Supporting Information

Poly(ε-caprolactone) Biocomposites Based on Acetylated Cellulose Fibers and Wet Compounding for Improved Mechanical Performance

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The Supporting information includes 7 total number of pages, 5 figures and 3 tables.

Solid state Nuclear Magnetic Resonance details

Cross-Polarization Magic Angle Spinning Carbon-13 Nuclear Magnetic Resonance (CP/MAS ^{13}C-NMR) spectra were recorded in a Bruker Avance III AQS 400 SB instrument operating at 9.4 T. All measurements were carried out at 295 (±1) K with a magic angle spinning (MAS) rate of 10 kHz. A 4-mm double air-bearing probe was used. Data acquisition was performed using a cross-polarization (CP) pulse sequence, i.e., a 2.95 microseconds proton 90-degree pulse and an 800 microseconds ramped (100–50 %) falling contact pulse, with a 2.5 s delay between repetitions. A SPINAL64 pulse sequence was used for ^{1}H decoupling. The Hartmann-Hahn matching procedure was based on glycine. The chemical shift scale was calibrated to the TMS-scale (tetramethylsilane, $(CH_3)_4Si$) by assigning the data point of maximum intensity in the alpha-glycine carbonyl signal to a shift of 176.03 ppm. 4096 transients were recorded on each sample leading to an acquisition time of about 3 h. The software for spectral fitting was developed at Innventia AB and is based on a Levenberg-Marquardt algorithm [27]. All samples were run as delivered (low water content) and were packed uniformly in a zirconium oxide rotor. Computations of degree of crystallinity were based on integrated signal intensities obtained from spectral fitting of the C4 spectral region [28]. The errors given for parameters obtained from the fitting procedure are the standard error of the mean with respect to the quality of the fit. The degree of substitution was estimated by spectral integration using the spectrometer software (Bruker TOPSPIN 3.0). The average degree of substitution was estimated by calibrating the integral over the cellulose spectral region (approximately 120 ppm to 40 ppm) to a value of 6, subsequently integrating the methyl carbon signal at about 21 ppm. The integration procedure was repeated five times. Fibril surface degree of substitution was calculated using the fibril surface-to-volume ratio obtained by spectral fitting of the C4-region.

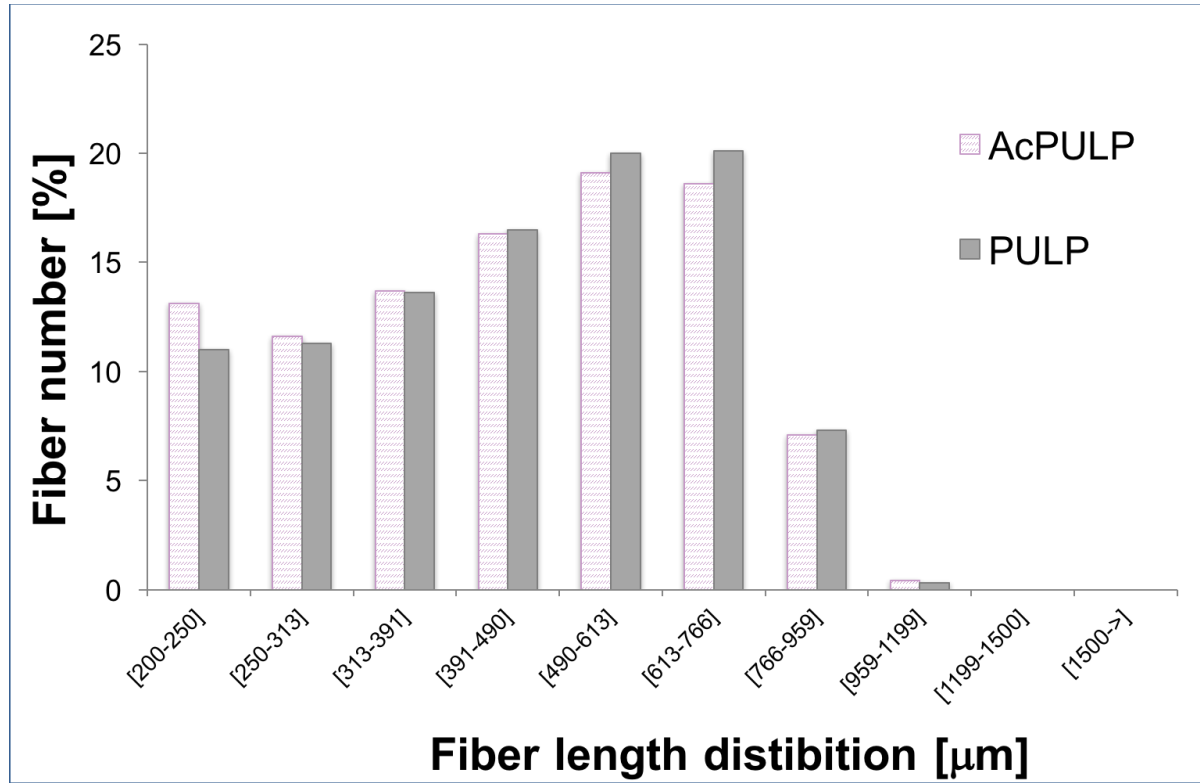**Fiber length distribution of the pulp before processing**

Figure S1. Fibre size distribution of the unmodified pulp and acetylated pulp.

