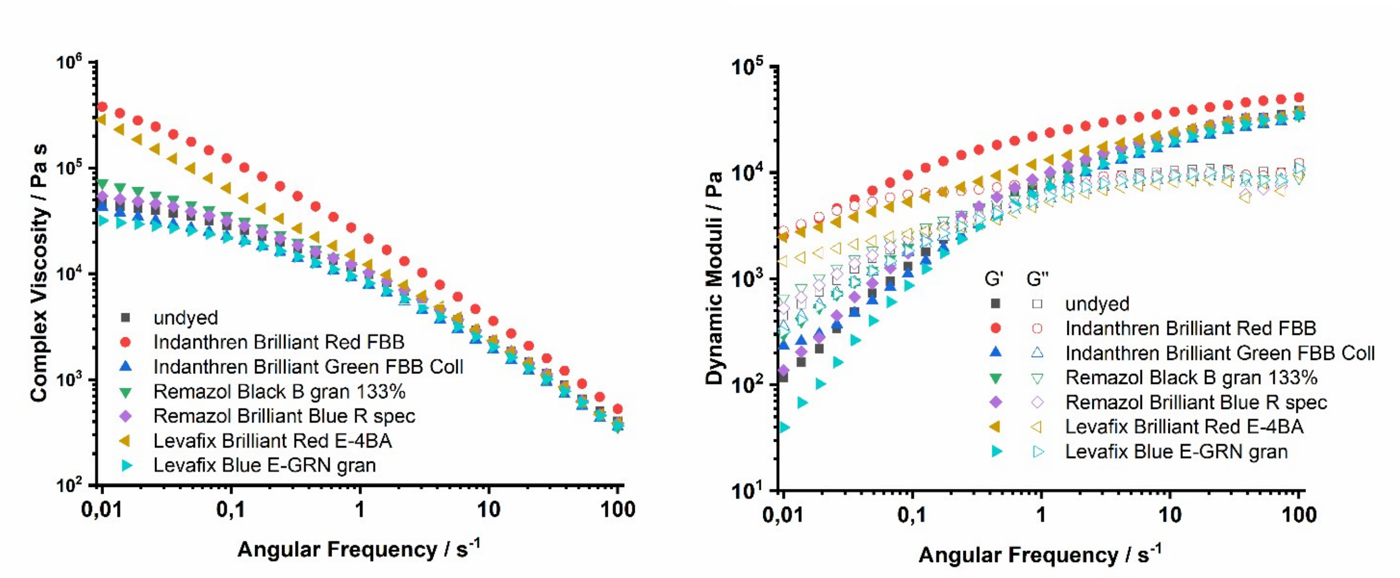


Figure S4 Rheogramms of the dyed post-consumer samples as a function of the angular frequency ω at 65°C. Left: Complex viscosities η*. Right: Storage and Loss Moduli (G',G'').

