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Assessing rheometry for measuring the viscosity-average degree of polymerisation of cellulose in paper degradation studies

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Abstract

In paper degradation studies, the viscosity-average degree of polymerisation (DP_v) is often used as a key indicator of the extent of degradation of cellulosic paper. DP_v can be deduced from the viscosity of dilute paper solutions, as typically measured through glass capillary viscometry. The current study proposes an efficient, alternative method to evaluate DP_v of cellulosic paper, which is based on rotational rheometry. The proposed methodology relies on the application of a shear flow in a thin film of cellulose solution to measure its dynamic viscosity, from which DP_v can be subsequently derived in a straightforward fashion. Rheometry allows to measure the viscosity for a range of shear rates, which results in multiple DP_v evaluations per sample, and thus in statistically representative data from an individual test. Further, rheometry typically requires considerably less paper mass per test than glass capillary viscometry, which makes the method attractive for paper degradation studies with limited sample availability. Also, rheometry measurements are less work-intensive than glass capillary viscometry measurements. The rheometry method has been applied to 4 hygrothermally aged cellulose paper samples and the unaged counterpart. The measurement results regarding the age-dependency of DP_v and the number of cellulose chain scissions are compared to those obtained by glass capillary viscometry, showing a very good agreement. At a longer ageing time, both experimental methods reveal a non-linear decrease in time of DP_v, and a non-linear increase in time of the number of cellulose chain scissions, which indicate that the cellulose ageing process is realistically captured. The agreement in measurement results further demonstrates that rheometry is an easy-to-use, accurate and efficient alternative for DP_v measurements by glass capillary viscometry.

Keywords Paper degradation, Ageing of cellulose, Degree of polymerisation, Glass capillary viscometry, Rheometry

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Introduction

Acid-catalysed hydrolysis is one of the main factors governing the degradation of paper [1, 2]. Hydrolysis reactions cause cleavage of the cellulose molecular chains through breakage of the glycosidic linkages, thereby resulting in a reduction of the average length of the cellulose chains, and thus in a reduction of the molecular weight [3–7]. This phenomenon has important consequences for the structural integrity of paper, as a decrease of the molecular weight is directly related to a reduction of the mechanical properties of cellulose, e.g., the tensile strength [8–11]. The extent of paper degradation is typically quantified in terms of the Degree of Polymerisation (DP), defined as the average number of monomeric units in the cellulose molecules, and its accurate determination plays an important role in paper ageing studies [12, 13].

In the literature, different methodologies have been proposed to assess ageing of paper samples. Size exclusion chromatography provides the molar mass distribution of cellulose, and consequently, the distribution of the DP and the polydispersity index [9, 14–16]. More often, the DP is evaluated by means of viscosity measurements on a dilute cellulose solution that is prepared by dissolving cellulose samples in a solvent. For this purpose, cadmium triethylene diamine dihydroxide, cuprammonium hydroxide or cupriethylenediamine can be used [17–19]. The procedure is based on *glass capillary viscometry*, which enables to determine the kinematic viscosity of the dilute cellulose solution in terms of the flow time that is needed for the fluid to pass through a capillary tube. From the kinematic viscosity, the intrinsic viscosity of the solution is determined next. By using the Mark-Houwink-Sakurada equation [20, 21], the *viscosity-average degree of polymerisation* (DP_v) is finally obtained as a function of the intrinsic viscosity. This method has been widely applied [15, 20–22], due to its relatively straightforward measurement procedure. However, viscosity measurements based on glass capillary viscometry may have certain limitations; specifically, these measurements can be carried out only at a predefined, constant shear rate, and the registration of the flow time is often performed manually, making the method work-intensive and time-consuming.

