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## RESEARCH

# 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. The  $DP_{v}$  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 the  $DP_v$  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 fluid to measure its dynamic viscosity, from which the  $DP_v$  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<sub>v</sub> evaluations per specimen, making the method statistically representative for each test with less experimental effort. The proposed viscometry methodology has been applied to 4 hygrothermally-aged cellulose paper samples and the unaged counterpart. The measurement results regarding the age dependency of the degree of polymerisation and the number of cellulose chain scissions are compared to those obtained by glass capillary viscometry, showing a very good agreement. Both experimental methods reveal a non-linear decrease in time of the degree of polymerisation, and a non-linear increase in time of the number of cellulose chain scissions, indicating 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

### 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 of the molecular weight [3, 4, 5, 6, 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, 9, 10, 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 the degree of ageing of paper samples. Size exclusion chromatography provides the molar mass distribution of cellulose, and consequently the distributions of the DP and the polydispersity index [9, 14, 15, 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, 18, 19]. The procedure departs from glass capillary viscometry measurements, in order to obtain 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  $(DP_y)$  is finally obtained as a function of the intrinsic viscosity. This method has been widely applied [20, 22, 15, 21], 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 stepwisely 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 a strong 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. This results in statistically representative data for each test and a less work intensive experimental procedure.

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

The paper is organized as follows. First, in Section "Experimental procedure", the sample preparation steps for both the rheometry and glass capillary viscometry methods 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 the  $DP_v$  are introduced. Section "Experimental results" presents the details of the dynamic viscosity measurements of two specific samples, as obtained by rheometry. Subsequently, the measurement results of the  $DP_v$  and the number of chain scissions are compared for the samples tested with the two methods. Finally, some concluding remarks are given in "Conclusions".

#### Experimental procedure

The procedure to evaluate the viscosity-average degree of polymerisation of cellulose from rheometry experiments and glass capillary viscometry experiments is performed on 4 hygrothermally-aged samples of cellulose paper and one unaged, cellulose paper sample. 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 transferred to the intrinsic viscosity of the cellulose polymers, which is eventually used to calculate the DP<sub>v</sub> of the paper samples by applying the well-known Mark-Houwink-Sakurada (MHS) 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 that were hygrothermally aged at 90 °C for 6, 12, 20 and 35 days, and on a reference, unaged paper sheet. The, accelerated ageing process was performed in 2014 using Lab-Line hybridization tubes (144 ml), according to the standard TAPPI T573 pm-09 [26]. 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 between 50 and 60% during the ageing process [27]. The samples were next kept at room conditions, at a temperature of  $21.5 \pm 1.5$  °C and a relative humidity of  $52\pm 2\%$ , 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], and the rheometry specimens 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 age category.

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 specific, the samples characterized by a longer ageing time are expected to have a lower DP, resulting in a lower viscosity for a constant concentration of the cellulose solution. Considering that a higher concentration results in a higher viscosity, a higher mass of paper is therefore used for the preparation of samples with longer

ageing time. The preparation procedure is based on cutting each piece of paper into roughly  $2 \text{ mm}^2$  pieces, followed by soaking these pieces for 30 minutes in 5 ml of demineralized water, after which 5 ml of CED is added. Each sample is then magnetically stirred for 30 minutes to ensure an adequate and complete dissolution process.

In order to obtain the intrinsic viscosity of each specimen, it is necessary to accurately measure the concentration of cellulose in the solution. To this purpose, before preparing the solution, the 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 the moisture was subtracted from the cellulose mass to attain an accurate determination of the polymer concentration. The equilibrium moisture content of the samples was determined from the isotherms measured at 21 °C using a TGA Q5000 SA sorption analyzer (TA Instruments). 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  $\gamma$ , while the ratio between the applied force F and the area of the boundary plate equals the corresponding shear stress  $\tau$ . Accordingly, the dynamic viscosity  $\eta$  is defined by

$$\eta = \frac{\tau}{\dot{\gamma}} , \qquad (1)$$

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, and the rotation of one of the discs 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  $\tau$ , and subsequently, through Eq.(1), the dynamic viscosity  $\eta$  of the liquid at the specific shear rate  $\dot{\gamma}$  are computed.

In case of Newtonian fluids, the viscosity is invariant under a growing 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 (sudden) 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 a 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 facility provides extra surface area in comparison to other geometries, such as a plate or a cone, which makes it suitable for accurately measuring relatively low viscosities. By using a pipette, for each measurement roughly 3.5 ml of the cellulose-CED solution is inserted in the rheometer's geometry. Subsequently, measurements are performed at shear rates of 10 to  $2000 \text{ s}^{-1}$ . The shear rate  $\dot{\gamma}$  is increased in an exponential fashion, using 25 steps to reach the predefined, maximum value. The duration of each step is 30 seconds, during which the torque is measured and the corresponding shear stress  $\tau$  is computed, thus leading via Eq.(1) to the dynamic viscosity  $\eta$ . It was verified that a period of 30 seconds 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  $\eta$ ; in fact, the dynamic viscosity obtained at each individual step can be regarded as an independent measurement value. Accordingly, a large number of measurement data is obtained from only a small number of experiments, resulting in statistically representative data for each test.

