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Pure cellulose paper ageing in sealed vessels. Autocatalytic depolymerization model revisited

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Abstract:

Purpose - *In the framework of the EU funded INVENVORG project (Thales Research Funding Program – NRSF), the natural and artificial ageing of bone, wood, textiles, parchment and paper were investigated.*

Design/methodology/approach - *In this work, the results of accelerated ageing on pure cellulose paper in sealed vessels are reported. The properties studied include the degree of polymerization (which was converted to the percentage of broken glyosidic bonds), the tearing resistance, the pH and the L* and b* coordinates of the CIEL*a*b* color system. Ageing was performed in sealed vessels at 90°C και 76% RH for periods of 20, 40, 60, 80, 100, 120 and 140 days.*

Findings - *The results indicated an overall deterioration of all paper properties, which accelerates with time because of the production of volatile acidic species (autocatalysis). The evolution of paper properties through time was modeled efficiently by use of the equations proposed by Zervos and Moropoulou (2005) for the autocatalytic acid hydrolysis of pure cellulose paper, which were shown that also apply for following the changes of tearing resistance. The applicability of the model equations was also verified for other paper properties, such as the percentage of broken bonds (δ%) and the L* and b* coordinates of the CIEL*a*b* color system.*

Index Terms - *Cellulose ageing model; autocatalysis; tearing resistance; pH; optical properties; sealed vessels*

I. Introduction

Various equations have been proposed to describe the evolution of paper and cellulose properties during accelerated ageing. The Ekenstam **[1]** equation (eq. 1) is the oldest, and its applicability and acceptance are almost universal. It can be derived either by assuming zero order kinetics or as an approximation of first order kinetics, and it applies to heterogeneous conditions, to acid hydrolysis in solutions and to thermal, photochemical and enzymatic degradation of cellulose, at the early stage of the reaction **[2-16]**.

$$\frac{1}{DP_t} - \frac{1}{DP_o} = kt \qquad (1)$$

where DP_t and DP_0 are the Degree of Polymerization values at times t and 0, t the time and k the rate constant.

Variations of eq. 1, but also other equations derived by other approaches, have also been introduced by Calvini, Ding and Wang and others **[17, 18, 19, 20, 21, 22, 23, 24, 16, 25, 26, 27, 28]**, taking into consideration autocatalysis and the slowing of the reaction because of the inaccessibility of the crystalline regions of cellulose.

In a previous paper **[21]**, a kinetic model which applied to the autocatalytic depolymerization of cellulose in sealed vessels was presented. The model introduced a generalized equation (eq. 2) that predicted the evolution of several properties of pure cellulosic paper during accelerated ageing at 80°C and 75% RH, namely the percentage of the broken glycosidic bonds (δ%), the folding endurance, tensile strength, tensile energy absorption, stretch at break and the L* and b* coordinates of the CIEL*a*b* color system.

$$P = P_o \pm C \cdot (2^{k \cdot t} - 1) \qquad (2)$$

where P_o and P are the values of the property P at time 0 and t, and C and k constants.

Equation 2, like the Ekenstam equation, holds for the early stage of degradation, until δ% reaches 0.6–0.7% with a corresponding DP of around 250, which is in the range of reported LODP (Leveling of Degree of Polymerization) values **[2, 5, 7, 16]**. The theoretical and mathematical evolution of the model equation is presented elsewhere **[21]**.

In the present paper, another paper strength property, tearing resistance, was also studied concerning its conformance to the model, and the predictive value of the model equations was reconfirmed for δ%, and the L* and b* coordinates of the CIEL*a*b* color system for different conditions of ageing in sealed vessels (90°C and 75% RH).

The framework of this study was the EU funded INVENVORG project (Thales Research Funding Program – NRSF), which investigated the natural and artificial ageing of bone, wood, textiles, parchment and paper **[29]**.

II. Related work

Whatman no 2 filter paper was used for the production of test strips, which has been used to model pure cellulose, since it consists of pure cotton cellulose with no additives, fillers or sizing[1]. Their size (7.6 X 6.5cm) was determined by the requirements of the determination of the tearing resistance.