In figure S1, the fiber length distribution is plotted; and the mean-arithmetic length ($\overline{L_a}$) and the mean-weighted length ($\overline{L_w}$) are provided by equations 1 and 2, respectively, where L_i represents the fiber length in each group and N_i the number of fibers in the group.

$$\overline{L_a} = \frac{\sum_i N_i L_i}{\sum_i L_i}$$ (Eq. 1)

$$\overline{L_w} = \frac{\sum_i N_i L_i^2}{\sum_i N_i L_i}$$ (Eq. 2)

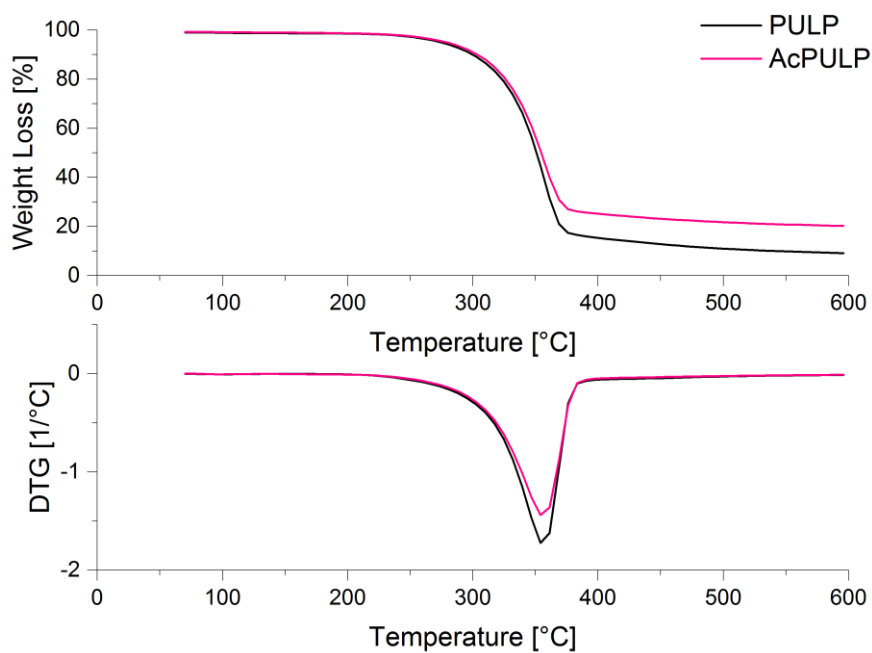**TGA of the fibers before processing**

Figure S2. TGA curves and their derivatives DTG of unmodified pulp and acetylated pulp

Visual aspect of the injection molded dumbbell specimens

Figure S3. Picture of the compounded and injected dumbbell specimens of the prepared biocomposites.

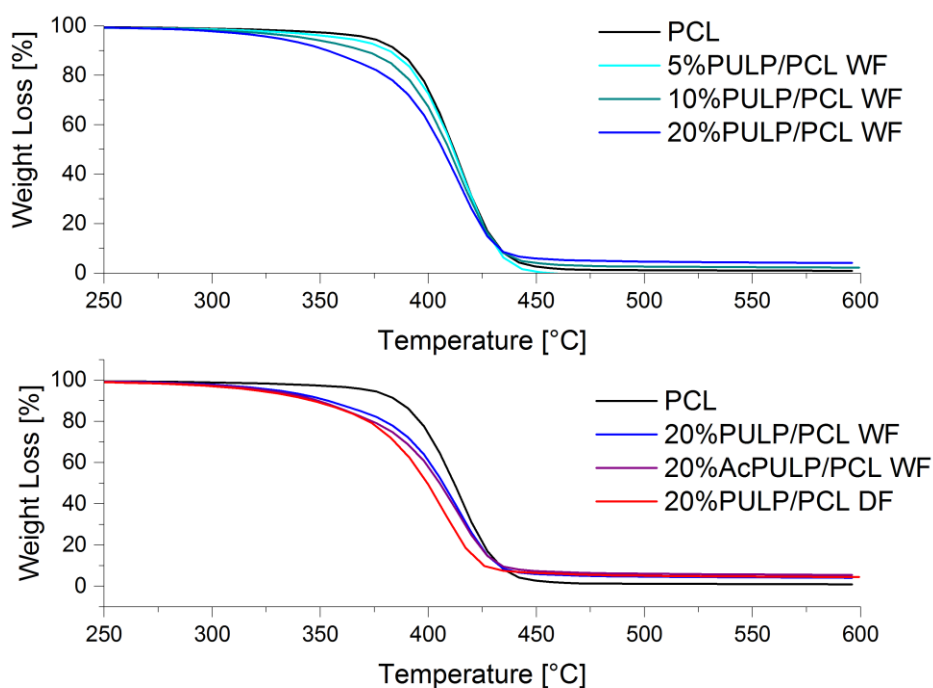**TGA results of the biocomposites**

Figure S4: TGA curves and their derivatives DTG of biocomposites.