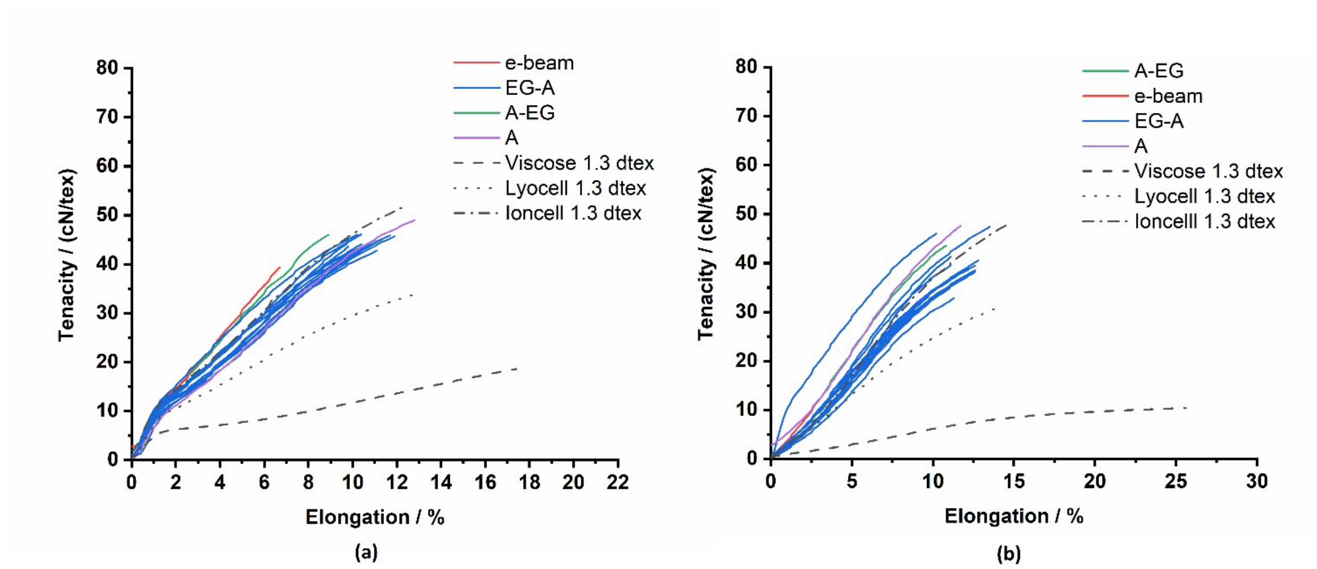
Table S2 summarizes the rheological properties of all spinning solutions close to their spinning temperatures at concentrations of 13-14%. It is shown that two of the e-beam samples as well as one acid pretreated sample were not spinnable. Most non-spinnable samples showed a high crossover point of the dynamic moduli (G',G'') as compared to the rest of the samples. The zero shear viscosities η0* of the post-consumer samples were on average higher than as compared to the pre-consumer dopes. As further illustrated here, the bad spinnability of Levafix Brilliant Red E-4BA can most likely be attributed to the strong gel character of the cotton solution, which is displayed in the high apparent zero shear viscosity and the absence of the cross-over point.

Table S2 Rheological properties of all samples tested for dry-jet wet spinning including spinnability, cotton concentration (wt%) of the spin dope, η0* zero shear viscosity (Pa s), storage and loss moduli G' and G'' (Pa) at their crossover point according to the spinning temperature T (°C).

	Sample	Spinnable	Cotton / wt%	T / °C	η_0* / Pa s	ω / (1/s)	G'=G'' / Pa
pre-consumer (dyed with Indanthren Blue BC 3%)	e-beam-1	yes	13	70	38535	0.85	7013
	e-beam-2	no	13	70	22473	1.29	6306
	e-beam-3	no	14	70	32269	1.08	7670
	A-EG-1	yes	13	70	16421	0.62	1633
	EG-A-1	yes	13	70	46127	0.32	2432
	EG-A-2	yes	13	70	45613	0.34	2533
	EG-A-3	yes	13	70	17319	0.67	1721
	EG-A-4	yes	14	70	58342	0.16	1502
	EG-A-5	yes	14	70	29139	0.47	2066
	EG-A-6	yes	14	70	51225	0.35	3123
	EG-A-7	yes	14	70	31298	0.27	1539
	EG-A-8	yes	14	70	20587	0.55	1847
	EG-A-9	yes	14	70	20190	0.59	2149
	EG-A-10	yes	14	70	16173	1.09	2270
	EG-A-11	yes	14	70	23207	0.80	2532
	EG-A-12	yes	14	70	50412	0.20	1813
	A-1	no	13	70	25335	1.16	4830
	A-2	yes	13	70	27739	0.65	2980
post-consumer	Undyed	yes	13	65	47490	0.42	4554
	Indanthren Brilliant Red FBB	yes	13	65	37213	0.76	4913
	Indanthren Brilliant Green FBB Coll	yes	13	65	41235	0.37	3484
	Remazol Black B gran 133%	yes	13	65	78176	0.29	4319
	Remazol Brilliant Blue R spec	yes	13	65	55899	0.18	3131
	Levafix Brilliant Red E-4BA	no	13	65	812180	n.a.	n.a.
	Levafix Blue E-GRN gran	yes	13	65	32709	0.51	4317

