Cotton Cellulose Ageing in Sealed Vessels. Kinetic Model of Autocatalytic Depolymerization

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INTRODUCTION

Cellulose ageing experiments are of great interest in many different technical and scientific contexts. Cellulosic insulation is used in oil-filled power transformers and high-voltage power cables. Cellulose is an important raw material in textile industry. It is also the main component of paper stored in libraries and archives. Thus, the ageing of cellulose governs the long-term performance of power transformers, textiles, books and documents. Cellulose ageing is studied by monitoring the degree of polymerization or selected mechanical properties of cellulose during ageing experiments.

It has been established beyond doubt that the initial stage of cellulose depolymerization follows equation 1 (Krassig and Kitchen, 1961; Fung, 1969; Shafizadeh and Bradbury, 1979; Feller et al., 1986; Fellers et al., 1989; Emsley and Stevens, 1994; Zou et al., 1994; Hill et al., 1995; Zou et al., 1996; Klemm et al., 1998, p. 86):

$$\frac{1}{DP_t} - \frac{1}{DP_o} = k\,t \tag{1}$$

where DP_o and DP_t are the number average degree of polymerization in times 0 and t and k the rate constant. Equation 1 has been derived by assuming first-order kinetics and an approximation to zero order kinetics. Zou at al. (1996) arrived to the same equation without any assumptions about the reaction order, by applying a generalized kinetic equation and assuming a constant bond breaking rate. The applicability of equation 1 is universal, since it can describe acidic degradation, light ageing and dry or moist thermal ageing in ovens (in vacuo, in nitrogen, air and oxygen) and in oil (Feller et al., 1986; Emsley and Stevens, 1994; Hill et al., 1995; Klemm et al., 1998).

It can be proved (see appendix 1) that, regardless of the reaction order and the kinetics of cellulose degradation, equation 2 gives the percentage δ% of the glycosidic bonds that break in time t.

$$\% \text{ broken bonds} = \delta\% = 100 \cdot \left(\frac{1}{DP_t} - \frac{1}{DP_o} \right) \tag{2}$$

By combining equations 1 and 2, equation 3 is derived, which indicates that the percentage of the broken bonds is a linear function of the reaction time.

$$\delta\% = k'\,t \tag{3}$$

A number of researchers monitored mechanical properties during ageing experiments, especially folding endurance, in order to study cellulose degradation. It has been found that in most of the cases, folding endurance is a linear function of time, following equation 4 (Browning and Wink, 1968; Gray, 1969, 1977; Walker, 1977; Williams et al., 1977; Roberson, 1981; Tang, 1981; Fellers et al., 1989).

$$FE_t = FE_o - \kappa\,t \tag{4}$$

Many different ageing tests have been devised for the study of cellulose ageing. The most widely accepted ageing test for paper is described in ISO 5630 - 3, which dictates ageing temperature of 80ºC and 65% relative humidity in a ventilated oven. In the case of ventilated ovens, the atmosphere of the oven is constantly renewed and the volatile degradation products of cellulose are removed. In such experimental setups, δ% and some mechanical and optical properties are linear functions of time, as indicated above. Recently, the idea of using sealed vessels has

been put forward (Shahani, 1995; Zou et al., 1996, ASTM D6819-02e2). The main argument behind this idea is that in most of the cases of natural ageing of cellulosic materials, the volatile degradation products of cellulose ageing are retained in the reaction space. This argument is valid in the case of books and archival material, but also in the case of power transformers. The retained volatile degradation products are supposed to be acidic, thus an autocatalytic effect in cellulose depolymerization had been expected when ageing takes place in sealed vessels, causing deviations from the linear models described above (Shahani, 1995; Baranski et al., 2000).

However, very few reports of such deviations for ageing in sealed vessels were found in the body of literature studied. The most important ones come from Shahani (1995), who found deviations from the linear dependence of folding endurance on time and acceleration of the reaction rate.

The experiments reported here verify the findings of Shahani and indicate that the hypothesis of autocatalysis in the case of cellulose ageing in sealed vessels is valid. A new kinetic model for ageing in sealed vessels and equations based on it that describe the change in δ% and different mechanical and optical properties of cellulose are proposed.