Thirty test strips were sealed in each of seven 3-liter glass jars equipped with a sealing spring and a silicon rubber ring, containing 150 ml of saturated solution of NaCl for the adjustment of the RH at 76% ±1% **[30]**. The jars were placed in an oven at 90 ±1 °C, in which they remained for 20, 40, 60, 80, 100, 120 and 140 days. The test strips were suspended with linen thread from the lid of the jar.

For the determination of the Tearing Resistance (TR), an Elmendorf instrument (Lorentzen and Wettre) was used. At least 10 measurements for each withdrawal time were performed. The samples were preconditioned and conditioned before the TR determination according to TAPPI T 402 om-88 **[31]** standard (23°C and 25% RH for 24 hours and 23±1°C and 50±2% RH respectively).

The color coordinates L* and b* of the CIEL*a*b* color system were determined by a Dr. Lange spectrocolor LMG 183 colorimeter. Five measurements were taken for every test strip at random places and the mean was calculated.

The surface pH of paper was determined by use of a flat contact electrode according to TAPPI T 529 om-04 **[32]**. Three measurements were taken at random spots of three paper strips and averaged.

The mean Degree of Polymerization (DP) was determined by viscometry, according to the ASTM D 1795-96 **[33]** standard. An Ubbelohde viscometer was kept in a thermostatic bath at 25±0.1°C, with a suitable capillary so that the efflux time was between 80-300 sec. Cellulose was dissolved in 0.5 M cupriethylenediamine hydroxide solution, manufactured by Merck. DP values were converted to δ% (percentage of broken bonds during ageing time t) by use of equation 3 **[3,21]**.

$$\delta\% = 100 \cdot \left(\frac{2}{DP_t} - \frac{2}{DP_o}\right) \qquad (3)$$

where DP_t and DP_0 are the Degree of Polymerization values at times t and 0, and δ% the percentage of broken bonds at time t.

The experimental setup utilized in the ageing experiments has been tested for possible leakage before. The experiments reported in the 2005 paper have been based on the same setup, and weight measurements of the glass jars before and after ageing indicated that there was no weight loss. The repeatability of the experimental results was tested at that time with parallel and consecutive ageing experiments, and the results obtained shown so statistically significant differences

III. Results and Discussion

The experimental (exp) and predicted (pred) values of the determined properties are presented in Table 1, together with the property evolution equation **[21]**, the values of the regression coefficients, the coefficient estimations and their standard errors.

The kinetic model of cellulose depolymerization used here **[21]** applies to the autocatalytic acid hydrolysis of cellulose in sealed vessels and can predict the evolution of several important properties of pure cellulose paper under the experimental conditions of the ageing experiment (T=90°C, RH=76%). The production of acidic species during paper ageing has been demonstrated by several researchers **[34, 35, 36, 37]** and has been verified for the experimental setup used here **[21]**. The production of acidic species is also supported by the pH values of the aged samples (table 1).

Table 1. Experimental (exp) and predicted (pred) values of the determined properties. The pH value of 2.8 is an outlier, the very low pH value resulting from probable sample contamination.

	TR (mN)		DP	δ%		L*		b*		pH
Days of ageing	TR-exp	TR-pred	DP	δ%-exp	δ%-pred	L*-exp	L*-pred	b*-exp	b*-pred	
0	692	676	1493	0	0	97.64	96.75	1.92	2.42	5.7
20	667	662	1208	0.032	0.028	95.18	95.96	3.28	2.95	5.4
40	608	631	902	0.088	0.080	94.29	94.70	4.06	3.76	5.2
60	549	564	615	0.191	0.172	92.39	92.73	5.47	5.02	4.7
80	438	416	447	0.313	0.340	90.65	89.63	6.07	6.95	4.8
100	87	92	256	0.647	0.640	84.38	84.75	10.23	9.93	**2.8**
120	87		223	0.763		83.98		10.12		3.7
140	43		182	0.965		77.33		12.47		3.4
model equation	$TR = TR_o - C(2^{kt} - 1)$			$\delta\% = C(2^{kt} - 1)$		$L^* = L^*_o - C(2^{kt} - 1)$		$b^* = b^*_o + C(2^{kt} - 1)$		
R^2	0.994			0.996		0.973		0.964		
	Estimate	Std. Error		Estimate	Std. Error	Estimate	Std. Error	Estimate	Std. Error	
P_0	676	16		-	-	96.75	0.77	2.42	0.57	
C	11.9	6.1		0.035	0.007	1.38	1.23	0.98	1.02	
k	0.025	0.020		0.043	0.003	0.033	0.011	0.031	0.013	

