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ABSTRACT

The effect of the degradation induced by the solvents for cellulose cuoxam and cadoxen and its dependency on the nature of the carbonyls in oxidatively-damaged cellulosics was investigated by combining a novel approach of sample regeneration and gel permeation chromatography coupled with carbonyl-selective labelling for reliable molecular characterization. The type of cellulosic pulp, degree and mode of oxidation and dissolution time were considered. Results show that the main discriminating factors in determining the degradation of oxidatively-damaged celluloses in alkaline dissolving media are: (1) the type of pulp, i.e. hemicellulose-containing pulps are more severely compromised; (2) of particular relevance, the prior oxidation mechanism, meaning not only the amount of oxidized moieties (greater oxidation, greater solvent-induced damage) but also their position on the chains (i.e. peroxide-oxidized cellulose is more unstable than hypochlorite-oxidized cellulose).

1. Introduction

In the pulp and paper industry, conventional viscometry still represents the standard approach to control the quality of bleached pulps. The solution viscosity of pulps, in fact, allows the simple and easily applicable evaluation of average molar mass information. Non-derivatizing cellulose solvents for viscometry most widely used include copper (II) complexes with ethylenediamine (cuen) or with ammonia (cuoxam, hereinafter also referred to as CuAM), and cadmium ethylenediamine hydroxide (cadoxen, hereinafter also referred to as CdEN) (Olsson & Westman, 2013; Saalwächter et al., 2000). It is worth remembering that these organometallic solvents are strongly alkaline (pH ≥ 12) and, although undesirably, they inevitably induce degradation of cellulose (Haskins & Hogsed, 1950) by beta-alkoxy elimination reactions starting from carbonyl groups ("oxidized spots") along the cellulose chains. The extent and the "circumstances" of these degradation processes – and thus the degree of errors made in the molar mass determination – is still a matter of discussion and the central topic of the present study.

Cuen is probably the most known and used cellulose solvent for viscosity measurements; hence a considerable amount of pertinent literature is available. Recently, studies on the influence of cuen on oxidized celluloses have also been published (Ahn, Zaccaron, Rosenau, & Potthast, 2019; Strlic, Kolar, Zigon, & Pihlar, 1998). Cuoxam and cadoxen, on the other side, are less frequently used in research labs for

molecular characterization of cellulosics, although being very common standards used in quality control in industrial pulp & paper labs. Pertinent literature on the molecular behavior of pulps in these two solvents is more limited than for cuen and, especially with regard to their effect on oxidized pulps, quite scarce (Achwal & Narayan, 1967; Blair & Cromie, 1977; Drábková, Ďurovič, & Škrdlantová, 2020; Milichovsky & Milichovska, 2008).

Cuoxam ([Cu(NH₃)₄](OH)₂) is a blue solution of cupric hydroxide in aqueous ammonia, known since 1857 as Schweizer's reagent. It had been used in the so-called cuprammonium process for the manufacture of rayon-type cellulosic fibers (mostly called copper silk, cuam rayon, or cuoxam rayon), and although this production largely decreased, it is still in use for cupro fiber production (tradename Bemberg™ fiber) (Kamide & Nishiyama, 2001). The dissolution of cellulose in cuoxam - similar to cuen - is attributed to the strong coordinative binding between the metal complex and the deprotonated hydroxyl groups of the anhydroglucose units of the polymer. Cellulose thus behaves as a chelating ligand towards the copper and dissolution is assumed to be the consequence of ligand exchange processes in the coordination sphere of the Cu central atoms (Burchard, Habermann, Klüfers, Seger, & Wilhelm, 1994; Fuchs, Habermann, & Klüfers, 1993; Seger & Burchard, 1994).

Cadoxen, [Cd(NH₂(CH₂)₂NH₂)₃][OH]₂, is a colorless solution, produced by dissolution of cadmium hydroxide in aqueous triethylenediamine. CAUTION! Cadoxen is known to be an acutely toxic compound

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upon contact with skin or inhalation! In contrast to cuen and cuoxam, no evidence has been provided of a carbohydrate-solvent complexes being formed upon dissolution. NMR investigations suggested that in this solvent rather an acid-base mechanism is involved in cellulose dissolution (Bain, Eaton, Hux, & Tong, 1980).

Various natural and/or artificial processes (e.g. pulping, bleaching, natural aging, exposure to atmospheric contaminants and other chemicals) lead to the oxidation of cellulosic hydroxyl groups to carbonyls (and at C-6 subsequently also to carboxyls). These functionalities represent "chemical instabilities" along the cellulose chains where chain cleavage preferably occurs, especially under alkaline conditions. This happens according to the so-called beta-alkoxy elimination mechanism, a fast reaction occurring wherever an oxidized group had been introduced before: already a single hydroxyl group in the cellulose chain, being oxidized to a carbonyl group, is sufficient to cause cleavage of the adjacent glycosidic bond. If this carbonyl group is placed in the middle of the cellulose molecule, for instance, the chain length is halved (Fengel & Wegener, 1983). Alkali-induced degradation is therefore more prominent in the case of oxidatively damaged pulps (Strlic et al., 1998). A more detailed description of the general beta-elimination mechanism characterizing oxidatively damaged celluloses and triggered by alkali can be found in the introduction of our previously published paper (Ahn et al., 2019).

As a logical consequence, viscometry, which determines only the values after alkali-induced degradation, provides underestimated molar masses (degrees of polymerization, DPs) of oxidized pulps. Therefore, values of (fast and easy) viscometry measurements - as usually obtained by pulp and paper companies as process control parameters - may not reflect the "real" molecular mass of the original pulps – because this can only be measured by means of non-degrading systems, such as *N,N*-dimethylacetamide / lithium chloride (DMAc/LiCl) in gel permeation chromatography (GPC) (Ahn et al., 2019; Potthast et al., 2015).

Despite those drawbacks of viscometry being well-known in general, a systematic methodical investigation of the extent of cellulose degradation in various solvents, in particular in cuoxam and cadoxen, is still missing. This applies equally to the parameters affecting the underestimation of molar mass values in viscometry, particularly in the case of oxidized pulps (Ahn, Henniges, Potthast, & Rosenau, 2015). The purpose of the present study is to investigate and compare the effects of the two long-known solvents for viscometry of cellulosics, cadoxen and cuoxam, on the molecular features of pulps at various degree of oxidation. The molar mass and the content of oxidized groups of the pulps were analytically determined by gel permeation chromatography (GPC) with group-selective fluorescence labeling (CCOA method) (Röhrling, Potthast, Rosenau, Lange, Borgards et al., 2002). This method, which is known to avoid any negative degradation effects, was applied both to the original oxidized pulps and to the pulps previously dissolved in the cuoxam / cadoxen and regenerated from these solvents. The results of these measurements will be explicated and the effects of these solvents on the hemicellulose fraction of the pulps as well as the role played by both mechanism and extent of oxidation will be discussed.