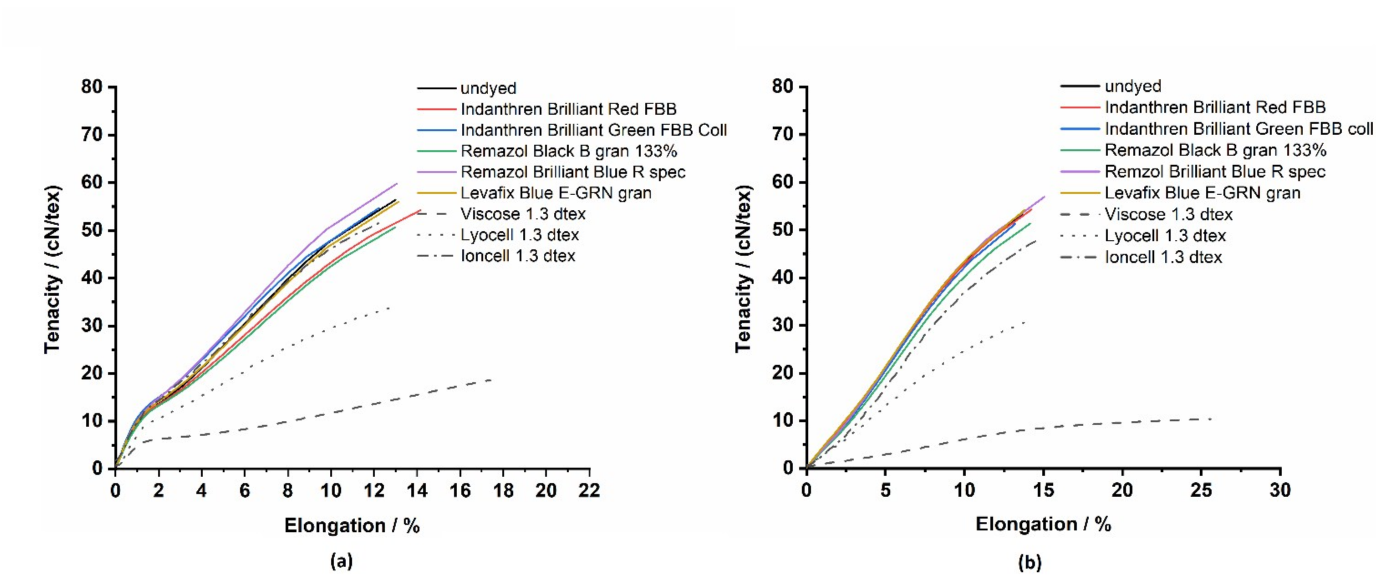
Fiber Properties

Figure S5 and Figure S6 display the average stress strain curves of all fibers spun from pre- and post-consumer waste, respectively. Both tenacities and elongations at break in conditioned and wet state were found to be higher for the samples spun from post-consumer fabrics than for the pre-consumer ones. The e-beam pretreated samples resulted in the worst fiber properties. Moreover, as shown, both commercial Viscose and Lyocell fibers exhibited significant lower tenacities, but to some extent higher elongations (Viscose). This is further confirmed by Table S3, which also includes a summary of the obtained Young's Moduli and Moduli of Toughness. The pre-consumer samples showed higher Young's Moduli and lower Moduli of Toughness than the regenerated post-consumer fibers.



The linear densities of all samples were in a similar range.

Figure S5 Average stress strain curves of all fibers spun from pre-consumer cotton according to the pretreatment empolyed (i.e. e-beam, A, A-EG). (a) in



conditioned state, (b) in wet-state

Figure S6 Average stress strain curves all fibers spun from post-consumer waste (dyed and undyed). (a) in conditioned state, (b) in wet state.

Table S3 Summary of all fiber properties spun from pre- and post-consumer cotton waste including linear density (dtex), breaking tenacity (cN/tex), elongation at break (%), Young's Moduli (GPa), and Moduli of Toughness (MPa) in conditioned and wet state.