THE MODEL - THEORETICAL CONSIDERATIONS

Assumptions

The model is valid under the following terms:
1. The percentage of the broken bonds is less then 1% of the glycosidic bonds that are present in the total amount of cellulose molecules. Under this condition, the total amount of the glycosidic bonds can be considered as being practically constant. This assumption is valid for the initial stage of cellulose hydrolysis (Feller et al., 1986; Klemm et al., 1998) and has been used for the establishment of equation 1.
2. All the glycosidic bonds are considered equal and their scission is random. This assumption is generally accepted (Major, 1958; Fung 1969; Zou et al., 1994).
3. Under the preceding terms, if autocatalysis does not occur, the rate of hydrolysis can be expressed as: $\dfrac{d[N]}{dt} = -k[N] = -k'$, N being the total number of glycosidic bonds, k, k´= rate constants, t = time. Since the rate of hydrolysis is constant, the time needed for the scission of any bond is constant and common for all bonds.
4. It is assumed that every μ (μ: positive integer) glycosidic bonds that break, an active hydrogen ion H^+ is produced. This assumption derives from the hypothesis that the rate of H^+ production is constant for the initial stage, if autocatalysis does not occur. Since kinetic data for the production of acidic species during cellulose hydrolysis are lacking, the hypothesis that the rate of H^+ production is proportional to the concentration of the glycosidic bonds seems reasonable (first order kinetics): $\dfrac{d[H]}{dt} = k[N]$, and because of term 1, $\dfrac{d[H]}{dt} = k' = \text{constant}$, since for the initial stage N ≈ constant.
5. The volatile products of paper ageing are acidic and in the case of circulating ovens are removed from the reaction vessels. However, if sealed vessels are used, the volatile acidic species remain in the reaction space and are absorbed

by cellulose. This assumption is supported by Shahani (1995) and has been verified by our findings, since the pH of the NaCl solutions used for the RH adjustment was found to be diminishing during the process of ageing.

Derivation of the Existing Zero-Order Kinetic model

Before discussing the kinetic model of the autocatalyzed hydrolysis of cellulose, we must examine if the linear dependence of $\delta\%$ on time can be derived under the preceding assumptions for ageing in circulating ovens.

The reaction of acid hydrolysis of cellulose can be schematically depicted as:

$$P + H^+ \rightarrow P_1{}' + P_1{}'' + H^+$$

The macromolecule of cellulose (P), under the influence of an already existing hydrogen ion H^+, splits in two shorter macromolecules. The sum of the DP of the new macromolecules equals the DP of the original. The hydrogen ion is regenerated. The reaction proceeds with the splitting of $P_1{}'$ and so on. The line of the reactions starting with P is catalyzed by the initial hydrogen ion. The produced volatile acidic species are carried away from the reaction space by the circulation of the oven. The sequence of these reactions is shown below:
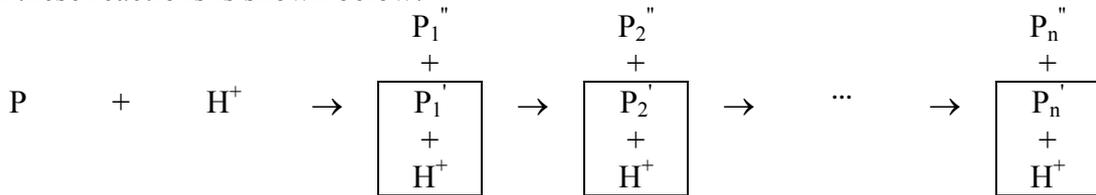
$$
P \quad + \quad H^+ \quad \rightarrow \quad
\boxed{\begin{array}{c} P_1{}'' \\ + \\ P_1{}' \\ + \\ H^+ \end{array}} \rightarrow
\boxed{\begin{array}{c} P_2{}'' \\ + \\ P_2{}' \\ + \\ H^+ \end{array}} \rightarrow \cdots \rightarrow
\boxed{\begin{array}{c} P_n{}'' \\ + \\ P_n{}' \\ + \\ H^+ \end{array}}
$$

Figure 1

This sequence can be depicted for simplicity as:

