

Electronic Supplementary Information

Influence of TEMPO-Oxidation on Pulp Fiber Chemistry, Morphology and Mechanical Paper Sheet Properties

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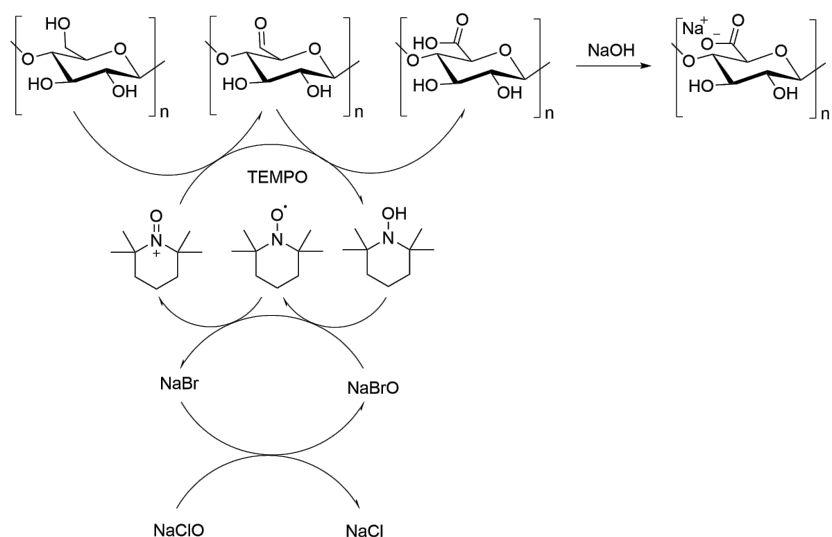


Figure S1: Reaction scheme of TEMPO-mediated cellulose oxidation, according to Saito et al. (2006).

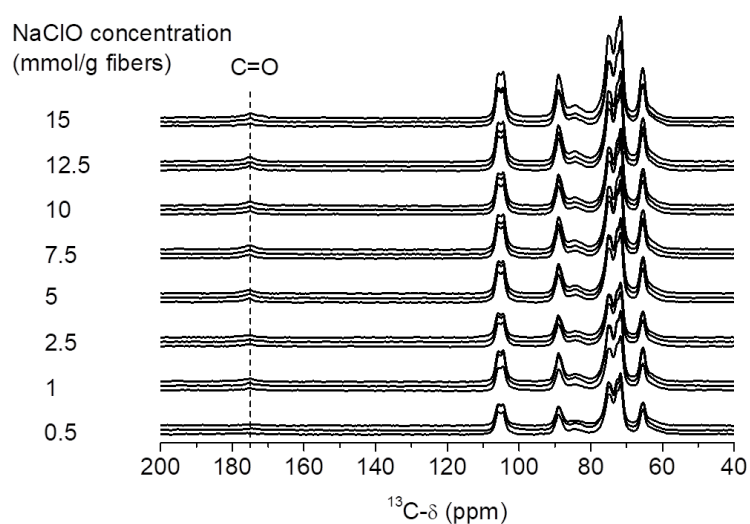


Figure S2: ^1H - \rightarrow ^{13}C CP MAS spectra of TEMPO oxidized fibers obtained with different NaClO concentrations between 0.5-15 mmol/g.

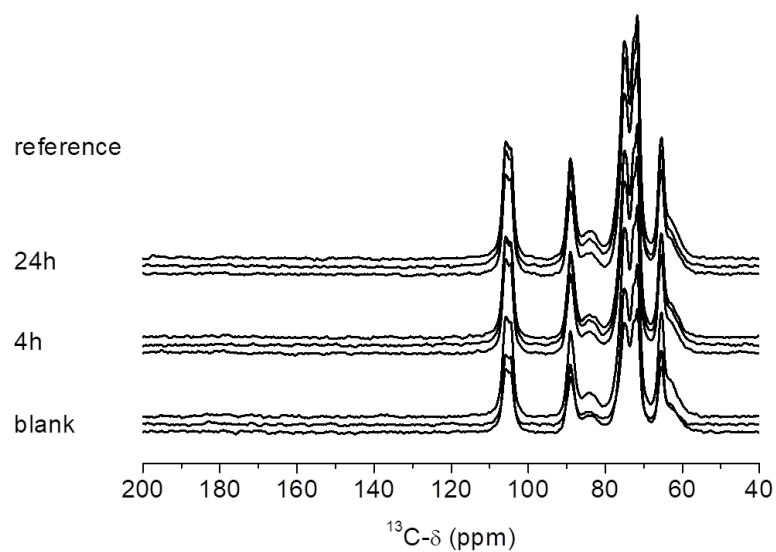


Figure S3: $^1\text{H} \rightarrow ^{13}\text{C}$ CP MAS spectra of blank fibers as well as reference fibers treated with NaOH at pH 10.5 for 4 and 24 h, respectively without the addition of catalyst and oxidant.