2. Materials and methods

2.1. Sample preparation

Two types of cellulosic pulp, cotton linters (CL) and a hardwood (beech) bleached sulfite pulp (HBSP), were oxidized to different extents (i.e., degree of oxidation, DO) with sodium hypochlorite (NaOCl) or hydrogen peroxide (H$_2$O$_2$) according to the optimized procedure reported in our previous publication (Ahn et al., 2019). An overview on the characteristics of the pulps investigated can be found in the supporting information in (Ahn et al., 2019). Numbers associated to each sample name refer to the oxidation degree (Table 1).

2.2. Dissolution in viscosity solvents & regeneration

Oxidized and non-oxidized samples (reference) were dissolved in cuoxam or cadoxen according to standard procedures (Zellcheming-MerkblattIV/52/71, 2020; Zellcheming-MerkblattIV/34/60, 1957) under magnetic stirring in the dark. The concentration of pulps in the dissolution media was 8 and 5 mg/mL for CuAM, and CdEN respectively, and dissolution times ranged from 30 up to 60 min depending on the protocols. In addition, different dissolution times were also tested for the non-oxidized reference pulps.

For subsequent GPC analysis, each dissolved sample was first regenerated using an aqueous bath containing 5% (v/v) acetic acid and 20 % (v/v) ethanol 96 %, thoroughly washed with deionized water and rinsed with ethanol 96 % in order to obtain stable cellulose EtOH-gels which were kept at + 4 °C for further usage.

2.3. Gel permeation chromatography (GPC) analysis

Oxidative functionalities (i.e. content and distribution) were investigated according to the CCOA technique (Potthast et al., 2003; Röhrling, Potthast, Rosenau, Lange, Borgards et al., 2002; and 2002b) by means of selectively fluorescence labelling of carbonyl groups.

Samples were dissolved in 9% (w/v) lithium chloride/*N,N*-dimethylacetamide (DMAc/LiCl) by solvent exchange (water – ethanol – DMAc) at room temperature. The molecular features, i.e. absolute molar masses, molar mass distributions (MMD) and content and distribution of oxidized moieties, were determined with a GPC/MALLS system constituted of: a degasser Dionex DG-2410 (Dionex Softron GmbH, Germering, Germany); autosampler HP 1100 (Agilent Technologies, Waldbronn, Germany); pulse damper Kontron pump 420 (Kontron Instruments, Rossdorf, Germany); fluorescence detector TSP FL2000 (Thermo Scientific Products, Darmstadt, Germany) for monitoring the CCOA label (λ_{ex} = 290 nm and λ_{em} = 340 nm); multiple-angle laser light scattering detector (MALLS) (Wyatt Dawn DSP, Wyatt Technologies, Santa Barbara, California, USA) with argon ion laser (λ_0 = 488 nm), and a refractive index detector (RI) (Shodex RI-71, Showa Denko Europe GmbH, Munich, Germany). As stationary phase, four GPC PLgel mixedA LS, 20 μm, 7.5 × 300 mm columns (Polymer Laboratories, currently Varian/Agilent) were used in series. Operating conditions: 1.00 ml min^{-1} flow rate, 100 μl injection volume, 45 min run time. DMAc/LiCl (0.9 %, w/V) filtered through a 0.02 μm Anopore inorganic membrane (Anodisc Sigma Aldrich) was used as the mobile phase.

The weight-average (Mw) and number-average (Mn) molar mass moments, the molar mass distributions (MMD), the total amount of carbonyl groups (C=O$_{tot}$) and the degree of substitution of oxidized functionalities (DS$_{C=O}$) were evaluated using Chromeleon (Thermo Fisher Scientific), Astra 4.73 (Wyatt Technologies) and GRAMS/32 AI (Thermo Fisher Scientific) software. Additionally, the theoretical amount of reducing end groups (REGs) and the along-chain carbonyls (C=O$_{ox}$) were estimated as previously reported (Potthast, Henniges, & Banik, 2008).

3. Results and discussion

In order to characterize the molecular parameters of the cellulosic pulps and to monitor how and to which extent they are affected by different alkaline cellulose solvents, GPC measurements in *N,N*-dimethylacetamide / lithium chloride (DMAc/LiCl) were used. Pulps dissolved in each viscosity solvent needed to be first regenerated in an aqueous bath and subsequently re-dissolved in 9% LiCl/DMAc. This approach allowed determining the presence and the extent of degradation induced by CuAM and CdEN since it has been proved that no degradation whatsoever occurs in the DMAc solvent system (Ahn et al., 2015, 2019; Henniges et al., 2014; Potthast et al., 2002). Hence, any change occurring to pulps at the molecular level was due to the

Table 1
Average Mw (kg mol^{-1}) and carbonyl group contents [b] of pulps under investigation, at different degree of oxidation (DO) [a]. Standard deviation is below 5% for Mw and C=O$_{tot}$, around 10 % for Mn, REGs and C=O$_{ox}$.

oxidant	NaOCl				H$_2$O$_2$			
DO	Mw kg mol^{-1}	C=O$_{tot}$ µmol g^{-1}	REGs µmol g^{-1}	C=O$_{ox}$ µmol g^{-1}	Mw kg mol^{-1}	C=O$_{tot}$ µmol g^{-1}	REGs µmol g^{-1}	C=O$_{ox}$ µmol g^{-1}
COTTON LINTERS (CL)								
0	172.7	3.1	9.1	−6.0	172.7	3.1	9.1	−6.0
1	167.2	9.0	9.7	1.1	148.8	9.6	10.2	0.6
2	150.6	19.9	10.6	12.3	125.9	19.1	12.3	8.3
3	142.5	29.2	11.1	21.2	112.3	27.2	15.5	11.8
4	132.0	41.6	12.7	31.4	93.7	41.9	17.0	25.7
HARDWOOD BLEACHED SULFITE PULP (HBSP)								
0	339.6	35.99	19.7	16.2	339.6	35.99	19.7	16.2
1	296.2	35.64	24.9	10.8	257.7	48.89	20.6	28.3
2	241.5	43.96	24.0	20.0	194.2	62.23	31.1	31.1
3	215.8	51.66	28.3	23.3	144	45.1	40.1	5.0
4	161.1	58.73	32.5	26.2	122	78.28	31.4	46.9

[a] Average values from three different samples and measurements.
[b] C=O$_{tot}$ = total carbonyl groups; REGs = reducing end groups (as estimated from Mn$_{GPC}$) (Potthast et al., 2008); C=O$_{ox}$ = along-chain carbonyls.

viscosity solvent used for the "first" dissolution.