Alternatively, the intrinsic viscosity of cellulose solutions can be determined by measuring the dynamic viscosity via *rotational rheometry*. In rheometry, the dynamic viscosity is obtained through the application of a shear flow in a thin film of the considered fluid [23]. The shear flow develops by step wisely increasing the shear rate, whereby viscosity evaluations can be performed as soon as the shear stress becomes constant through reaching a steady state. Cellulose solutions typically exhibit Newtonian behaviour at relatively low concentrations [24, 25], whereby shear thinning remains absent and the dynamic viscosity stays constant over a considerable range of shear rates. By performing measurements at the separate shear rate steps, for each individual sample *multiple* dynamic viscosity evaluations are obtained in an efficient manner. Accordingly, a large number of (statistically representative) measurement data is acquired from an individual test. Moreover, a rheometry test typically requires less paper mass than required for a glass capillary viscometry test; this is an essential advantage of rheometry, specifically in degradation studies whereby the availability of samples is limited.

Despite the above-mentioned advantages, to date rheometry has not been explored for the evaluation of DP_v in paper degradation studies. Accordingly, the present study aims at assessing a rheometry-based method for the evaluation of the viscosity of cellulose solutions, from which subsequently DP_v of cellulose of paper samples can be determined. To this purpose, 4 hygrothermally aged cellulose paper samples and one unaged counterpart are tested. The validity of the method is verified by comparing the obtained DP_v values of cellulose solutions and the corresponding number of cellulose chain scissions with those obtained from glass capillary viscometry measurements. The results demonstrate that rheometry is an accurate and efficient measurement technique that is useful in paper degradation studies.

The paper is organized as follows. First, in "Experimental procedure" section, the sample preparation steps for both the rheometry and glass capillary viscometry experiments are described, followed by a summary of the main theoretical concepts underlying the two measurement methodologies. Next, the procedure to evaluate the intrinsic viscosity and DP_v is introduced. "Experimental results" section presents the details of the dynamic viscosity measurements of two specific samples, as obtained by rheometry. Subsequently, the measurement results of DP_v and the number of chain scissions are compared for the samples tested with the two methods. Finally, concluding remarks are given in "Conclusions".

Experimental procedure

The procedure to evaluate DP_v of cellulose from rheometry experiments and glass capillary viscometry experiments is performed on 4 hygrothermally aged samples of cellulose paper and one unaged counterpart. First, the paper samples are dissolved to attain a dilute solution of molecularly dispersed polymeric cellulose chains. The dynamic (or kinematic) viscosity of this dilute cellulose solution is measured, and subsequently converted to the intrinsic viscosity of the cellulose polymers, which is eventually used to calculate DP_v of the paper samples by applying the well-known Mark-Houwink-Sakurada

equation. The individual experimental steps and the underlying equations are successively described below.

Sample preparation

The measurements were carried out on a set of Whatman No. 1 filter paper sheets. Whatman No. 1 filter paper is 100% cotton paper, made of cotton linters without sizing and fillers. Its chemical composition is fully based on cellulose, i.e., it does not contain hemicellulose or lignin. The use of Whatman No. 1 filter paper is common in paper conservation studies since its simple composition enables an accurate assessment of degradation mechanisms. Moreover, it is widely commercially available. The considered samples were hygrothermally aged at 90 °C for 6, 12, 20, and 35 days; further, a reference, unaged paper sheet was used. The accelerated ageing process was performed in 2014 using Lab-Line hybridization tubes (144 ml), according to the standard TAPPI T573 pm-09 [26] that is commonly applied in paper conservation studies. The samples were part of the same pool of Whatman No. 1 samples as those studied in [7, 11]. The relative humidity (RH) in the tube is buffered by the paper and typically stabilizes around 50% during the ageing process [27]. The samples were subsequently kept in a dark room under ambient conditions (21.5 ± 1.5 °C and 52 ± 2% RH), until they were prepared for the viscosity measurements presented in this paper.