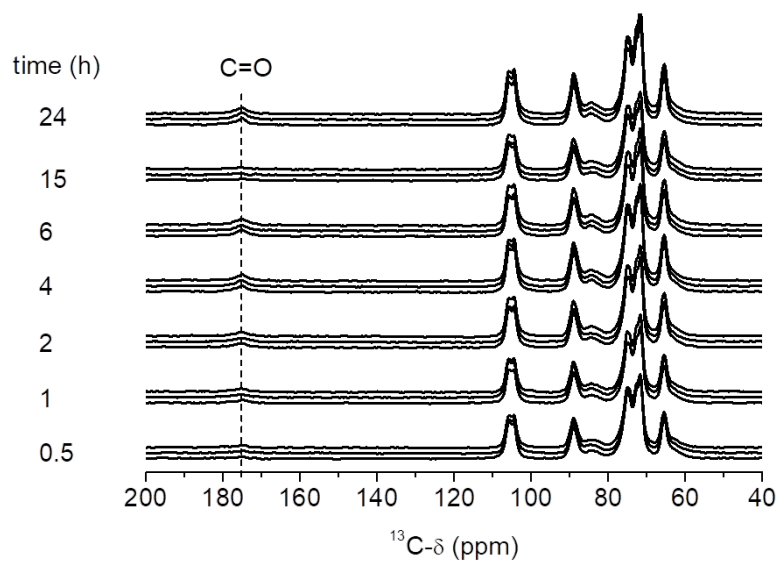


Figure S4: $^1\text{H} \rightarrow ^{13}\text{C}$ CP MAS spectra of TEMPO oxidized fibers obtained with different reaction times between 0.5-24 h.

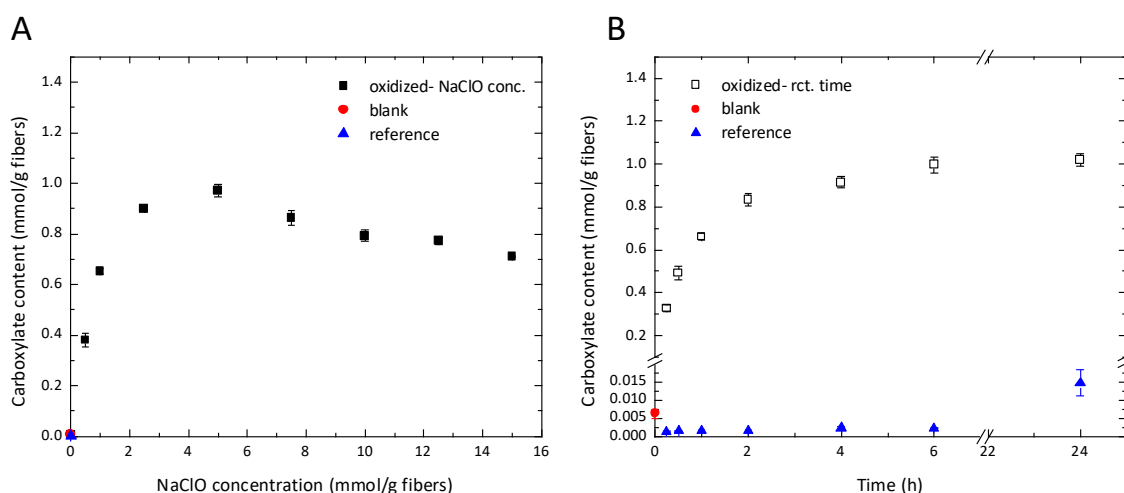


Figure S5: Carboxylate content as a function of NaClO concentration (A) and reaction time (B). For the oxidized samples, cotton linters were treated with various amounts of NaClO for 4 h at pH 10.5 (A) and 5 mmol NaClO, for various reaction times with NaOH at pH 10.5 (B). For the reference samples, cotton linters were treated for 4 h (A) and various times (B) at pH 10.5 without the addition of further reactants. The blank samples are untreated cotton linters.

The conductivity titrations were performed by suspending dry TEMPO-oxidized fibers (50-100 mg) in MilliQ water (55 mL). 0.01 M NaCl (5 mL) and 0.1 M HCl (1 mL) were added and a conductivity titration with Methrom Titrando 905 and the Metrohm Conductivity module 856 was performed using 0.01 M NaOH. To correct for *carbon dioxide* impurities in NaOH, a blank value of the water/NaCl/HCl mixture without addition of TEMPO-oxidized fibers was acquired before every titration.

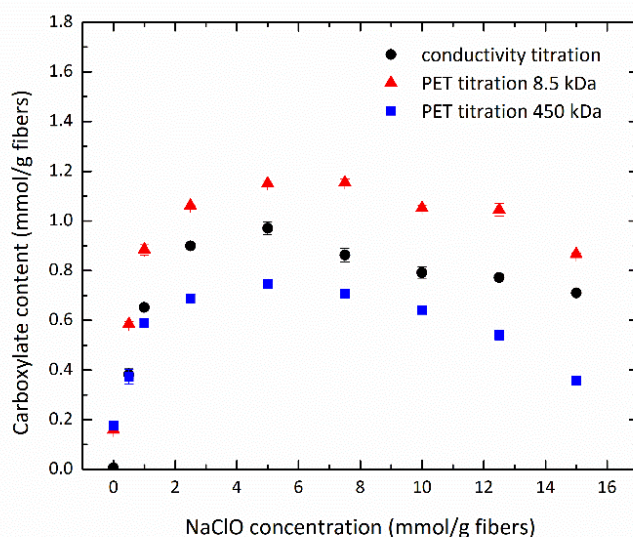


Figure S6: Carboxylate content as a function of NaClO concentration obtained by conductometric titration using 0.01 M NaOH (black dots), and polyelectrolyte titration using PDADMAC with a molecular weight of 8.5 kDa (red triangles), respectively 450 kDa (blue squares). All fibers are oxidized using 5 mmol/g NaClO and 4 h oxidation time.