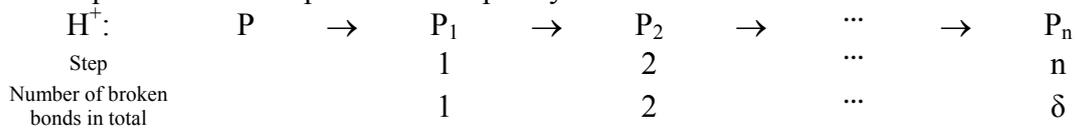| H^+:	P	$\rightarrow$	P_1	$\rightarrow$	P_2	$\rightarrow$	$\cdots$	$\rightarrow$	P_n
Step			1		2		$\cdots$		n
Number of broken bonds in total			1		2		$\cdots$		δ

Figure 2

The initial hydrogen ion H^+ is placed on the left of the reaction line and for every step only one of the fragments is presented, the one that splits in the next step. One glycosidic bond breaks in every step.

For every active hydrogen ion, an equation like the above one can be written. We can thus conclude that the total number of split bonds must be proportional to the initial concentration of the active H^+. Since the time needed for the splitting of any bond is constant, the number of split bonds (δ) after n steps in time t is proportional to t:

$$\delta = n = K\,t,$$

$$\delta\% = 100\,b\,[H^+]_o\,\frac{\delta}{N_o} = 100\,b\,[H^+]_o\,\frac{K\,t}{N_o} \Rightarrow$$

$$\delta\% = k'\,t \tag{5}$$

where: $\delta\%$ the percentage of the split bonds, N_o the total number of initial glycosidic bonds, $[H^+]_o$ the initial concentration of the active hydrogen, K and b constants and

$$k' = 100\,b\,[H^+]_o\,\frac{K}{N_o}$$

Thus, the preceding assumptions, in the case of ageing in circulating ovens lead to the accepted model of zero-order reaction for the initial stage of cellulose hydrolysis (linear dependence of $\delta\%$ on time of ageing)

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Derivation of a Kinetic model based on Autocatalysis

a. In the case of sealed vessels, the reaction sequence is triggered by one active hydrogen ion H^+. According to assumptions 4 and 5, every μ reactions (in the following example, $\mu = 3$) a new active hydrogen ion is produced, which initiates a new branch of reaction. This hydrogen ion is depicted at the beginning of the new branch (the lower branch in figure 3). The upper branch continues with the original active H^+:

The split bonds in total after n steps of this sequence equal the sum of the bonds that split in every step:

$$\delta = \mu\,2^0 + \mu\,2^1 + \mu\,2^2 + \ldots + \mu\,2^{n-1} = \mu\,(2^0 + 2^1 + 2^2 + \ldots + 2^{n-1}) = \mu\,(2^n - 1)$$

(since $x^n - 1 = (x - 1)(x^{n-1} + x^{n-2} + \ldots + x + 1)$, application for $x = 2$)