3.1. Native (non-oxidized) pulps

The dissolution behavior of pulps in the various viscosity solvents is not expected to be identical. We first investigated the impact that these organometallic solvents have on the dissolution of model native cellulosic materials.

Quite as expected, pulps dissolved in alkaline solvents suffer from degradation even in their native, non-deliberately oxidized forms (Fig. 1), with the wood pulp (HBSP) being more severely affected than the cotton linters (CL). Compared to the non-degrading DMAc solvent system, in fact, native materials showed a decrease below 10 % (CL) and around 30 % (HBSP) of their average Mw when CuAM and CdEN were used as solvents. These results are comparable with the behavior

Fig. 1. Results of GPC analysis on native cotton linters (CL) and hardwood bleached sulfite pulp (HBSP) dissolved in different cellulose solvents and regenerated as reported in Section 2.2: weight-average molar masses, Mw (kg mol^{-1}, bars) and amount of carbonyl groups (µmol g^{-1}), i.e. total amount of carbonyls (◆, black), along-chain carbonyls (●, red) and (theoretical) reducing end groups (■, blue). The error bars refer to the relative standard deviation, SD: SD = 5 % for Mw and C=O$_{tot}$, SD = 10 % for REGs and C=O$_{ox}$. NOTE: negative values of along-chain carbonyls (red) indicate that no C = O$_{chain}$ are present (i.e. REGs values outnumber the total C=O). Literature data for cuen (Ahn et al., 2019) have been added for comparison (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

shown by native pulps in copper ethylenediamine (cuen), another widely used alkaline solvent for viscometric determination of the DP of cellulosics (Ahn et al., 2019).

A deeper insight into the solvent-induced degradation mechanism than by the numbers in Fig. 1 can be achieved by the molar mass distributions (MMD, Fig. 2). On the one hand, native CL showed some sign of induced degradation, but the left-shift of the molar mass distribution (MMD) was moderate and more pronounced for cuoxam than for cadoxen (Fig. 2). On the other hand, the MMD for HBSP changed quite remarkably when the pulp was dissolved in the alkaline metal complexes (grey curves, Fig. 2). The high molar mass fractions were clearly compromised. Additionally, the disappearance of the shoulder on the left side of the distributions (grey graphs and inset in Fig. 2, right), is indicative of hemicellulose loss upon dissolution. Overall, a remarkable decrease in the average molar masses of HBSP dissolved in the viscosity solvents was observed (Fig. 1), with cadoxen having a less negative impact by slightly better preserving the high-Mw regions (Fig. 2, right).

The duration of the dissolution in the metal-complex solvents also has a negative impact on the integrity of the pulps. In general, the longer the dissolution time, the stronger the extent of the solvent-induced damage, which indicates a further oxidation / beta-elimination cycle during dissolution and storage (Ahn et al., 2015). For CL the Mw loss is limited, whereas for the HBSP the loss is quite pronounced in both solvents and occurs already after a very short time (above 20 % loss after 10 min) (Fig. 3).

The dissolution process in the organometallic solvents is generally rather fast, i.e. within five minutes (Ahn et al., 2019). Any additional time the pulp stays in contact with the alkaline medium compromises the polymer from a molecular viewpoint. Unfortunately, standard protocols for the determination of the viscosity-DP commonly recommend at least 30 min of dissolution time, in an attempt to be as general and widely applicable as possible. However, especially in industrial practice, methods applied by different companies are hardly comparable. It happens, in fact, that different protocols are used by different companies for the same dissolution medium, possibly recommending different dissolution times and further "adapting" the protocol. This – unfortunately rather uncontrollable – variability affects the reliability of the resulting viscosity-DP value and inevitably adds up to the solvent-induced underestimation of the actual DPv, in particular when "non-tricky" (i.e. easily dissolvable) pulps are considered which would get by with much shorter dissolution times. In order to obtain more reliable and accurate data, such long contact times with alkaline media should only applied to pulps that are difficult to dissolve.
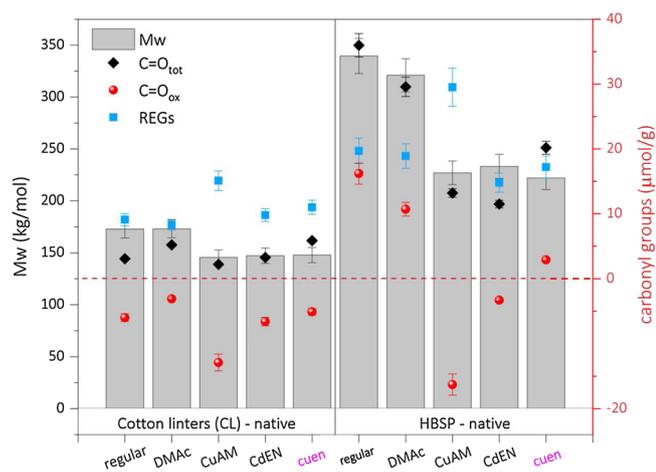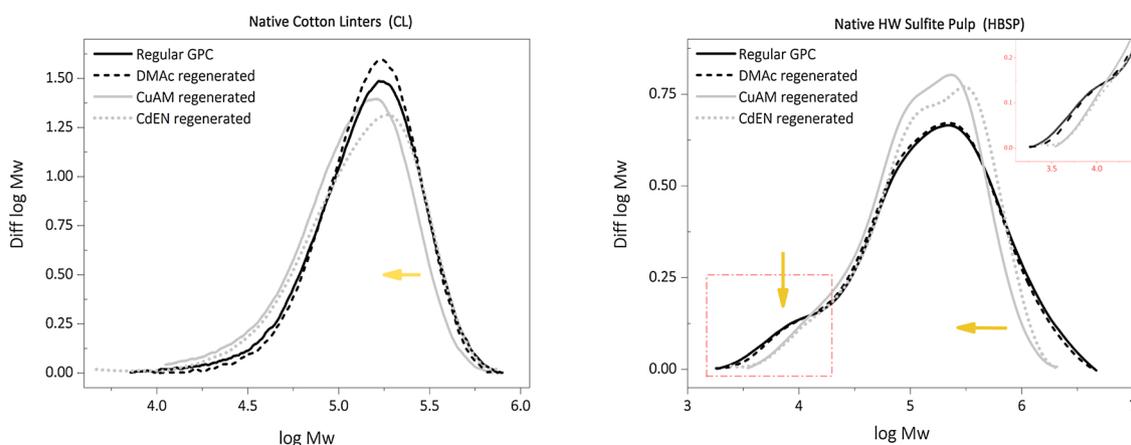
Fig. 2. Molar mass distributions (MMD) from GPC analysis of native (non-oxidized) cotton linters (left) and hardwood bleached sulfite pulp (right). Dissolution effect of different solvents: DMAc/LiCl, non-regenerated (solid curve, black), DMAc/LiCl, regenerated (dashed curve, black), CuAM (solid curve, grey), CdEN (dotted curve, grey). The inset in the right graph zooms in the changes in the low-MM regions of HBSP.
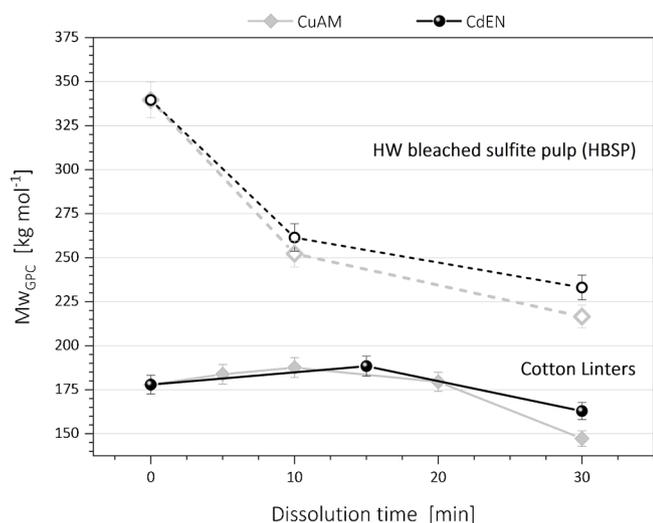