With the above paper specimens, the sample preparation for glass capillary viscometry was performed based on the standard ASTM D1795-13 [19]. The rheometry samples were prepared according to the standard IEC 60450 [28]. The two standards are merely different regarding the specific temperature prescribed during the viscosity measurement, i.e., the glass viscometry and rheometry were performed at 25 °C (ASTM) and 20 °C (IEC), respectively. Further, for both types of experiments, three samples were prepared per ageing time.

Different dilute cellulose solutions were prepared using cupriethylenediamine (CED) as a solvent. Specifically, paper samples of 14 to 47 mg were dissolved in 10 ml of 50% water-diluted CED. The use of different concentrations is required to guarantee that the viscosity of all samples falls within a range that is suitable for the performance of accurate viscosity measurements with the viscometer. In fact, samples characterized by a longer ageing time are expected to have a lower DP_v, which at a constant cellulose concentration results in a lower viscosity. Since a higher concentration results in higher viscosity, a higher mass of paper was used for the preparation of samples with a longer ageing time. The preparation procedure was based on cutting each piece of paper roughly into 2 mm^2 pieces, followed by soaking these pieces for 30 min in 5 ml of demineralized water, after which 5 ml of CED was added. Each sample was then magnetically stirred for 30 min to ensure an adequate and complete dissolution process, immediately after which the viscosity measurement (rheometry or glass capillary viscometry) was performed.

In order to obtain the intrinsic viscosity of each sample, it is necessary to accurately measure the concentration of cellulose in the solution. To this purpose, before preparing the solution, the hygrothermally aged, pre-cut paper pieces were weighed with a precision of 0.01 mg. Subsequently, the moisture content of the paper specimens was measured and the mass of water was subtracted from the cellulose mass to attain an accurate determination of the polymer concentration. The equilibrium moisture content of the paper samples was determined from the isotherms measured at 21 °C using a TGA Q5000 SA sorption analyzer (TA Instruments). Separate samples were used for evaluating the moisture content and the degree of polymerization.

More details of the measurement procedure can be found in the supplementary material of [11].

Rheometry

Rheometry is an experimental method that enables to measure the viscosity of a liquid by inducing a controlled shear flow. This is done by applying a force F on a boundary plate that is in contact with the surface of the fluid, which results in a gradient of deformation from that surface to the opposite, stationary surface. This gradient of deformation corresponds to a (simple) shear strain γ, while the ratio between the applied force F and the area of the boundary plate equals the corresponding shear stress τ. Accordingly, the dynamic viscosity η is defined by

$$\eta = \frac{\tau}{\dot{\gamma}}, \tag{1}$$

with $\dot{\gamma}$ the shear (strain) rate. Note that in the current study rotational rheometry is employed, whereby the shear flow is applied in a rotational manner. In particular, a thin film of liquid is enclosed in between two circular discs or concentric cylinders, and the rotation of one of the discs or cylinders induces a shear flow in the liquid. The torque needed for the application of a constant rotational speed is measured, from which the applied shear stress τ, and subsequently, through Eq. (1), the dynamic viscosity η of the liquid at the specific shear rate $\dot{\gamma}$ are calculated.

In the case of Newtonian fluids, the viscosity is invariant under an increasing shear rate. Fluids that deviate from Newtonian behaviour, i.e., non-Newtonian fluids, often exhibit a behaviour referred to as shear thinning, which is characterized by a decrease of the viscosity

when exceeding a (sufficiently high) critical shear rate. This effect may be ascribed to small structural changes within the fluid, such as the disentanglement of polymer chains, which facilitate shearing and thereby reduce the viscosity [23]. Dilute solutions of cellulose in CED, however, are expected to exhibit Newtonian behaviour with a constant dynamic viscosity over a considerable range of shear rates.