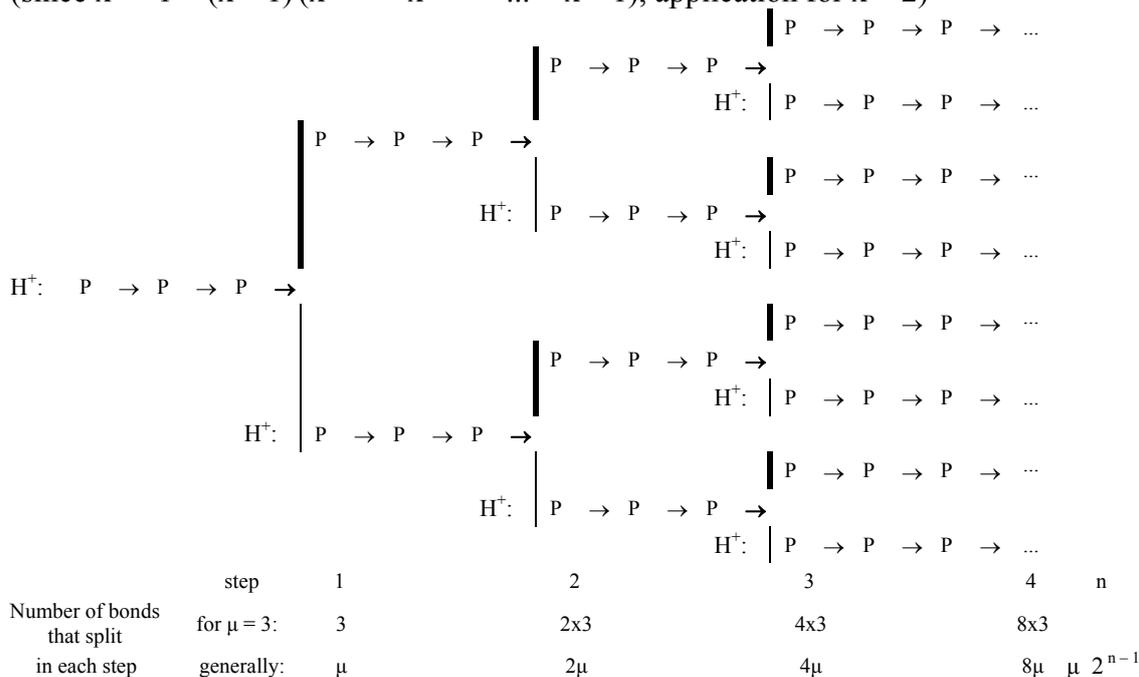|	step	1	2	3	4	n
Number of bonds that split in each step	for $\mu = 3$:	3	2x3	4x3	8x3	
	generally:	μ	2μ	4μ	8μ	$\mu\,2^{n-1}$

Figure 3. Reaction sequence of the autocatalyzed hydrolysis of cellulose

Considering as above that the total percentage of the split bonds is proportional to the initial concentration of hydrogen ions and taking into account that since the time needed for the splitting of each bond is constant the number of steps in time t is proportional to t, we end up with:

$$\delta\% = 100\,b\,[H^+]_o\,\frac{\delta}{N_o} = 100\,b\,[H^+]_o\,\frac{\mu(2^{kt} - 1)}{N_o} \Rightarrow$$

$$\delta\% = a\,(2^{kt} - 1) \tag{6}$$

where $\delta\%$ is the percentage of the split bonds, N_o the total number of glycosidic bonds, $[H^+]_o$ the initial concentration of active H^+, k and b constants and

$$a = 100\,b\,[H^+]_o\,\frac{\mu}{N_o}$$

b. The same results can be reached by considering the reaction of acid hydrolysis and the following differential equations describing the rate of splitting of glycosidic bonds and the rate of production of H^+:

$$P + H^+ \rightarrow P_1{}' + P_1{}'' + H^+$$

$$\frac{d[N]}{dt} = -k'_1[N][H^+] \tag{7}$$

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$$\frac{d[H^+]}{dt} = k'_2[N][H^+] \tag{8}$$

where N is the total number of glycosidic bonds and k_1' και k_2' rate constants.

According to assumption no 1, the concentration of glycosidic bonds [N] is nearly constant for the initial stage and equations 1 and 2 can be written:

$$\frac{d[N]}{dt} = -k_1[H^+] \tag{9}$$

$$\frac{d[H^+]}{dt} = k_2[H^+] \tag{10}$$

$$(10) \Rightarrow [H^+] = [H^+]_o\, e^{k_2 t} \tag{11}$$

$$(9),(11) \Rightarrow \frac{d[N]}{dt} = -k_1[H^+]_o\, e^{k_2 t} \Rightarrow [N]-[N]_o = -\frac{k_1[H]_o}{k_2}e^{k_2 t} + \frac{k_1[H]_o}{k_2} \Rightarrow$$

$$\frac{[N]_o - [N]}{[N]_o} = \frac{k_1[H]_o}{k_2[N]_o}e^{k_2 t} - \frac{k_1[H]_o}{k_2[N]_o} \Rightarrow \frac{[N]_o - [N]}{[N]_o} = \frac{k_1[H]_o}{k_2[N]_o}(e^{k_2 t} - 1) \Rightarrow$$

$$\delta\% = A(e^{k_2 t} - 1) \tag{12}$$

$$\text{since } \frac{[N]_o - [N]}{[N]_o}100 = \delta\% \text{ and } A = \frac{k_1[H]_o 100}{k_2[N]_o}$$

Equation 6 can be written as:

$$\delta\% = a(e^{\ln 2 k t} - 1) \tag{13}$$

With A = a και k_2 = k ln2, equation 6 and 13 are identical.