The model, according to the limitations set for its theoretical development, applies for values of δ% (percentage of broken bonds) below 0.6-0.7 (which corresponds to DP values around 250). At that point starts the attack on cellulose crystallites, the rate of the hydrolysis reaction drops due to stereochemical hindrance and the

[1] https://www.gelifesciences.com/en/gb/shop/whatman-laboratory-filtration/cellulose-filter-papers

model ceases to apply **[21]**. As fig. 1 indicates, the limitation discussed above is verified by the experimental data, since the reaction starts to slow down at values of δ% around 0.6% – 0.7%. According to the above, the applicability of the model was tested for the first 100 days of ageing corresponding to values of δ% < 0.7 (DP > 250). Figure 2 presents the plots of TR (Tearing resistance), δ% (percentage of broken bonds), and L* and b* coordinates of the CIEL*a*b* color system against time of ageing. The high values of the regression coefficients presented in table 1 indicate that the fit of the experimental values to the model equation is quite satisfactory.

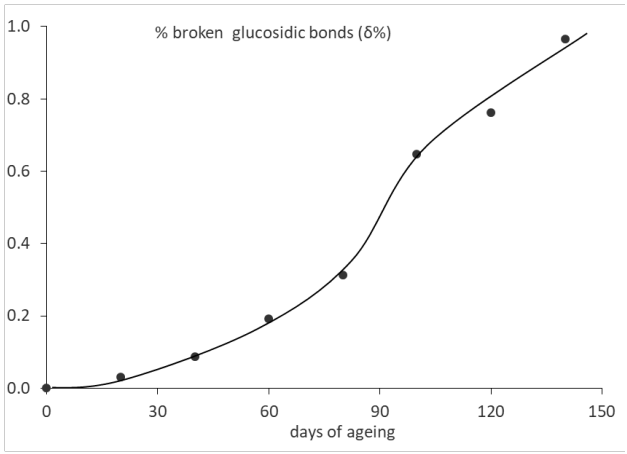

Figure 1. Plot of δ% (percentage of the broken bonds) against time

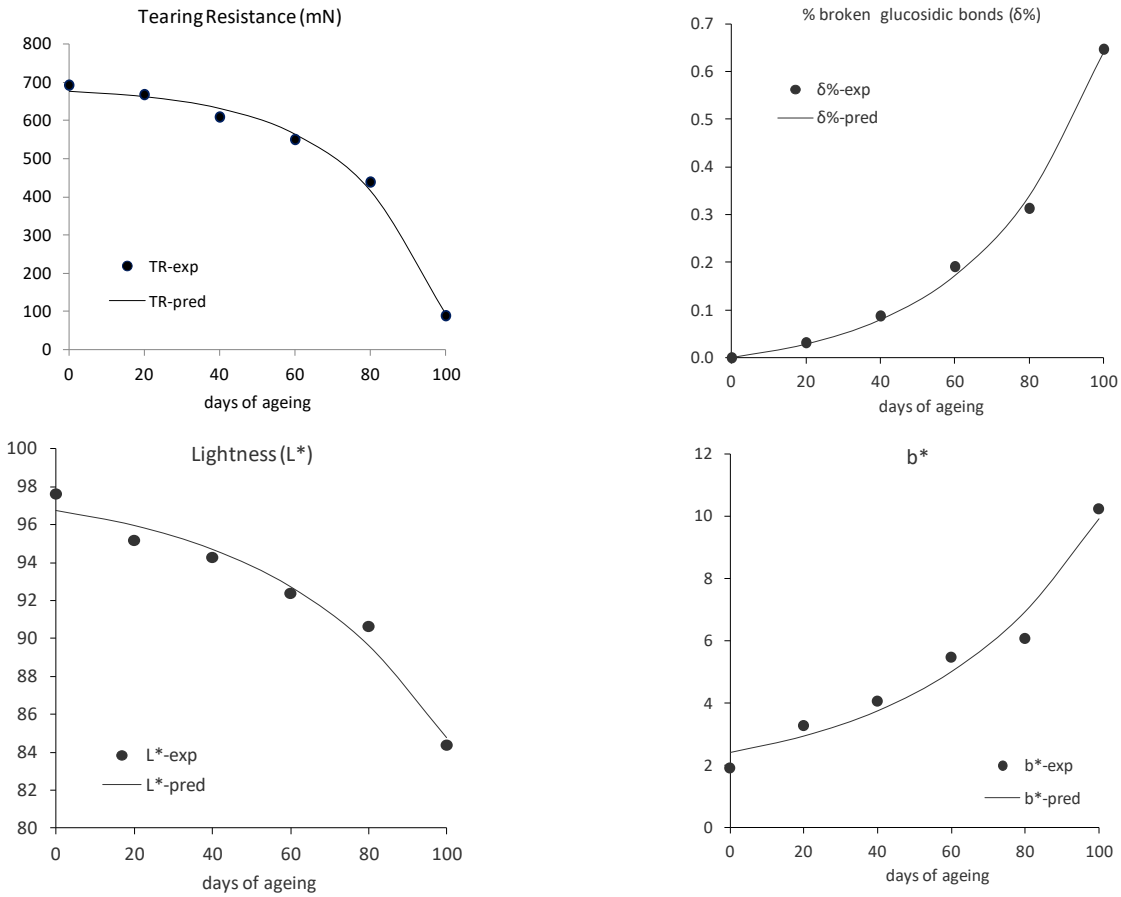

Figure 2. Plots of TR (Tearing resistance), δ% (percentage of broken bonds), and L* and b* coordinates of the CIEL*a*b* color system against time of ageing. Experimental (exp, dots) and predicted (pred, lines) values.