In the present work, the rheometry measurements were performed with an Anton Paar MCR 501 rotational rheometer equipped with a double-wall Couette geometry (DG26.7-SS). This geometry provides an extra surface area in comparison to other geometries, such as a disk or a cone, which makes it suitable for accurately measuring relatively low viscosities. For each measurement, approximately 3.5 ml of the cellulose-CED solution was inserted in the rheometer's geometry. Note that this amount is about one third of the 10 ml CED solution needed for the glass capillary viscometry test, which thus effectively reduces the paper mass needed for sample preparation by $(1 - 3.5/10) \times 100\% = 65\%$, to between 5 and 17 mg (with the specific mass depending on the ageing time). The use of a relatively low amount of paper material makes rheometry attractive for degradation studies with limited sample availability. After insertion of the CED solution in the rheometer, measurements were carried out at shear rates of 10 to 2000 s^{-1}. The shear rate $\dot{\gamma}$ was increased in an exponential fashion, using 25 steps to reach the predefined, maximum value. The duration of each step was 30 s, during which the torque was measured and the corresponding shear stress τ was computed, leading via Eq. (1) to the dynamic viscosity η. It was verified that a period of 30 s was sufficient for reaching steady-state flow conditions. By applying a stepwise increase of $\dot{\gamma}$, a single experiment provides different values of the dynamic viscosity η; in fact, the dynamic viscosity obtained at each individual step can be regarded as an independent measurement value. Accordingly, a large number of (statistically representative) measurement data is obtained from an individual test.

Glass capillary viscometry

Glass capillary viscometry is an experimental method for evaluating the viscosity of a fluid, and is based on the measurement of the flow time, called the *efflux time*, of a defined liquid volume flowing through a capillary tube. The method makes use of the Hagen-Poiseuille equation, which provides the pressure drop Δp for an incompressible Newtonian fluid that flows through a tube with a constant cross-section as [29]:

$$\Delta p = \frac{8\eta V L}{\pi\, t\, R^4}\,, \tag{2}$$

where η is the dynamic viscosity of the fluid, V is the flow volume, R and L are the respective radius and length of the tube, and t is the efflux time. In glass capillary viscometers, the driving force for flow is the hydrostatic pressure of a liquid column. Accordingly, the pressure difference can be written as $\Delta p = \rho g h_m$, where ρ is the density of the liquid, g is the gravitational acceleration and h_m is the height of the liquid head above the capillary entrance of the viscometer. Inserting the above relation for Δp in Eq. (2), and reformulating the resulting expression, allows to write the kinematic viscosity $\nu = \eta/\rho$ as

$$\nu = C_0 t \qquad \text{with} \qquad C_0 = \frac{\pi R^4 g h_m}{8 L V}\,, \tag{3}$$

whereby the specific value of the factor C_0 essentially depends on the characteristics of the viscometer used and thus can be determined by calibration. In the current study, a Cannon-Fenske Routine 100 viscometer was used, with a calibration factor of $C_0 = 0.01468\ mm^2\ s^{-2}$ at a temperature of 40 °C. For each specimen, the efflux time was measured using a stopwatch. The measurements were repeated until three consecutive readings corresponded within 0.1 s, which were then averaged. The kinematic viscosity was subsequently determined from the average efflux time via Eq. (3). The measurements were performed in the viscosity regime where the Hagenbach-Couette correction factor, which accounts for pressure losses at the capillary ends, can be neglected. In specific, the range of kinematic viscosities ν of dilute cellulose solutions in CED are bounded by a maximum value of approximately $3.0\ mm^2\ s^{-1}$ [24, 25]. In accordance with the technical specifications of the experimental setup used for performing the glass viscometry experiments, this maximum viscosity value relates to a maximum efflux time t of 200 s and a minimum shear rate $\dot{\gamma}$ of $612\ s^{-1}$. Depending on the state of degradation of each sample, the concentration c of the dilute cellulose solution was carefully selected to ensure that the experimental results fall within the above range of values.