EXPERIMENTAL - DESCRIPTION OF AGEING METHODOLOGY

In this study, we used Whatman No 2 filter paper for the production of samples. Whatman filter paper has been widely used to model pure cellulose, since it consists of pure cotton cellulose with no additives, fillers or sizing (Anonymous 2001). Due to the inhomogeneity of Whatman paper, it was decided that the experimental setup should not be based on the assignment of different treatments to different leaves (or group of leaves). Instead, the paper was cut in test-strips (15±0.1 mm wide, larger for the determination of the optical properties), which were then randomly assigned to different periods of ageing.

The ageing of the samples took place in 3 lit. glass jars, equipped with a sealing spring attached on the lid. For the sealing of the jars, silicon rubber rings were used. Artificial ageing of silicon rubber for 25 days at 105ºC indicated that this material is stable. No change in weight, color or mechanical strength was observed. The relative humidity inside the jars was adjusted around 75% by use of saturated NaCl solutions. The jars were washed with a weak acid solution for the removal of any alkaline residue and then with deionized water. A Pyrex glass containing 100 ml of deionized water and 70 g of NaCl was placed in each jar. The paper strips were suspended vertically by a stainless steel wire. The glass jars were sealed, left for equilibration for 3 days and then placed inside an oven set at 80±1ºC. According to Greenspan (1997), the relative humidity at that temperature over a saturated NaCl solution in a sealed vessel is set at 76±1%.

Two series of experiments were performed. The first served for the rough estimation of the most suitable ageing periods. Both experiments gave almost

identical results, so only the results of the second experiment are presented here. The ageing times for the first experiment were 40, 80, 120, 160 and 240 days and for the second experiment 30, 60, 90, 120 and 150 days. A separate jar was used for each ageing time.

Tensile Strength, Tensile Energy Absorption, Stretch at Break and Folding Endurance were determined according to the appropriate ISO standard (ISO 1924-2 and 5626). The samples were first preconditioned at 23ºC and 25% RH for 24 hours and then conditioned at 23ºC and 50% RH for another 24 hours (TAPPI TEST METHOD T 402). At least 10 determinations for every mechanical property were performed.

For the Tensile Properties, a computer-operated instrument made by Zwick was used. The rate of the jaws displacement was 20 mm/min and the initial distance of the jaws was 180 mm. Test strips 21 cm long with a width of 15±0.1 mm were used.

Folding Endurance is equal to the logarithm of the number of double folds. An M.I.T. instrument made by Tinius Olsen, operating at a rate of 175 double folds per minute and a spring tension of 0.5 Kp was used for the determination of the number of double folds. Test strips 15 cm long and 15±0.1 mm wide were used.

The reported values of the so-called viscosity-average degree of polymerization of the cellulose samples were determined according to ASTM 1795-96 standard and are the average of at least two determinations. The 0.5 M cupriethylenediamine hydroxide solution that was used was manufactured by Merck. The weight average degree of polymerization (DP_w) is approximately equal to the viscosity-average degree of polymerization (DP_v) (Klemm et al., 1998). For natural samples of cellulose, DP_w is approximately twice the number average degree of polymerization ($DP_w \approx 2\ DP_n$) (Michie et al., 1961; Shafizadeh et al., 1979).

For the determination of the optical properties of the samples, a spectrophotometer manufactured by Dr. Lange, model "spectrocolor LMG 183", was used. The L* and b* coordinates of CIEL*a*b* color system were determined.

The cold-extraction pH was determined according to ISO 6588. Twice distilled water (Merck) was used, having a conductivity of 0.60 μS/cm. The reported values are the average of two determinations.

pH OF PAPER AND OF THE NaCl SOLUTIONS

The pH changes of paper and of the NaCl solutions that were used for controlling the RH inside the jars are presented in tables 1 and 2 and figures 4 and 5. The measured drop of the pH of the NaCl solutions indicates that volatile acidic species are produced, verifying the validity of assumption no 5. The predicted values have been calculated by linear regression ($R^2 = 0.949$ for paper, $R^2 = 0.968$ for the NaCl solutions). The equations of the straight lines are: pH = 7.5205 – 0.0198 d for paper, pH = 5.0179 – 0.0146 d for the NaCl solutions, where d = days of ageing.