In the previous report, it was shown theoretically that the pH of paper under those conditions of ageing (sealed vessels, autocatalysis) drops linearly with time **([21]**, eq. 14). The fitting of the experimental values of the previous study to a linear model gave inconclusive results but worked quite well with the pH values obtained by the present study, verifying what theory predicted (fig. 3). As mentioned above, the model works until δ% approaches 0.6 - 0.7%. In many contexts, such as in paper conservation, this limitation is not important, because at that point, the mechanical properties related to the usability of paper information substrates (mainly folding endurance) drop to such low values that the paper is not usable anymore **[38]**.

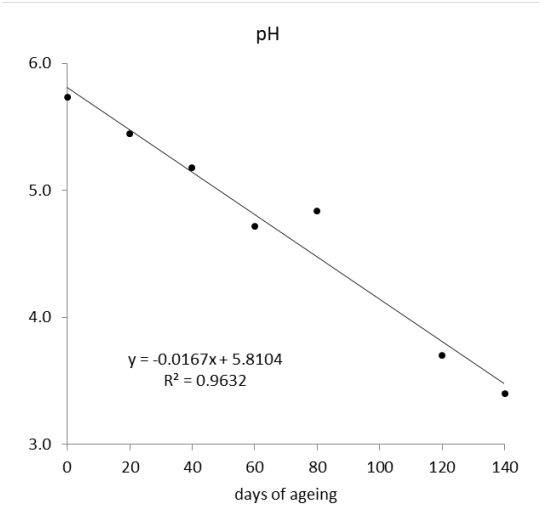

Figure 3. Surface pH of paper against time. The fit is satisfactory, as indicated by the high value of R^2. The pH value of 2.8 is an outlier (see table 1) and was not taken into account.

IV. Conclusions

Accelerated ageing in sealed vessels results in an overall deterioration of important paper properties, which accelerates with time because of the production of volatile acidic species (autocatalysis). The evolution of pure cellulose paper properties can be modeled efficiently by use of the equations presented above. In this work, it was shown that the model of autocatalytic acid hydrolysis suggested by **[21]** can be effectively applied for following the changes of tearing resistance. The applicability of the model was also verified for other paper properties, such as the percentage of broken bonds (δ%) and the L* and b* coordinates of the CIEL*a*b* color system.

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