		Conditioned					**Wet**			
	Sample	Titer / dtex	Tenacity / (cN/Tex)	Elongation / %	Young's Modulus / GPa	Modulus of Tougness / MPa	Tenacity / (cN/Tex)	Elongation / %	Young's Modulus / GPa	Modulus of Tougness / MPa
pre-consumer (dyed with Indanthren Blue BC 3%)	e-beam-1	1.4±0.2	40.3±2.7	7.4±1.4	16.37±2.78	25.6±6.7	33.7±3.3	7.25±1.03	8.3±1.6	17.4±3.6
	e-beam-2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	e-beam-3	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	A-EG-1	1.0±0.1	45.5±2.8	8.9±1.1	17.11±3.4	34.8±5.7	45.0±3.5	11.5±1.3	8.5±1.5	41.9±5.9
	EG-A-1	1.2±0.1	45.0±3.6	11.4±0.7	17.7±2.9	45.1±5.5	32.9±2.7	11.5±0.9	5.0±0.8	29.1±4.0
	EG-A-2	1.4±0.2	44.9±3.6	10.5±0.9	15.2±2.1	39.7±6.1	47.0±3.9	13.4±1.2	6.8±1.2	51.9±7.1
	EG-A-3	1.0±0.1	46.2±4.6	10.6±0.4	15.1±3.1	41.0±4.4	41.7±3.5	11.5±1.2	5.8±1.2	35.2±5.0
	EG-A-4	1.4±0.2	42.2±3.0	11.1±1.2	17.0±2.8	41.8±7.1	39.0±3.3	13.1±1.8	5.6±0.7	41.5±9.4
	EG-A-5	1.2±0.2	45.3±3.5	11.7±1.0	14.1±2.9	45.5±6.9	40.8±2.6	13.2±1.4	5.4±0.7	42.3±5.9
	EG-A-6	1.4±0.1	45.4±2.0	12.0±0.9	16.0±3.1	47.7±5.5	38.2±2.6	12.8±1.1	5.7±2.4	38.9±5.7
	EG-A-7	1.2±0.1	43.1±3.0	10.3±0.3	19.3±2.3	40.2±6.5	39.0±4.3	12.4±2.0	6.9±0.8	40.6±11.3
	EG-A-8	1.1±0.1	42.8±5.6	10.2±2.4	15.1±3.7	38.8±11.8	39.6±2.9	12.9±1.2	6.2±1.4	42.6±6.8
	EG-A-9	1.0±0.1	44.4±3.0	10.0±1.2	16.2±3.3	38.8±6.7	40.1±2.1	11.6±1.3	6.6±0.9	37.6±6.6
	EG-A-10	1.1±0.2	45.8±3.5	10.4±1.4	18.6±2.1	44.1±8.2	38.2±2.9	12.2±1.5	6.1±0.7	38.2±8.9
	EG-A-11	1.2±0.1	44.0±2.8	10.6±1.4	17.1±2.1	41.3±6.3	39.7±2.1	12.8±1.3	5.7±0.9	40.8±6.4
	EG-A-12	1.3±0.1	42.3±2.3	10.6±1.3	16.3±1.6	40.0±7.0	38.0±2.1	12.4±1.2	5.5±0.6	37.9±5.3
	A-1	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	A-2	1.2±0.1	48.5±4.1	12.8±1.3	13±3.3	53.6±9.2	47.4±4.1	12.4±3.1	7.2±1.5	49.1±15.9
post-consumer	Undyed	1.2±02	56.4±4.3	13.0±1.4	12.4±2.5	64.2±11.1	53.4±4.0	13.7±1.1	7.7±0.7	60.6±9.6
	Indanthren Brilliant Red FBB	1.4±0.4	54.4±8.4	14.3±1.0	12.5±2.2	69.5±13.0	54.3±2.3	14.3±1.1	7.3±0.3	64.9±8.0
	Indanthren Brilliant Green FBB Coll	1.3±0.2	54.7±4.4	12.3±1.9	14.4±2.3	60.0±13.9	51.2±6.0	13.2±1.5	7.3±0.7	55.6±13.0
	Remazol Black B gran 133%	1.4±0.4	50.7±8.8	13.1±1.4	12.0±2.2	59.6±13.2	51.4±2.6	14.2±1.5	7.0±0.6	59.9±9.4
	Remazol Brilliant Blue R spec	1.2±0.2	59.8±4.1	13.1±1.6	13.2±2.5	69.5±13.0	57.0±4.4	15.1±2.1	7.7±1.2	72.5±13.1
	Levafix Brilliant Red E-4BA	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	Levafix Blue E-GRN gran	1.2±0.2	56.0±4.7	13.1±1.9	13.2±2.5	64.8±14.1	54.3±4.3	13.8±1.8	7.5±0.5	62.5±12.6

Recycling of fibers from denim fabrics

Raw material. From thirteen denim fabrics provided by a textile recycling center the denim fabric sample #3 (Lee Cooper Jeans, Figure S7) was selected for the production of new fibers using the Ioncell™ process. The other denim fabrics only differed in DP and color depth, so that it can be assumed that the recycling would have been successful for other fabrics as well. The successfully spun staple fibers were spun into yarns and finally knitted into a fabric from which a blue scarf was made.