#### Glass capillary viscometry

Glass capillary viscometry is an alternative 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. Its origin stems from the Hagen-Poiseuille equation, which provides the pressure drop  $\Delta p$  for an incompressible Newtionian fluid that flows through a tube with a constant cross-section as [29]:

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

where  $\eta$  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  $\rho$  is the density of the liquid, g is the gravitational acceleration and  $h_m$  is the heigth of the liquid head above the capillary entrance of the viscometer. Inserting the above relation for  $\Delta p$  in Eq. (2), and reformulating the resulting expression, allows to write the kinematic viscosity  $\nu = \eta/\rho$  as

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

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, which is characterized by a calibration factor  $C_0 = 0.01468 \text{ mm}^2 \cdot \text{s}^{-2}$  at a temperature of 40 °C. For each specimen, the efflux time was measured until three consecutive measurements provide values of which the mutual difference was less than 0.1 s. The kinematic viscosity was subsequently determined from the average of these three efflux times 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  $\nu$  of dilute cellulose solutions in CED are bounded by a maximum value of approximately 3.0 mm<sup>2</sup> s<sup>-1</sup> [24, 25]. In accordance with the technical specifications of the experimental set-up 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<sup>-1</sup>. Depending on the state of degradation of each sample, the concentration c of the dilute cellulose solution is carefully selected to ensure that the experimental results fall within the above range of values.

#### Intrinsic viscosity

In order to determine the viscosity-average degree of polymerisation from the rheometry and glass capillary viscometry experiments, the measured viscosity values first need to be transferred 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  $\eta_s$  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  $\eta_s$  follows from

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

with  $\eta$  and  $\eta_{solv}$  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, 31, 32]. However, it is common practice to obtain [ $\eta$ ] based on a *single* concentration measurement. For this purpose, Martin's formula is used [33, 22]:

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

where k is Martin's constant, which is equal to 0.13 and 0.14 for the case 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  $\eta_s$  appearing in the left-hand side of Eq.(6) is computed via Eq.(5), by substituting the dynamic viscosities  $\eta$ and  $\eta_{solv}$  as obtained via Eq.(1). Conversely, in the glass caplillary viscometry experiment the specific viscosity is determined as follows. When the difference in the densities of the dilute solution and solvent is minor and ignorable (which is the case for the cellulose solutions used in the present study), from the definition of the kinematic vicosity  $\nu = \eta/\rho$ , 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  $\eta_s$  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  $\eta_s$  by using the tabular data provided in the standard ASTM D1795-13, which leads to the same result.

#### Viscosity-average degree of polymerisation

From the intrinsic viscoity  $[\eta]$  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 (MHS) equation

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

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 Section "Experimental procedure" were performed on paper samples characterized by different ageing conditions. First, the dynamic viscosity measurements obtained by rheometry are presented for two specific specimens. Next, the  $DP_v$  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. 1(a)) and Specimen 2 (Fig. 1(b)), 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 Section "Experimental procedure", these measurement results are suitable for determining the  $DP_{\rm v}$  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 the  $DP_{v}$ .

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  $\mu$ Nm, for which the corresponding, 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  $3.34 \times 10^{-3}$  Pa · s and  $0.003 \times 10^{-3}$  Pa · s, respectively. For Specimen 2, the mean value and standard deviation across the measurement region in Fig. 1b are  $2.78 \times 10^{-3}$  Pa · s and  $0.005 \times 10^{-3}$  Pa · s, respectively.

#### Comparison of results from rheometry and glass capillary viscometry experiments

Figures 2(a) and (b) respectively show the viscosity-average degree of polymerisation and the number of chain scissions as a function of ageing time, as determined



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

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. Clearly, the spread in the measurement results is generally small, which confirms that the measurements have been performed with high precision.

In the rheometry experiments, the viscosity of the 3 specimens 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. In comparison to the glass capillary viscometry experiments, whereby the 3 samples per age category only lead to 3 viscosity evaluations, it may be concluded that in the rheometry experiments the measurement data is obtained much more efficient.

Observe from Fig. 2a that the  $DP_v$  decreases as a function of ageing time, from which it indeed follows that the cellulose samples degrade with age. The agedependent trends of the  $DP_v$  determined by the two measurement methods generally exhibit a very good agreement; the glass viscometry measurements only lead to slightly lower values of the  $DP_v$ , which may thus be due to the fact that the rheometry and glass viscometry measurements are 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]. In specific, the higher temperature prescribed for the glass viscometry measurements leads to slightly lower viscosity values, which in turn results in slightly lower  $DP_v$  values.