Intrinsic viscosity

In order to determine DP_v from the rheometry and glass capillary viscometry experiments, the measured viscosity values first needed to be converted to the so-called *intrinsic viscosity*. The intrinsic viscosity $[\eta]$ of a dilute solution is a measure of the contribution of the solute, i.e., the cellulose polymeric chains, to the viscosity of the

solution. It is defined by the ratio between the specific viscosity η_s and the concentration c of the cellulose solution, evaluated in the limit of an infinitely dilute solution $c \to 0$, i.e.,

$$[\eta] = \lim_{c \to 0} \frac{\eta_s}{c}, \tag{4}$$

where the specific viscosity η_s follows from

$$\eta_s = \frac{\eta - \eta_{solv}}{\eta_{solv}}, \tag{5}$$

with η and η_{solv} the dynamic viscosities of the solution and the solvent, respectively. From its definition given by Eq. (4), the intrinsic viscosity can be determined by performing dynamic viscosity measurements at different concentrations close to zero, and next extrapolating the result to zero concentration [30–32]. However, it is common practice to obtain $[\eta]$ based on a *single* concentration measurement. For this purpose, Martin's formula is used [22, 33]:

$$\eta_s = [\eta]\, c\, 10^{k[\eta]c}, \tag{6}$$

where k is Martin's constant, which is equal to 0.13 and 0.14 for the cases of glass capillary viscometry and rotational rheometry, respectively. This slight difference in the value of k is due to the fact that the glass viscometry measurements are performed based on the ASTM D1795-13 standard [19] and the rheometry measurements are based on the IEC 60450 standard [28].

In the rheometry experiment, the specific viscosity η_s appearing in the left-hand side of Eq. (6) is computed via Eq. (5), by substituting the dynamic viscosities η and η_{solv} as obtained via Eq. (1). Conversely, in the glass capillary viscometry experiment, the specific viscosity is determined as follows. When the difference in the densities of the dilute solution and that of the solvent is small and negligible (which is the case for the cellulose solutions used in the present study), from the definition of the kinematic viscosity $\nu = \eta/\rho$, the specific viscosity in Eq. (5) can be alternatively determined as $\eta_s = (\nu - \nu_{solv})/\nu_{solv}$. Combining this relation with Eq. (3) allows to write the specific viscosity as:

$$\eta_s = \frac{t - t_{solv}}{t_{solv}}, \tag{7}$$

where t and t_{solv} are the efflux times of the cellulose solution and the solvent, respectively. The specific viscosities η_s following from the rheometry and glass viscometry experiments and the concentrations c of the corresponding samples are next inserted in the (nonlinear) Martin's equation, Eq. (6), which is solved in an iterative fashion to obtain the intrinsic viscosity $[\eta]$. It is noted that for the glass viscometry experiment the value of $[\eta]$ can also be determined from η_s by using the tabular data provided in the standard ASTM D1795-13, which leads to the same result.

Viscosity-average degree of polymerisation (DP_v)

From the intrinsic viscosity $[\eta]$ of the specimen, the corresponding value of the viscosity-average degree of polymerisation DP_v is calculated from the inverse of the Mark-Houwink-Sakurada equation:

$$[\eta] = K\,(DP_v)^{\alpha}, \tag{8}$$

whereby the two empirical constants are taken as $K = 0.91$ and $\alpha = 0.85$ [20].

Experimental results

The rheometry and glass capillary viscometry experiments described in "Experimental procedure" section were performed on paper samples subjected to different ageing times. First, the dynamic viscosity measurements obtained by rheometry are presented for two specific specimens. Next, DP_v and the number of chain scissions measured for the test samples are discussed and compared for the two measurement methods.

Dynamic viscosity versus shear rate from rheometry experiments

Figure 1 illustrates the dynamic viscosity as a function of the applied shear rate, as obtained from the rheometry experiments for two specific specimens made of Whatman No. 1 filter paper. The specimens are referred to as *Specimen 1* (Fig. 1a) and *Specimen 2* (Fig. 1b), and respectively correspond to the minimum and maximum exposure times of 6 and 35 days selected in the accelerated ageing procedure.