Figure S7: Jeans from Lee Cooper, sample #3: warp dyed with Indigo, weft natural undyed cotton

Pretreatment of the raw material. The used denim fabric structure consisted of Indigo dyed warps (vertically woven) and white wefts (horizontally woven). Since the average DPv of 4395 was well above the target value between 1095 and 1300 for dry jet wet spinning, the fibers were treated with endoglucanases to adjust the DP. The enzymatic hydrolysis was carried out with Biotouch C 800 (BT), an endo-1,4-β-D-glucanase, which is frequently used in textile finishing or stone washing of cellulose fibers. The enzymatic treatments were conducted at pH 5.3, 55ºC and a dosage of 20000 CMU/g at 1% consistency. The chosen enzyme did not prove to be very suitable for DP degradation so that much more drastic (and costly) conditions than those mentioned for the DP adjustment of white waste cotton had to be applied to achieve the target DPv. The kinetics of the DPv degradation are shown in Figure S8.

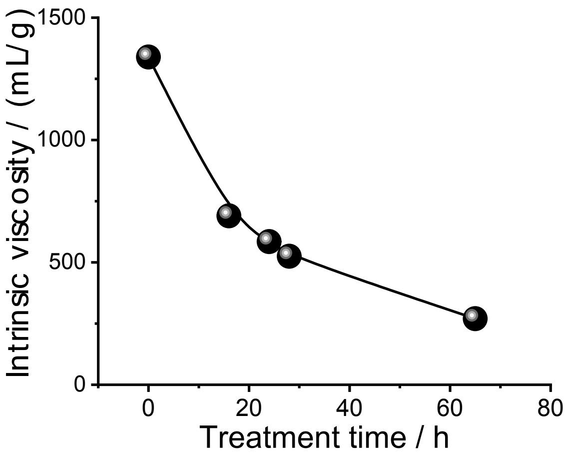


Figure S8: Intrinsic viscosity over time of cellulosic fibers derived from jeans sample #3 treated with endoglucanases (Biotouch C 800) at fixed concentration of 20000 CMU/g, temperature of 55ºC and 1% consistency.

For the preparation of the spinning dope an appropriate amount of ground sample material #3 was subjected to enzyme treatment for 28 h according to the conditions outlined in Figure S8. The resulting intrinsic viscosity of the enzyme treated sample #3 was 525 mL/g (DPv = 1280).

Dope and fiber preparation. The pretreated denim sample #3 was dissolved in [DBNH][OAc] to obtain a 13 wt% spinning dope using a vertical kneader as described in the Materials and Methods section. The undissolved particles were removed by press filtration prior to the rheological characterization. The temperature dependency of the viscoelastic properties of the dope is shown in Figure S9. The rheological properties are similar to those of the spinning solutions prepared from the enzymatically treated freshly dyed white cotton samples (Table 2), which are characterized by relatively low dynamic moduli (below 2000 Pa) caused by the broad molecular weight distribution of the cellulose sample (Mn = 45.9 kDa, Mw = 180.9 kDa; PDI = 3.9). A broad molecular weight distribution is indicative of an enzyme treated samples.

Table S4: Main results from rheological dope characterization (from oscillatory measurements) and the characterization of the Ioncell™ fibers spun from the cellulose solutions.

Sample	Rheology						Conditioned		
	Cotton / wt%	T / °C	η_0 / Pa s	ω / s^{-1}	G'=G'' / Pa	DR	Titer /dtex	Tenacity / cN/tex	Elongation / %
Sample #3	13	80	32795	0.27	1243	10	1.3	41.8±2.7	8.2±0.7
Sample #3/S7	13	85	26451	0.52	1882	9	2.3	36.9±2.9	9.6±0.9