The amount of paper degradation can be qualitatively 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  $S = 1/\text{DP} - 1/\text{DP}_0$ , whereby  $\text{DP}_0$  is the initial degree of polymerisation [8, 3, 5]. The two measurement methods lead to a similar trend, showing that the number of chain scissions S increases progressively with age, exhibiting nonlinearity at higher degradation range.

According to the Ekenstam's kinetic model for the degradation of linear polymers [34, 35, 13], the number of chain scissions S is expected to vary linearly as a function of the ageing time, with the slope k representing the rate constant for glycosidic bond cleavage. This linear behaviour has often been observed in accelerated ageing experiments performed in paper degradation studies, see for example, [1, 8]. Note that the curve in Fig. 2b appears to be close to linear only during the first 10 days of accelerated ageing. A non-linear cleavage development at longer ageing times has also been observed in other experimental works on paper degradation [4, 16], and although not completely understood, has been attributed to an acid catalyzed hydrolysis reaction whereby the nature of the reactant changes continuously [4].

#### 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 the  $DP_v$ , which is based on rotational rheometry experiments. This measurement method enables to determine the



Figure 2: Comparison of degree of polymerisation 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 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.

dynamic viscosity through the application of a shear flow in a thin film of the considered fluid. From the dynamic viscosity, the intrisinc 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 tested sample. This efficiency of the method results in statistically representative data for each test. The proposed viscometry method has been applied to 4 hygrothermally-aged samples of cellulose paper and one unaged, cellulose paper sample. The measurement results for the degree of polymerisation and the number of chain scissions as a function of ageing have been compared to those obtained by glass capillary viscometry, showing a very good agreement. Both experimental methods reveal a non-linear decrease in time of the degree of polymerisation, and a non-linear increase in time of the number of cellulose chain scissions at higher degradation levels, indicating 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.

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#### References

- 1. Nevell, T.P.: Degradation of cellulose by acids, alkalis, and mechanical means. Cellulose Chem. Appl. 223 (1985)
- Stephens, C.H., Whitmore, P.M., Morris, H.R., Bier, M.E.: Hydrolysis of the amorphous cellulose in cotton-based paper. Biomacromolecules 9(4), 1093–1099 (2008)
- Zou, X., Uesaka, T., Gurnagul, N.: Prediction of paper permanence by accelerated aging i. kinetic analysis of the aging process. Cellulose 3(1), 243–267 (1996)
- 4. Emsley, A.M., Heywood, R.J., Mushtaq, A., Eley, C.M.: On the kinetics of degradation of cellulose. Cellulose 4(1), 1–5 (1997)
- 5. Calvini, P., Gorassini, A., Merlani, A.L.: On the kinetics of cellulose degradation: looking beyond the pseudo zero order rate equation. Cellulose 15(2), 193–203 (2008)
- 6. Ding, H.-Z., Wang, Z.: On the degradation evolution equations of cellulose. Cellulose 15(2), 205-224 (2008)
- Tétreault, J., Dupont, A.-L., Bégin, P., Paris, S.: The impact of volatile compounds released by paper on cellulose degradation in ambient hygrothermal conditions. Polymer degradation and stability 98(9), 1827–1837 (2013)
- Zou, X., Gurnagul, N., Uesaka, T., Bouchard, J.: Accelerated aging of papers of pure cellulose: mechanism of cellulose degradation and paper embrittlement. Polymer degradation and stability 43(3), 393–402 (1994)
- Emsley, A., Heywood, R.J., Ali, M., Xiao, X.: Degradation of cellulosic insulation in power transformers. part 4: Effects of ageing on the tensile strength of paper. IEE Proceedings-Science, Measurement and Technology 147(6), 285–290 (2000)
- Čabalová, I., Kačík, F., Gojný, J., Češek, B., Milichovský, M., Mikala, O., Tribulová, T., Ďurkovič, J.: Changes in the chemical and physical properties of paper documents due to natural ageing. BioResources 12(2), 2618–2634 (2017)
- Tétreault, J., Bégin, P., Paris-Lacombe, S., Dupont, A.-L.: Modelling considerations for the degradation of cellulosic paper. Cellulose 26(3), 2013–2033 (2019)
- Strlič, M., Grossi, C., Dillon, C., Bell, N., Fouseki, K., Brimblecombe, P., Menart, E., Ntanos, K., Lindsay, W., Thickett, D., France, F., De Bruin, G.: Damage function for historic paper. part III: Isochrones and demography of collections. Heritage Science 3(1), 1–11 (2015)
- Parsa Sadr, A., Bosco, E., Suiker, A.S.J.: Multi-scale model for time-dependent degradation of historic paper artifacts. International Journal of Solids and Structures, 111609 (2022)
- Strlič, M., Kolar, J.: Size exclusion chromatography of cellulose in Licl/N, N-dimethylacetamide. Journal of biochemical and biophysical methods 56(1-3), 265–279 (2003)
- Dupont, A.-L., Mortha, G.: Comparative evaluation of size-exclusion chromatography and viscometry for the characterisation of cellulose. Journal of Chromatography A 1026(1-2), 129–141 (2004)
- Dupont, A.-L., Réau, D., Bégin, P., Paris-Lacombe, S., Tétreault, J., Mortha, G.: Accurate molar masses of cellulose for the determination of degradation rates in complex paper samples. Carbohydrate polymers 202, 172–185 (2018)
- 17. TAPPI: 230 om-08, Viscosity of Pulp (Capillary Viscometer Method). Technical Association of the Pulp and Paper Industry (2008)
- ISO: Pulps Determination of limiting viscosity number in cupri-ethylenediamine (CED ) solution . Standard, International Organization for Standardization (2010)
- 19. ASTM: D1795-13, Standard test method for intrinsic viscosity of cellulose. ASTM (2013)