The polyelectrolyte titrations were conducted by suspending 20 mg of fibers (5 mmol/g NaClO) in 10 ml water (MilliQ grade) using a laboratory stirrer with vane rotor. Subsequently, 15 ml *polydiallyldimethylammoniumchloride* (PDADMAC) solution ($C_{PDADMAC} = 0.0025$ N) was added and

the suspension rotated for 8 h to ensure complete adsorption. After that, 8 ml of the supernatant was collected and titrated by polyelectrolyte titration using a *potassium polyvinyl sulfate* (PVS) standard solution ($c_{PVS} = 0.0025$ N). The amount of carboxylate groups of the TEMPO oxidized fibers was calculated by calculating the amount of adsorbed PDADMAC on the fibers from the amount of remaining PDADMAC in the supernatant, titrated by the PVS standard solution (Form. I-III).

$$n_{COO^-} = n_{PDADMAC_{total}} - (n_{PDADMAC_{supernatant}} \cdot 3.125) \quad (I)$$

$$n_{PDADMAC_{supernatant}} = n_{PVS} \quad (II)$$

$$n_{PVS} = V_{PVS} \cdot c_{PVS} \quad (III)$$

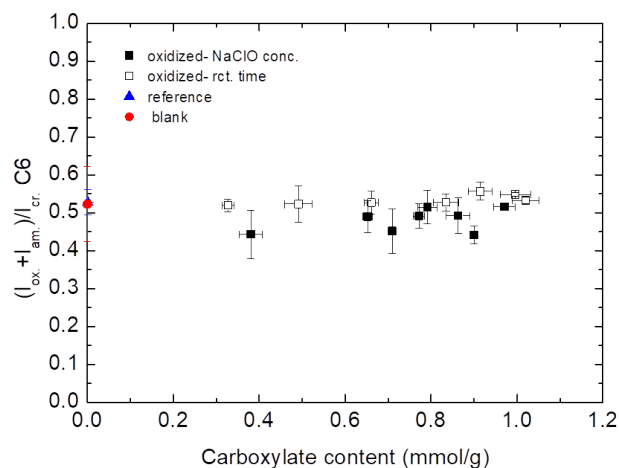


Figure S7: Ratio of the sum of $C_{6,am.}$ ($I_{am.} C_6$) and $C=O$ ($I_{ox.}$) to $C_{6,cr.}$ ($I_{cr.} C_6$) plotted as function of the carboxylate content obtained by $^1H \rightarrow ^{13}C$ CP MAS NMR. For the oxidized samples, cotton linters were prepared with various NaClO amounts (full squares), resp. different oxidation times (empty squares) at pH 10.5. For the reference samples, cotton linters were treated with NaOH for 4 h at pH 10.5 without the addition of TEMPO and NaClO (full triangles). The blank samples refer to untreated cotton linters (full circles).

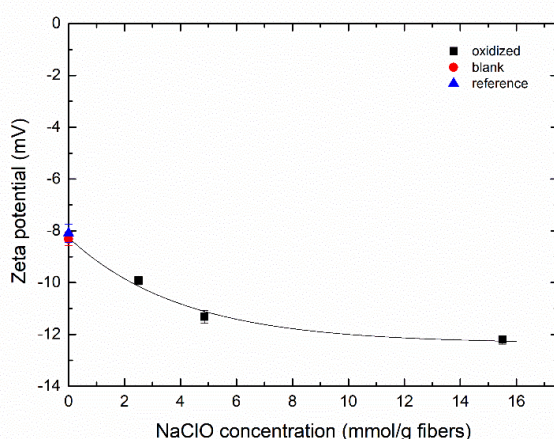


Figure S8: Zeta potential of TEMPO-oxidized (black squares), blank (blue triangle) and reference fibers (red circle) as a function of NaClO concentration. Blank fibers were used without further modification, reference fibers were treated with NaOH at pH 10.5 without the addition of catalyst and oxidant.

For the Zeta potential measurements, fiber suspensions were prepared by suspending 0.03 g in 10 mL 0.1 mM *potassium chloride* (KCl) solution using a laboratory stirring device. For the measurement, a Stabino device from Particle Metrix GmbH was used that operates according to the streaming potential measurement principle.

References

Saito, T.; Okita, Y.; Nge, T. T.; Sugiyama, J.; Isogai, A. (2006): TEMPO-mediated oxidation of native cellulose: Microscopic analysis of fibrous fractions in the oxidized products. In: *Carbohydrate polymers* 65 (4), S. 435–440.