Fig. 3. Influence of the dissolution time for native cotton linters (solid data points and lines, bottom) and HBSP (hollow data points and dashed lines, top) in the alkaline solvents CuAM (◆, grey) and CdEN (●, black).

3.2. Effect of oxidation

Beside possible externally induced oxidation (e.g. aging, environmental stressors), pulps can naturally carry some oxidative groups due their production history (pulping, bleaching, storage). Such functionalities can be detrimental to the molecular stability of pulps upon dissolution in alkaline media due to beta-alkoxy elimination reactions. Therefore, we deliberately partially oxidized cotton linters (CL) and hardwood bleached sulfite pulps (HBSP) in order to simulate oxidatively damaged samples and to ascertain to which extent the determination of their Mw (or better, the DP) by viscometry is still acceptable.

Since different oxidative groups can be introduced to cellulosic materials, we used two different oxidants, allowing for a better simulation of different oxidation mechanisms affecting pulps and for a wider understanding of the underlying alkali-induced degradation. Specifically, sodium hypochlorite and hydrogen peroxide were used. The former is reported to cause the formation of aldehyde and carboxyl groups at C6 of the glucopyranose rings together with keto functions at C2 and C3 (Ivanov, Kaverzneva, & Kuznetsova, 1953; Lewin & Epstein, 1962). Hydrogen peroxide, instead, primarily causes the oxidation of secondary alcohols at C2 and C3 to ketones and virtually forms "keto-cellulose" (Lewin & Ettinger, 1969; Zeronian & Inglesby, 1995). Both oxidized CL and oxidized HBSP, upon contact with the

organometallic solvents, exhibited a significant decrease in the molar mass as a consequence of the increased degree of oxidation: the Mw of the most severely oxidized samples (i.e. sample "ox 4″") drops about additional 30 % and 60 % for CL and HBSP, respectively, as compared to the native references (supplementary data, Table S1). GPC analysis additionally confirmed this effect of the organometallic, alkaline solvents. In general, dissolution in both cuoxam and cadoxen was highly detrimental to the molecular integrity of the oxidized pulps. Fig. 4 presents the trends in the Mw of oxidized CL and HBSP after dissolution in cuoxam (◆ pink) and cadoxen (● green) in comparison to the pulps regularly dissolved in DMAc/LiCl (Fig. 4, "original").

In case of an ideal non-degrading dissolving system, the graphs are expected to coincide with the diagonal (1:1) line. This behavior was actually nearly exhibited by the pulps "regenerated & redissolved" in DMAc/LiCl (■ grey), which we included for reference. Even though some sign of degradation may be seen with the grey curves not perfectly matching a 1:1 relationship, the non-degrading nature of this solvent could be generally confirmed even on oxidized pulps, when the intrinsic error associated with the measurements (i.e SD) was taken into account. The linear fittings for cuoxam-dissolved and cadoxen-dissolved samples, on the contrary, remarkably deviated from the diagonal 1:1 line. Hence, pronounced degradation of the pulps occurred and molecular information gathered from these dissolved samples are incorrect and misleading, compared to the "true" Mw value (as nearly obtained from DMAC/LiCl-dissolved pulps).

The effect of alkalinity on oxidized samples is more remarkable on wood pulps (i.e. HBSP) than on cotton linters, as abovementioned (Section 3.1) and seen in Fig. 4. Taking Fig. 2b into consideration, this is most likely due to a combined degradation mechanism, affecting both large cellulose molecules (left-shift of the MMD, supplementary data, Fig. S1) and the very alkali-sensitive hemicellulose portions, so that the MMD changed from tri- to monomodal indicating the loss of these fractions (supplementary data, Fig. S1).

In our study, two different oxidants and different degrees of oxidation were investigated for each pulp in the different solvents. Fig. 5 reports a comparison between DO = 2 and DO = 4 (cf. Table 1 for details).EFFECT OF THE OXIDANT