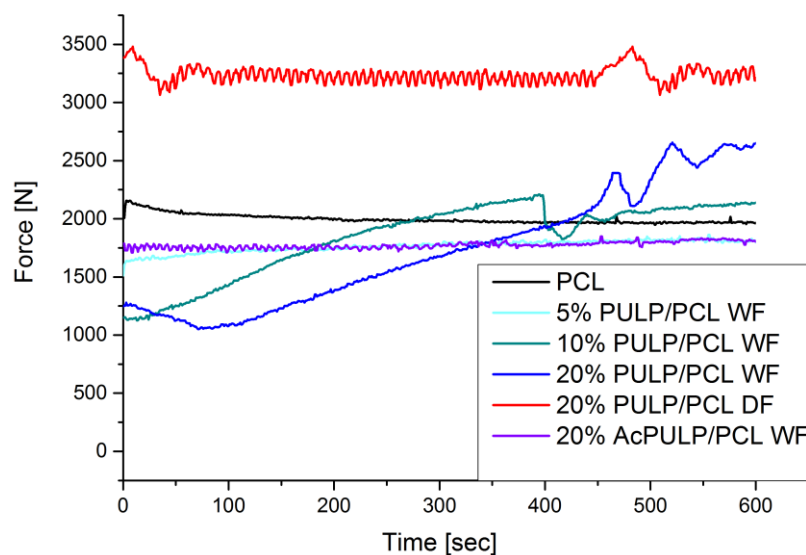**Screw force recorded during melt compounding**

Figure S5. Screw force as a function of the processing time recorded during the melt compounding of the biocomposites and the neat PCL.

CHCl₃ SEC results

Table S1. List of the different material melt processed and the corresponding molecular weights, polydispersity and the peak value of the SEC curve **M_{z+1} of the PCL matrix before and after processing recovered from the soluble fraction after Soxhlet extraction of the biocomposites (considering the main population).

SAMPLE	Processing time (min)	*Initial water content (%)	Mw	Đ	**Mz+1
PCL	0	0	166370	1.5	280589
PCL_DF	30	0	159160	1.5	259412
PCL_WF	30	20	158790	1.4	256730
PCL_WF	10	50	165280	1.4	262660
PCL from 5% PULP/PCL-WF	10	15	177600	1.3	272850
PCL from 10% PULP/PCL-WF	10	26	174180	1.3	267850
PCL from 20% PULP/PCL-WF	10	41.5	173660	1.3	263210
PCL from 20% AcPULP/PCL-WF	10	41.5	160530	1.3	261160
PCL from 20% PULP/PCL-DF	10	0	167093	1.3	249770
PCL from 20% AcPULP/PCL-DF	10	0	169100	1.3	251750

*The wet PULP used in the biocomposites has the 22% in dry content.
**This value is reported in order to avoid the possible integration errors and used to compare the molecular weight of the different polycaprolactone chains used in the present study.

DSC results of the biocomposites

Table S2. Main thermal properties recorded from the biocomposites at 20 wt% of modified or unmodified pulp from DSC analysis

	xPCL [wt%]	T_g* [°C]	T_m [°C]	ΔH_m [J/g]	χ* [%]
PCL	1	-44	59	62	46
20%PULP PCL_WF	0.8	-48	63	52	48
20%AcPULP PCL_WF	0.8	-47	64	51	47
20%PULP PCL_DF	0.8	-47	65	53	49

*Crystallinity of The PCL was calculated by the equation: $\chi = 100\ (\Delta Hm/xPCL\ \Delta H_0)$. where $\Delta H_0 = 135.65$ J/g [Kambutter. F. B, Warner. F., Russel, T. Br Stein, R.S., J. Polym. Sci., Polym. Phys. Ed., 14].

Fiber length distribution

Table S3 – Fiber size analysis for the pristine PULP and AcPULP and for the fibers recovered from the insoluble fraction of Soxhlet extraction in THF of the 20%PULP/PCL compounded in dry or wet feeding and the wet fed 20%AcPULP/PCL.

SAMPLE	Average fiber length[a] (µm)	Average diameter[b] (µm)	Average aspect ratio
PULP	1315	30 ± 10	44
AcPULP	1275	30 ± 10	43
Fibers from 20%PULP/PCL WF	465	<10*	>47
Fibers from 20%PULP/PCL DF	352	<10*	>35
Fibers from 20%AcPULP/PCL WF	550	<10*	>55

[a] Mean arithmetic length assessed by a fiber analyzer.

[b] The average diameter of the fibers was assessed by SEM microscopy analysis, based on 100 measurements.

* Fibers with diameter ranging from 10 µm to nanometric size were observed by SEM microscopy.