Equation 10 can be transformed to the following equation:

$$pH = pH_o - m\ t, \hspace{4cm} (14)$$

which suggests that the pH of paper should depend linearly on the time of ageing. Supposing that the hydrogen ion concentration of the NaCl solutions is proportional to the concentration of the hydrogen ion in the paper, it seems reasonable that equation 14 should also apply to the NaCl solutions. Although the calculated regression coefficients are high enough, the fits are far from perfect, especially for paper, where the pH seems to decrease more rapidly than predicted by the linear model. Thus, the experimental evidence is not conclusive, concerning the applicability of eq, 14 to the pH values.

pH of paper

	0	30	60	90	120	150
experimental	7.23	6.95	6.58	6.08	5.06	4.30
predicted	7.52	6.93	6.33	5.74	5.14	4.55

Table 1. Experimental and predicted values of the pH of paper
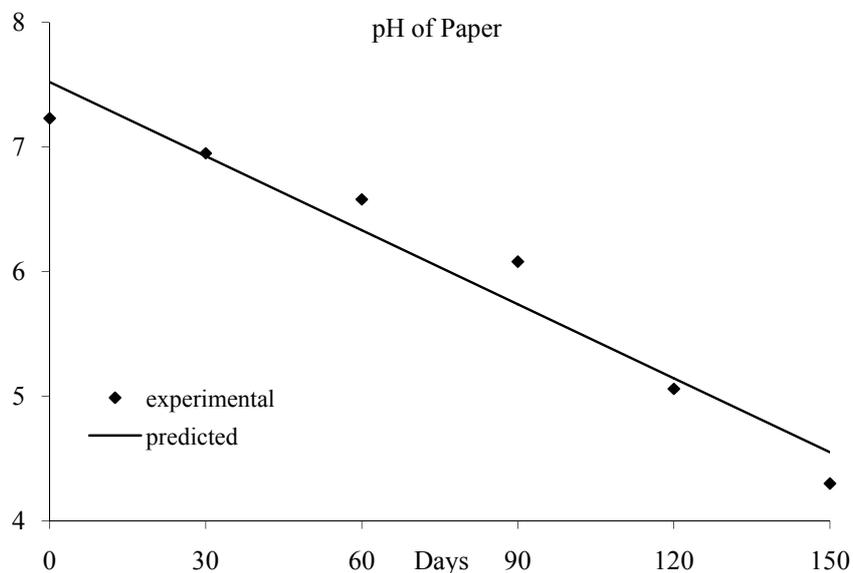
Figure 4. Plot of the pH of paper against time

pH of NaCl solutions

	0	30	60	120	150
experimental	5.20	4.35	4.18	3.18	2.94
predicted	5.02	4.58	4.14	3.27	2.83

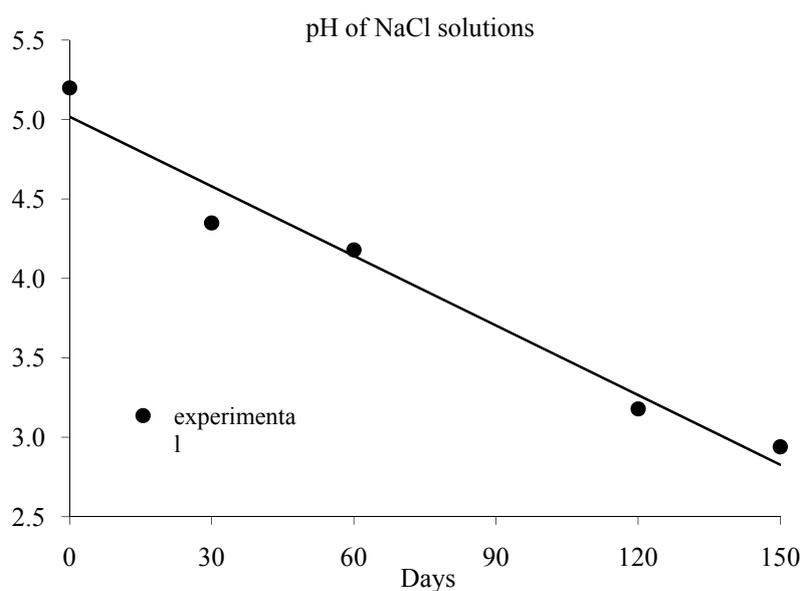Table 2. Experimental and predicted values of the pH of the NaCl solutions