In Fig. 1 three different regions are distinguished, which are delimited by the vertical dashed lines. The first region corresponds to a low shear rate, whereby the value of the torque applied by the rheometer to reach the desired shear rate typically lies outside the accuracy range of the rheometer. This results in a high noise-to-signal ratio for the measured viscosity values, which therefore are left out of consideration. In the second region, the dynamic viscosity reaches an approximately constant value that is independent of the applied shear rate, as characteristic of a Newtonian fluid. As explained in "Experimental procedure" section, these measurement results are suitable for determining DP_v of the cellulose. The third region corresponds to a relatively high shear rate and typically is characterized by a significant drop in the measured viscosity due to shear thinning, see Fig. 1a, or by a monotonic increase in the viscosity as a result of inertia effects,

see Fig. 1b. Hence, the viscosity values measured in this region are omitted in the determination of DP_v.

In correspondence with the above observations, within the second region the workable range of the applied torque has been identified to lie between 10 and 100 μNm, for which the measured dynamic viscosities are indicated in Fig. 1 by the red solid circles. The range of these measurement points is designated in the figure as the *measurement region*. The size of the measurement region proved to be adequate for all samples tested, as it always fell within the second region in which the dynamic viscosity is approximately constant. For Specimen 1, the mean value and standard deviation of the dynamic viscosity, as evaluated across the measurement region denoted in Fig. 1a, are 3.34×10^{-3} Pa s and 0.003×10^{-3} Pa s, respectively. For Specimen 2, the mean value and standard deviation across the measurement region in Fig. 1b are 2.78×10^{-3} Pa s and 0.005×10^{-3} Pa s, respectively.

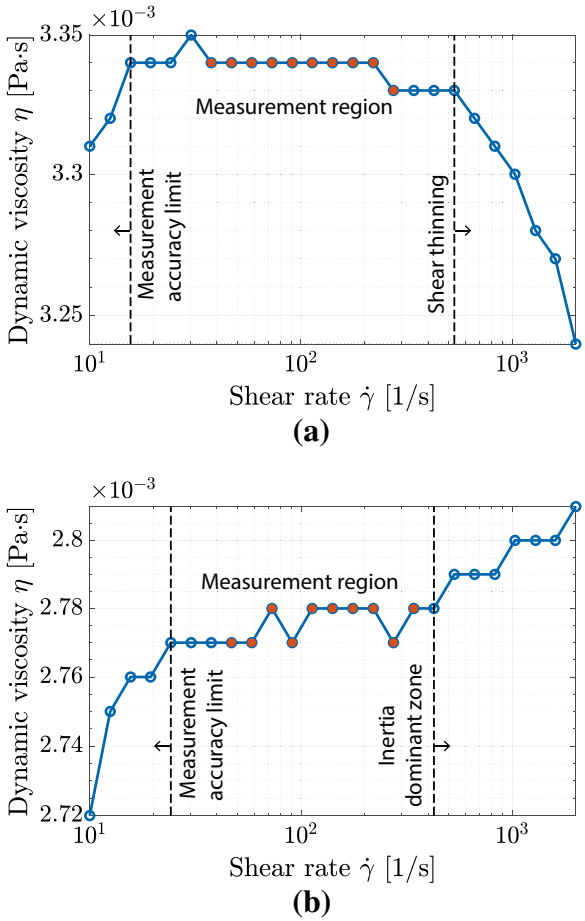

Fig. 1 Dynamic viscosity as a function of the shear rate as measured by rotational rheometry for **a** *Specimen 1*—artificially aged for 6 days, and **b** *Specimen 2*—artificially aged for 35 days. The measurement region used for determining the dynamic viscosity is indicated by means of red solid circles