- For the H_2O_2-oxidized samples, a greater Mw loss was evident for both pulps (at the same DO) when compared to the corresponding hypochlorite-treated ones. This phenomenon was particularly evident for HBSP.
- H_2O_2-oxidized cotton linters exhibited comparable Mw values regardless of the dissolution solvent whereas for the corresponding NaOCl-oxidized samples, regular and DMAc-regenerated pulps
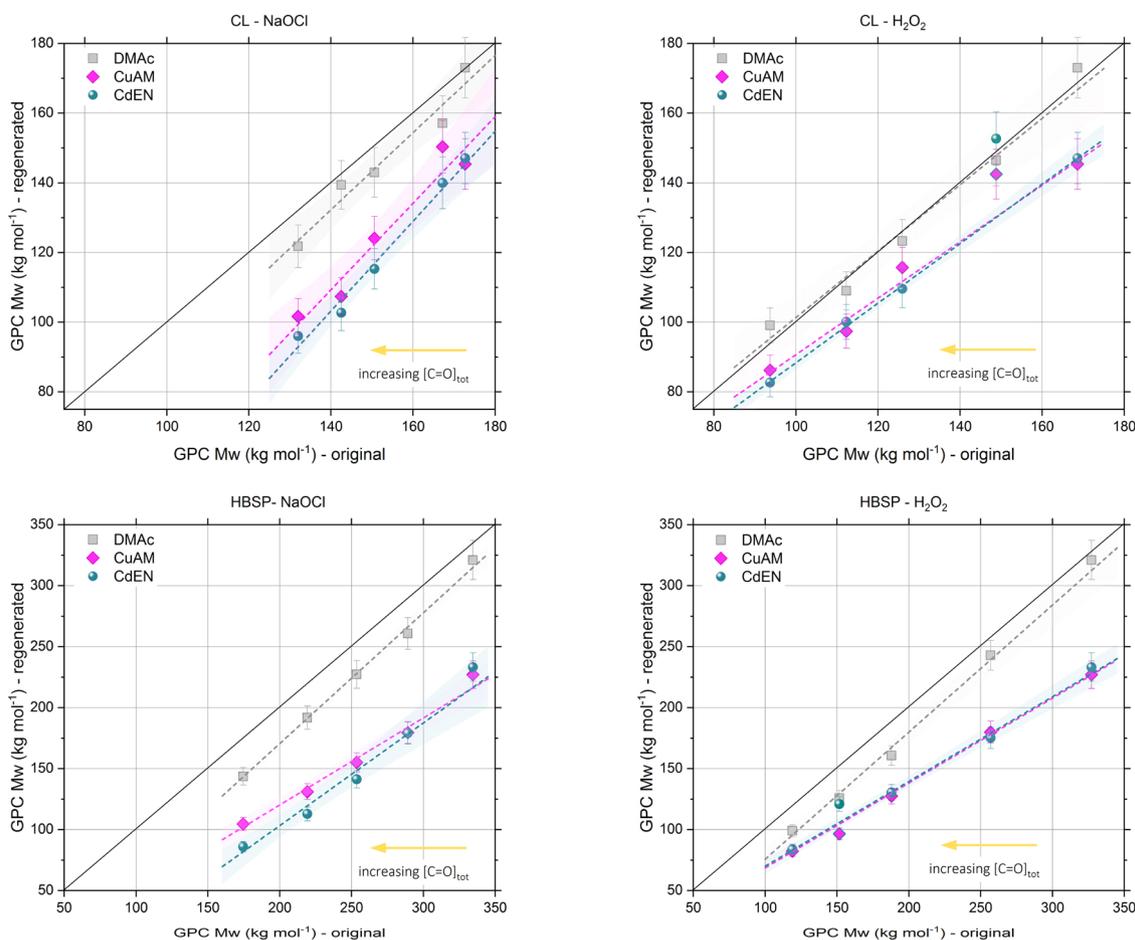
Fig. 4. Relationship between the weight-average molar masses (Mw, kg mol^{-1}) of cotton linters (top) and hardwood bleached sulfite pulp (bottom) regularly dissolved in DMAc/LiCl 9% (original, x axis) and after regeneration (y axis). Regeneration after dissolution in different solvents, i.e. DMAc/LiCl (■ grey), cuoxam (◆ pink) and cadoxen (● green). In each graph, from right to left, experimental data of pulps with increasing amount of total carbonyl groups are given (yellow arrow). The error bars refer to the relative standard deviation, SD = 5 % (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

retain higher Mw than the alkaline-dissolved ones.

An explanation can be derived from the different oxidation mechanism of the two oxidizing agents. H_2O_2-oxidation mostly results in ketones at C2 and C3 which are very sensitive towards alkaline environments and therefore very prone to beta-alkoxy elimination. Hypochlorite causes less keto group introduction and more pronounced formation of C6-carboxyl, the latter being innocent with regard to induction of beta-alkoxy eliminations. When the oxidized keto moieties are located near the middle of the cellulose backbone, the consequence of the chain cleavage is a pronounced decrease of the Mw (depolymerization).EFFECT OF THE SOLVENT/PULP

- After dissolution in the alkaline solvents CuAM and CdEN, the carbonyls along the chain (C=O$_{ox}$) are generally lower than after dissolution in DMAc/LiCl, because the chains have been "cleaned" (and degraded) upon the alkali-treatment (beta-alkoxy elimination and subsequent chain cleavage). The chain cleavage is reflected in the increase of the corresponding REGs;
- The alkaline solvents have a quite drastic effect on all oxidized pulps (and for all oxidants used) as highlighted by the Mw values, which were generally lower than for the corresponding DMAc-dissolved samples. This was additionally confirmed by the higher numbers of REGs for alkaline-dissolved CL and HBSP: more REGs mean an increased number of polymer chains, and thus fragmentation (one new REG, of the new cellulose chain, is formed when alkali-induced

chain cleavage occurs at the alkali-labile carbonyl spot in the "old", oxidized chain);
- Peroxide-oxidized pulps generally retain a larger amount of along-chain carbonyls (C=O$_{ox}$) after dissolution in cadoxen as compared to H_2O_2-pulps dissolved in cuoxam. This observation correlated readily with the higher basicity and nucleophilicity of cuoxam relative to cadoxen.
- For hypochlorite oxidation, pulps dissolved in cuoxam have in general a higher portion of surviving along-chain carbonyls (C=O$_{ox}$) than the corresponding ones dissolved in cadoxen.

These results are generally in line with previous research reports (Hosoya, Bacher, Potthast, Elder, & Rosenau, 2018) on viscosity experiments which state that degradation in DMAc/LiCl is the smallest, moderate in cadoxen and the highest in cuoxam (Brown & Wikström, 1965; Dawsey & McCormick, 1990; Henley, 1961; Vink, 1959).