- 20. Evans, R., Wallis, A.: Comparison of cellulose molecular weights determined by high performance size exclusion chromatography and viscometry. In: Proc Fourth Int Symp Wood Pulping Chem Paris, vol. 1, pp. 201–5 (1987)
- Łojewski, T., Zieba, K., Łojewska, J.: Size exclusion chromatography and viscometry in paper degradation studies. new Mark-Houwink coefficients for cellulose in cupri-ethylenediamine. Journal of Chromatography A 1217(42), 6462–6468 (2010)
- Abdel-Azim, A.-A.A., Atta, A.M., Farahat, M.S., Boutros, W.Y.: Determination of intrinsic viscosity of polymeric compounds through a single specific viscosity measurement. Polymer 39(26), 6827–6833 (1998)
- 23. Morrison, F.A.: Understanding Rheology vol. 1. Oxford university press New York, ??? (2001)
- Gericke, M., Schlufter, K., Liebert, T., Heinze, T., Budtova, T.: Rheological properties of cellulose/ionic liquid solutions: from dilute to concentrated states. Biomacromolecules 10(5), 1188–1194 (2009)
- Lu, F., Song, J., Cheng, B.-W., Ji, X.-J., Wang, L.-J.: Viscoelasticity and rheology in the regimes from dilute to concentrated in cellulose 1-ethyl-3-methylimidazolium acetate solutions. Cellulose 20(3), 1343–1352 (2013)
- 26. TAPPI: T573 pm-09, accelerated temperature aging of printing and writing paper by dry oven exposure apparatus. Technical Association of the Pulp and Paper Industry (2009)
- Sawoszczuk, T., Barański, A., Łagan, J.M., Łojewski, T., Zieba, K.: On the use of ASTM closed vessel tests in accelerated ageing research. Journal of cultural heritage 9(4), 401–411 (2008)
- IEC-60450: Measurement of the Average Viscometric Degree of Polymerization of New and Aged Cellulosic Electrically Insulating Materials. NORMA, IEC Geneva, Switzerland (2004)
- 29. Pfitzner, J.: Poiseuille and his law. Anaesthesia **31**(2), 273–275 (1976)
- Huggins, M.L.: The viscosity of dilute solutions of long-chain molecules. IV. dependence on concentration. Journal of the American Chemical Society 64(11), 2716–2718 (1942)
- Kraemer, E.O.: Molecular weights of celluloses and cellulose derivates. Industrial & Engineering Chemistry 30(10), 1200–1203 (1938)
- Schulz, v.G., Blaschke, F.: Eine Gleichung zur Berechnung der Viscositätszahl für sehr kleine Konzentrationen, [Molekulargewichtsbestimmungen an Makromolekularen Stoffen, IX]. Journal für Praktische Chemie 158(1-8), 130–135 (1941)
- 33. Martin, A.: Toward a referee viscosity method for cellulose. Tappi 34(8), 363-366 (1951)
- Ekenstam, A.: Über das Verhalten der Cellulose in Mineralsäure-lösungen, I. Mitteil.: Die Bestimmung des Molekular-gewichts in Phosphorsäure-Lösung. Berichte der deutschen chemischen Gesellschaft (A and B Series) 69(3), 549–552 (1936)
- Ekenstam, A.: Über das Verhalten der Cellulose in Mineralsäure-lösungen, II. Mitteil.: Kinetisches Studium des Abbaus der Cellulose in Säure-Lösungen. Berichte der deutschen chemischen Gesellschaft (A and B Series) 69(3), 553–559 (1936)