Comparison of results from rheometry and glass capillary viscometry experiments

Figure 2a, b show DP_v and the number of chain scissions as a function of ageing time, respectively, as determined by rheometry (solid blue line) and glass capillary viscometry (dashed orange line). The average measurement values are indicated by circles and the maximum and minimum measurement values by error bars. The spread in the measurement results is generally small, indicating that pure cellulose paper is characterized by a very low uncertainty in DP_v measurements and that the

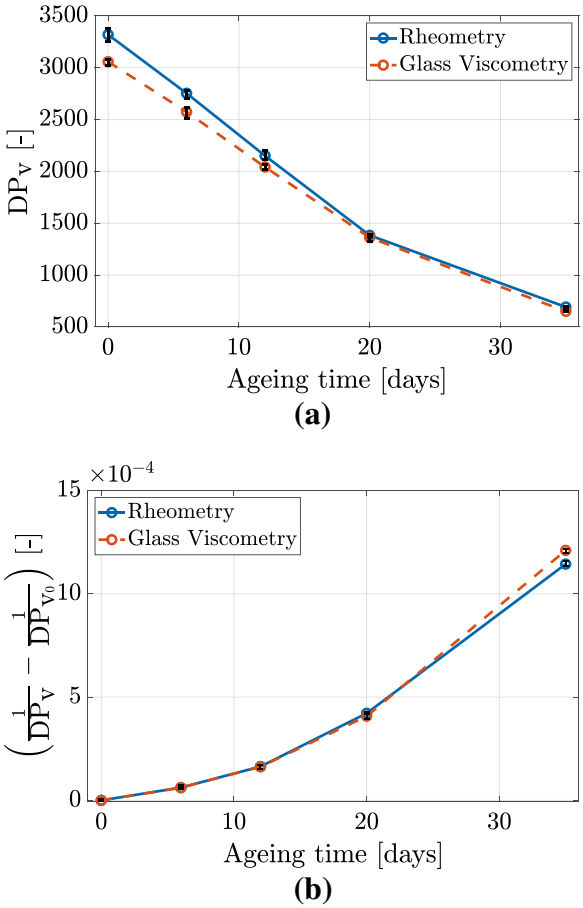

Fig. 2 Comparison of DP_v of hygrothermally aged Whatman No. 1 paper, obtained from rotational rheometry experiments (solid blue line) and glass capillary viscometry experiments (dashed orange line). **a** Viscosity-average degree of polymerisation DP_v and **b** number of chain scissions $S = (1/DP_v - 1/DP_{v0})$ as a function of ageing time. The circles represent the average measurement values and the error bars represent the maximum and minimum measurement values of each of the 5 age categories, which are based on respectively 30 and 3 measurements for the rheometry and glass capillary viscometry experiments

measurements have been performed with high precision. Obviously, the uncertainty in DP_v values measured for real paper samples, which have a more heterogeneous composition, may be expected to be larger.

In the rheometry experiments, the viscosity of the three samples of a specific age has been evaluated at about 10 different values of the shear rate (as reflected by the red solid circles in Fig. 1), thus resulting in approximately 30 viscosity evaluations per age category. Conversely, in the glass capillary viscometry experiments only one viscosity measurement is obtained per sample, leading to three viscosity evaluations per age category. Consequently, rheometry is much more efficient in acquiring measurement data for the viscosity than glass capillary viscometry.

Observe from Fig. 2a that DP_v decreases as a function of ageing time, confirming the degradation of the samples with age. The age-dependent trends of DP_v determined by the two measurement methods generally exhibit a very good agreement; the glass viscometry measurements lead to slightly lower values of DP_v, which may be due to the fact that the rheometry and glass viscometry measurements were performed at somewhat different temperatures of 20 °C and 25 °C, respectively, as dictated by the respective standards ASTM D1795-13 [19] and IEC 60450 [28]. Specifically, the higher temperature prescribed for the glass viscometry measurements provides slightly lower viscosity values, which in turn results in slightly lower DP_v values.