An in-depth analysis of the oxidized functionalities revealed some additional details on the reaction behavior upon both oxidation and alkali-dissolution of cotton linters.OXIDATION

Fig. 6 depicts the molecular features of oxidized cotton linters under non-degrading analytical conditions, i.e. the actual Mw and the content of oxidized functionalities without any interference from the dissolution media. The comparison between the two oxidants is clear:

- The amount of total carbonyls introduced by the whole oxidation process is essentially the same between H2O2 and NaOCl (orange
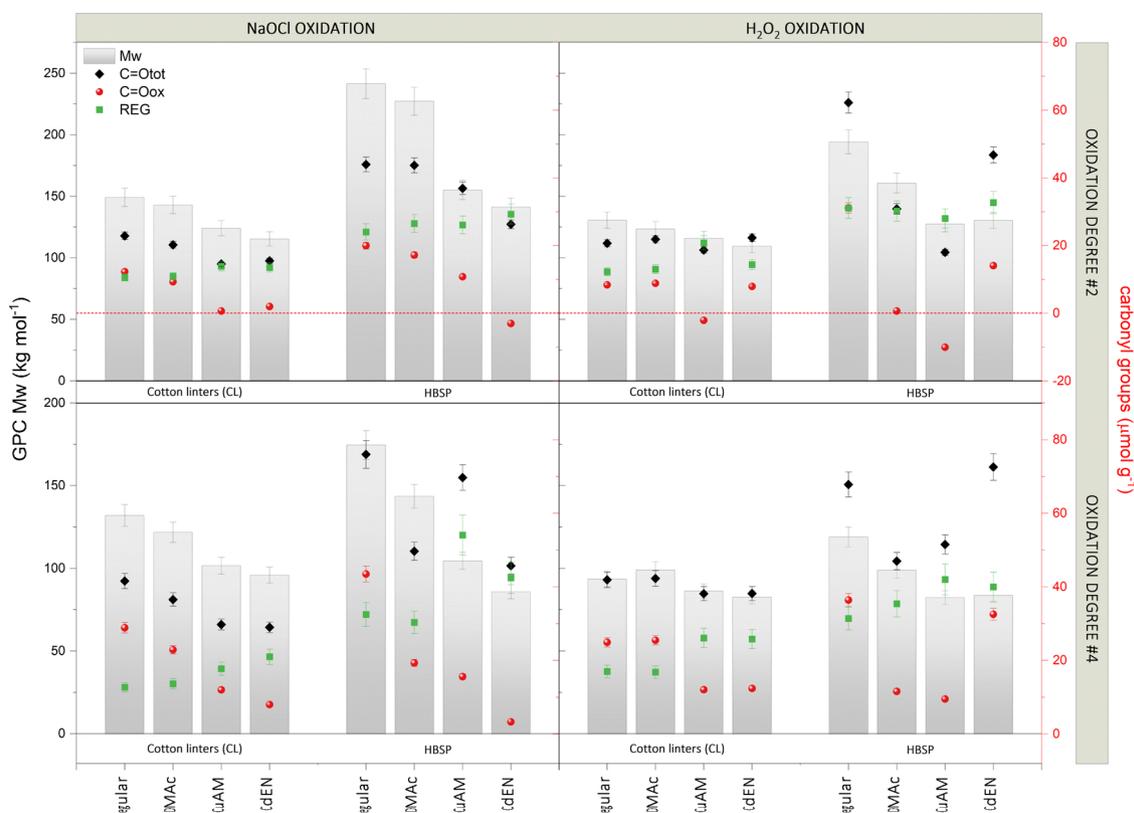
Fig. 5. Effect of the oxidant (columns, NaOCl and H₂O₂) and the degree of oxidation (rows, degree 2 and 4, cf. Table 1) on cotton linters (CL) and hardwood bleached sulfite pulp (HBSP). Bars, weight-average molar masses (Mw, kg mol-1); scatter data, carbonyl groups (µmol g-1): total amount (◆ black), along-chain carbonyls (● red), reducing end groups (■ green). The error bars refer to the relative standard deviation, SD: SD = 5 % for Mw and C=O$_{tot}$, SD = 10 % for REGs and C=O$_{ox}$. The two-way ANOVA statistics confirmed that the population means of both factors (i.e. oxidants and solvents) are significantly different (p < 0.05) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

areas in Fig. 6)
- But, the Mw range covered is wider in H2O2-pulps (i.e. carbonyls are more "spread out"), indicating a more severe depolymerization of cellulose upon oxidation with this oxidant.

ALKALI-DISSOLUTION

By correlating the amount of total carbonyls (CO$_{chain}$ + REGs) in regularly analyzed pulps (no alkali-induced degradation, x axis) and in pulps after dissolution in organometallic solvents (alkali-induced degradation & "wash-out" effect, y axis) (Fig. 7) it was clear that:

- a linear correlation between the extent of oxidation and the solvent´s degradation effect existed for both CuAM and CdEN and both oxidants;
- the decisive factor with regard to cellulose degradation upon dissolution is the oxidant rather than the dissolution solvent. The differences in solvent basicity or nature of interactions with cellulose was obviously less decisive. The slopes of the linear regression for peroxide pulps is close to 1 ($y = mx + c$; CuAM: m = 0.98; c = 0.79; R^2 = 0.99, CdEN: m = 1.06; c = 0.07; R^2 = 0.98) while it is clearly smaller than 1 for hypochlorite pulps ($y = mx + c$; CuAM: m = 0.67; c = 0.18; R^2 = 0.99; CdEN: m = 0.64; c = 1.11; R^2 = 0.99) regardless the organometallic solvent used. This implies that the type and/or location of carbonyls in HOCl-oxidized pulps caused a significantly stronger degradation than peroxide oxidation.

When the three sub-groups of oxidized moieties in celluloses (i.e. CO$_{tot}$, CO$_{chain}$, REGs) are considered in more detail, some unexpected observations can be drawn. The use of strong alkaline solvents is expected to largely "clean" the polymer from the along-chain carbonyls through beta-elimination. However, some along-chain carbonyls remain on the backbone, as indicated in Fig. 8 by the orange-shaded areas which represent the "residual" along-chain carbonyls after dissolution of the oxidized pulps in each organometallic solvent. In particular,