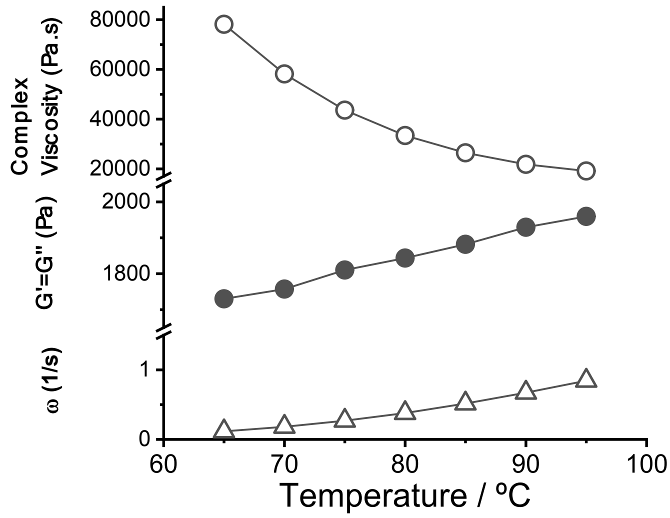


Figure S9: Temperature dependency of the 13wt% solution of enzymatically pretreated denim Sample #3: Zero shear viscosity η0* (Pa s), dynamic moduli at their crossover point (G',G'') and angular frequency at the COP, ω (1/s)

Spinnability (DR up to 15) and fiber properties are comparable to those obtained from the dyed and enzymatically pretreated white pre-consumer cotton fibers (s. Table 2 vs Table S4).

Color difference. The CIE colorimetric coordinates L*, a*, b* were determined to compare the dye intensity of the raw material, the enzymatically pretreated samples and the staple fibers. As expected, there is a significant color change in reference to the initial denim Sample #3. However, the color difference is already caused by the enzymatic treatment and continues during the spinning process.

The color change, expressed as ΔE, is, however, in the same order of magnitude as the fiber samples produced from freshly dyed pre-consumer cotton waste s.(Table 4 vs. Table S5). Essentially, the color tone is retained, but part of the color is leached out by the spinning process.

Table S5: Color difference in the CIELab space of the worn denim jeans after enzymatic treatment and after fiber spinning

Sample	L*	a*	b*	ΔE
Raw material #3	33.2	-2.5	-10.1	-
#3 enzyme treated, 28h	49.7	-4.5	-14-1	17.1
#3/S7 enzyme treated, 28 h	44.1	-2.8	-13.3	11.4
#3 fibers, DR 10	29.0	-6.5	2.7	14.0
#3/S7 fibers, DR 9	37.2	-9.3	-11.0	8.0

Note: The applied sample preparation is not optimized and the numerical results are doubtful. The samples were formed into a spherical shape, which was then pressed beneath the measuring instrument. As a result, the surface of the fibers is quite uneven, which partly falsifies the measurement. The CIELab measurement results of the fiber sample "#3 fibers, DR10" suggest a black color. In normal daylight, however, the color of the spun fibers appears blue to slightly cyan.

Yarn spinning. The spun fibres were treated with a spin finish and then subjected to yarn production as described in the Materials and Methods section. The relatively small amount of fibers allowed only the production of a relatively thick yarn with a titer of 38.1 ±2.0 tex. The fiber properties are shown in table S6 and Figure S10.

Table S6: Mechanical properties of the yarn spun from staple fibers derived from a worn denim fabric, Sample#3.

Sample	Titer / tex	Torsion Twist / m^{-1}	Elongation / %	Tenacity / (cN/tex)
#3/S7 fibers, DR9	38.1±2.0	Z	625	18.1±2.8

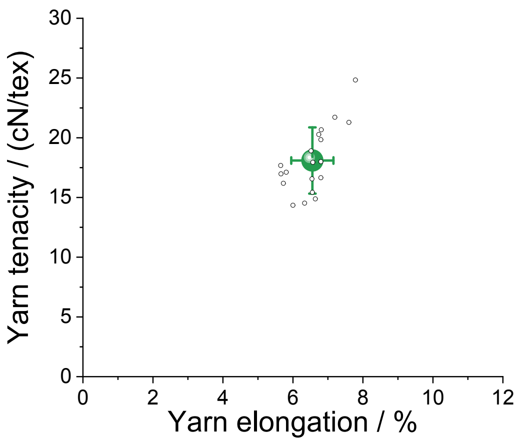


Figure S10: Individual and average stress-strain values of a 38.1 tex Z-shaped yarn with a twist of 625/m.

The yarn properties are slightly lower than those of yarns made from a standard Lyocell staple fibre. The lower utilization of the staple fiber strength for the yarn strength is again due to the low fiber quantity.

Knitted scarf. The fabric was knitted by a flatbed weft knitting machine as described in the Materials and Methods section.