The extent of paper degradation can be quantitatively assessed from the number of broken polymeric bonds, which depends on time and governs the kinetics of cellulose degradation. Accordingly, in Fig. 2b the number of scissions per anhydroglucose unit S is considered as a function of ageing time, with $S = (1/DP_v - 1/DP_{v0})$, where DP_{v0} is the initial value of DP_v [3, 5, 8]. The two measurement methods lead to a similar trend, showing that the number of chain scissions S increases progressively with age.

According to Ekenstam's kinetic model for the degradation of linear polymers [13, 34, 35], the number of chain scissions S is expected to vary linearly as a function of the ageing time, with the slope representing the rate constant for glycosidic bond cleavage. This linear behaviour has often been observed in accelerated ageing experiments performed in paper degradation studies [1, 8]. Note that the curve in Fig. 2b appears to be close to linear only during the first 10 days of accelerated ageing. The non-linear evolution of the number of chain scissions at a longer ageing time has also been reported in other experimental works on paper degradation [16, 36, 37], and, although not completely understood, has been attributed to an acid-catalyzed hydrolysis reaction, whereby the nature of the reactant changes continuously [2].

Conclusions

The viscosity-average degree of polymerisation DP_v is a commonly used parameter for quantifying the extent of paper degradation, and is often determined by means of glass capillary viscometry experiments. This article presents an efficient and accurate alternative method for measuring DP_v, which is based on rotational rheometry experiments. This measurement method enables to determine the dynamic viscosity through the application of a shear flow in a thin film of the considered fluid. From the dynamic viscosity, the intrinsic viscosity can be deduced, which subsequently provides the viscosity-average degree of polymerisation DP_v via the Mark-Houwink-Sakurada equation. Within a single experiment, rheometry measurements can be performed over a range of shear rates, thereby resulting in multiple evaluations of the viscosity of the test sample. Accordingly, rheometry is very efficient in acquiring measurement data on viscosity. Moreover, a rheometry test typically requires less paper mass than a glass capillary viscometry test, making rheometry an attractive method in paper degradation studies with limited sample availability. Further, rheometry measurements are less work-intensive than glass capillary viscometry measurements.

The proposed rheometry method has been applied to 4 hygrothermally aged cellulose paper samples and one unaged counterpart. The measurement results for DP_v and the number of chain scissions as a function of ageing time have been compared to those obtained by glass capillary viscometry, showing a very good agreement. At longer ageing times, both experimental methods reveal a non-linear decrease in time of DP_v and a non-linear increase in time of the number of cellulose chain scissions, which confirm other experimental studies and indicate that the cellulose ageing process is realistically captured. The agreement in measurement results further proves that rheometry is an easy-to-use and efficient alternative for DP_v measurements by glass capillary viscometry.

Abbreviations

DP	Degree of polymerisation
DP_v	Viscosity-average degree of polymerisation
TAPPI	Technical association of the pulp and paper industry
ASTM	American Society for Testing and Materials
IEC	International Electrotechnical Commission
CED	Cupriethylenediamine

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Author contributions
SM has contributed to the conception and design of the work, acquisition, analysis and interpretation of the data, and has drafted and revised the manuscript. A-LD has contributed to conception and design of the work and interpretation of the data, has drafted part of the manuscript, and has revised the entire manuscript. RC as contributed to conception and design of the work and interpretation of the data, and has revised the manuscript. SP-L has contributed to acquisition, analysis, and interpretation of the data and has revised the manuscript. JPMH has contributed to the conception and design of the work, and interpretation of the data, and has revised the manuscript. ASJS has contributed to funding acquisition, the conception and design of the work, and interpretation of the data, and has revised the manuscript. EB has contributed to funding acquisition, the conception and design of the work, and interpretation of the data, and has revised the manuscript. All authors read and approved the final manuscript.

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Availability of data and materials
Data will be available upon request.

Declarations

Competing interests
The authors declare that they have no competing interests.

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