- peroxide pulps seem to retain larger amount of CO$_{chain}$ as compared to NaOCl-oxidized ones. According to literature, H₂O₂ introduces primarily ketones at C2 and C3 (ketocellulose) while NaOCl introduces in addition aldehydes and COOH at C6. According to our data, oxidized functionalities introduced by H₂O₂ are likely less prone to be "released" by the alkaline media. Celluloses oxidized by H₂O₂ will contain a considerable amount of C2/C3 diketo structures, which by contrast are rather rare in hypochlorite-oxidized pulps. The usual alkali-induced beta-elimination mechanism does not occur in the case of C2/C3 dicarbonyls and, consequently, neither does the removal of these carbonyls nor the concomitant chain cleavage. It is thus highly likely that the higher amount of "retained" along-chain carbonyls in H₂O₂-oxidized pulps is due to C2/C3-diketo structures which elude beta-alkoxy degradation. Notwithstanding this relative stability, it should be noted that such structures are far from being inert – in fact, they readily undergo follow-up chemistry such as benzilic-type rearrangements. However, this requires more strongly alkaline media than the viscosity solvents are able to provide. We are currently attempting to prove the hypothesis of diketo structures being the along-chain carbonyl "survivors", by a combination of experimental work and computation similar to previous studies on beta-eliminations from different positions of the anhydroglucose units (Hosoya et al., 2018).
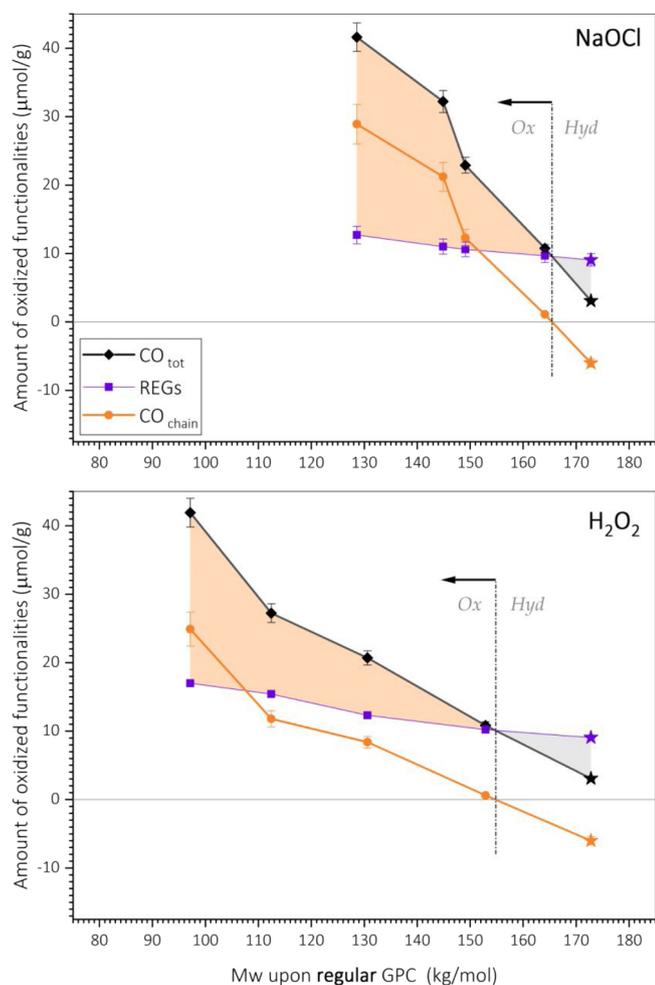- along-chain carbonyls survive a cuen-treatment (Ahn et al., 2019)

Fig. 6. Cotton linters. Amount of oxidized groups (carbonyls detected by GPC_{CCOA}) in CL, introduced by oxidation with NaOCl (top) and H_2O_2 (bottom) related to the Mw as measured by GPC on regularly-dissolved and analyzed samples (no alkali-induced degradation and no regeneration). The reference (native, non-oxidized pulp) is indicated with ★. Orange-shaded areas represent the amount of carbonyls along the cellulose backbone; "*Ox*" and "*Hyd*" indicate that a primarily oxidative or hydrolytic degradation of cellulose, respectively, occur, as estimated from the difference between total C=O and REGs (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

Fig. 7. Cotton linters. Relationship between the total amount of carbonyl groups (CO_{tot}, $\mu mol\ g^{-1}$) in regularly-dissolved oxidized pulps (i.e. no solvent-induced degradation, x axis) and in pulps dissolved in the solvents for viscosity (i.e. alkali-induced beta elimination), cuoxam (filled symbols, straight lines) and cadoxen (empty symbols, dashed lines). Oxidants: H_2O_2 (black) and NaOCl (green). Best-fit lines of experimental data and linear regression parameters are indicated (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

substantial amount of oxidized functionalities and which "responds" differently to the alkaline environment than the cellulose part was too strong.

4. Conclusion

This study reports a detailed investigation of the harmful effect of oxidative damage of cellulosic pulps which are dissolved in organometallic alkaline solvents for viscosity measurements, cuoxam and cadoxen. Particular attention is paid to the changes on the molecular level. We quantify, for the first time, the effect of the solvent-induced degradation and its dependency on the nature of the carbonyls in the cellulosics.

In general, with the amount of carbonyl groups increasing in oxidized pulps, the degradation in the alkaline viscosity measurement media becomes more severe as compared to native, non-oxidized pulp samples, seen by an additional Mw loss of about 30 % and 60 % for CL and HBSP, respectively. This provides solid evidence of the detrimental effect of these solvents which induce scissions of alkali-labile linkages, compromising the molecular integrity of the pulps (average molar masses decreased).

Some important detailed conclusions can be drawn from this study:

- Native model pulps degrade in a similar way upon contact with cuoxam or cadoxen;
- Organometallic solvents for cellulose dissolution and viscosity determination compromise the average molar masses of pulps more severely if the pulps contain hemicellulose (i.e. HBSP vs. CL). Cadoxen seems to be slightly less aggressive in this regard. Its lower basicity relative to cuen or cuoxam translates into a lower dissolution power towards hemicelluloses.
- Regarding the oxidation of pulps, not just the extent of oxidation but also the location of introduced oxidized functionalities within the AGU and along the chain – which are determined by the type of oxidant – play an important role. Hydrogen peroxide oxidizes

better than one in cuoxam or cadoxen.

Finally, the data on the effect of cuoxam and cadoxen on oxidized celluloses are quite in agreement with our results on cuen (Ahn et al., 2019) thus confirming our previous conclusion that depolymerization of oxidatively-damaged celluloses in alkaline media depends on the oxidation mechanism (Fig. 8):

- *Hypochlorite pulps*: the decrease in the Mw upon increasing oxidation is levelled-off by the removal of all alkaline-labile carbonyls. Further oxidation does not cause further damage (size-constraint). As visible in Fig. 8 left for extended oxidation (i.e. most left-sided point in the graphs), despite the sharp increase in carbonyl concentration, the corresponding decrease in Mw is limited (up to about 100 kg/mol).
- *Peroxide pulps*: the decrease in Mw seemed to be more constant over a wider range of molar masses (down to 80 kg/mol).

Unfortunately, the complex nature of HBSP (hemicellulose content, trimodal MMD) hampered an analogous analysis for this wood pulp. The interference of the hemicellulose fraction which carries a
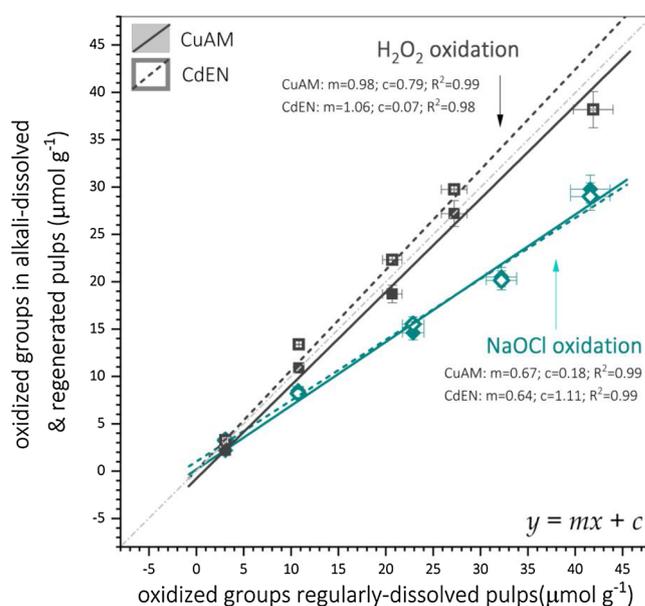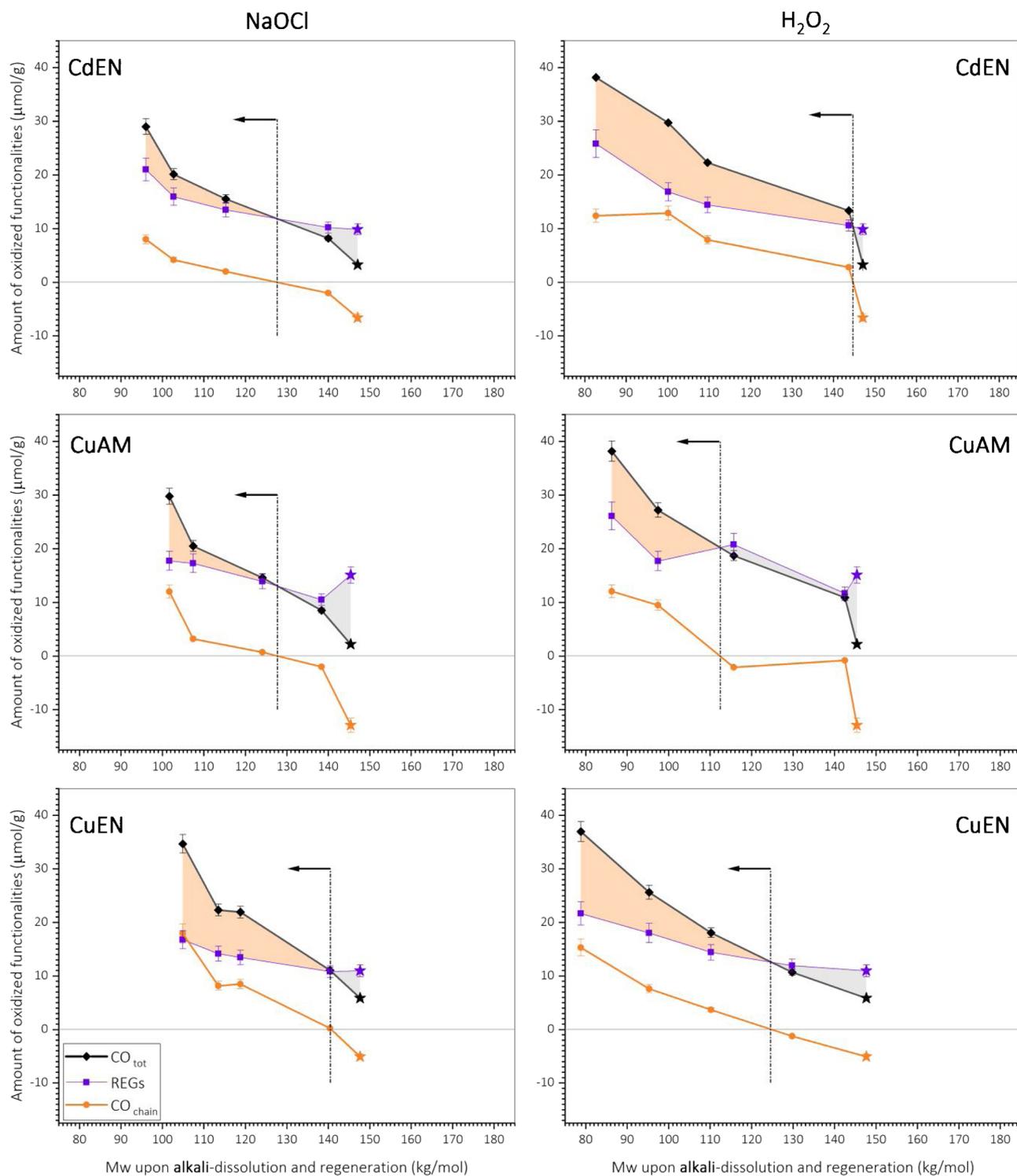
Fig. 8. Amount of oxidized functionalities (CO_{tot}, black; CO_{chain}, orange; REGs, purple) of oxidized cotton linters (CL) after dissolution and regeneration from organometallic solvents related to their corresponding Mw (kg mol^{-1}). Comparison by oxidant (left, NaOCl; right, H_2O_2) and solvent (top, CuAM; bottom, CdEN). Reference (native, non-oxidized pulp) is indicated with ★. Orange-shaded areas represent the amount of carbonyls along the cellulose backbone (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

cellulose in a more central position which leads in all cases to a smaller final DP (80 kg mol^{-1}) as compared to HOCl, which reaches only 100 kg mol^{-1} at the same extent of oxidation. The larger number of surviving carbonyls for peroxide-oxidized pulps is presumed to be due to C2/C3-diketo structures which do not undergo beta-alkoxy elimination processes, a hypothesis which is currently tested by model compound work and computations;

- Oxidized materials are severely attacked by both alkaline metal complexes, the damage (chain cleavage) increasing with increasing oxidation degree;
- H_2O_2-oxidized samples generally exhibit higher extent of solvent-induced degradation (i.e. higher MM loss) as compared to hypochlorite-oxidized ones, which is due to the fact that H_2O_2 affects mainly C2 and C3 while hypochlorite also affects C6. The rates for

beta-elimination from C-6, C-2 and C-3 are about 1:5:22 (Hosoya et al., 2018), hence elimination from C-2/C-3 (which are interchangeable in alkaline media) is about 20 times faster than from C-6, explaining the high lability of H_2O_2-oxidized pulps.

Thanks to a more advanced analytical approach and experimental design than hitherto possible, our study was able to shed some light on the topic of viscosity measurements and their problems, highlighting for the first time the complex interrelation between the viscometry solvents cuoxam and cadoxen, the type of pulp substrate, and the oxidation mode.

CRediT authorship contribution statement

Acknowledgments

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.carbpol.2020.116251.

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