Figure 5. Plot of the pH of NaCl solutions against time

APPLICATION OF THE MODEL TO THE EXPERIMENTAL DATA

From the results of the DP measurements and by using equation 2, we calculated the percentage of the split bonds (δ%). The resulting figures of δ% were fit in the model equation 6 by use of the statistical package SPSS v. 8 for Windows. The results are presented in table 3 and figure 6. The very high value of the regression coefficient (R^2 = 0.998) indicates that the model works quite well. The estimated values of the constants are: a = 0.0190 and k = 33.75×10^{-3}.

t (days)	DP_v	experimental δ%	predicted δ%
0	1810	0.0000	0.0000
30	1587	0.0156	0.0194
60	1266	0.0474	0.0584
90	845	0.1263	0.1373
120	472	0.3130	0.2962
150	277	0.6125	0.6170

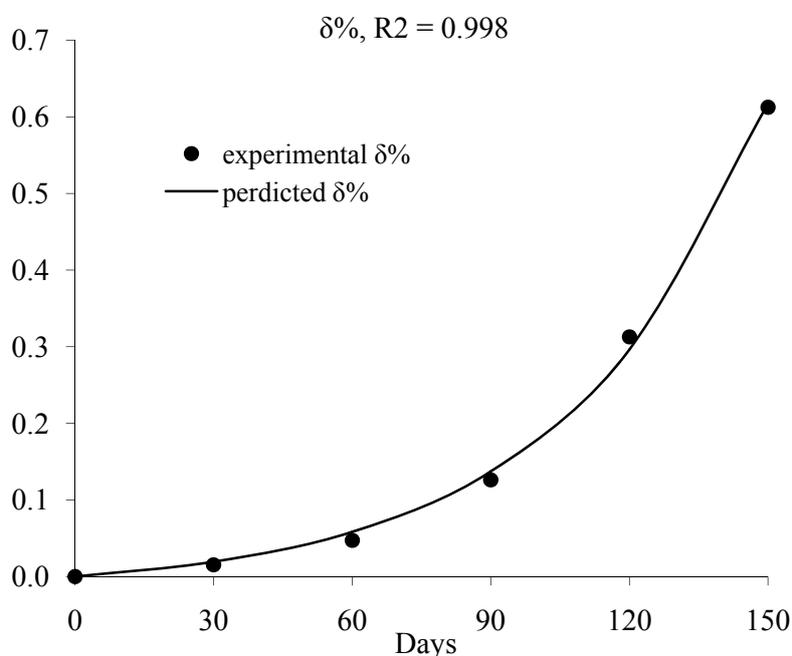Table 3. Viscosity-average degree of polymerization (DP_v), experimental and predicted values of δ%.

Figure 6. Plot of δ% against time

Figure 7 presents the dependence of δ% on the time of ageing for the preliminary ageing experiment. From the graph, we notice a deceleration of the upward trend of δ% at a value of δ% $\approx 0.6 - 0.7$ around 150 - 160 days of ageing. This value of δ% is lower than 1% (term no 1 is fulfilled); it corresponds to DP_v around 250 and marks the lowest value of DP that our model is valid for the specific cellulose samples. Such values of DP are reported by other scientists (Krassig and Kitchen, 1961; Shafizadeh and Bradbury, 1979; Feller et al., 1986 and others report values ranging between 400 and 200) and are considered to represent the so-called Limiting Value of the Degree of Polymerization (LODP), the value of the DP of cellulose crystallites. Around these values (that depend primarily on the source and the processing of the cellulose samples) the attack on the crystalline regions starts and the rate of depolymerization decreases.
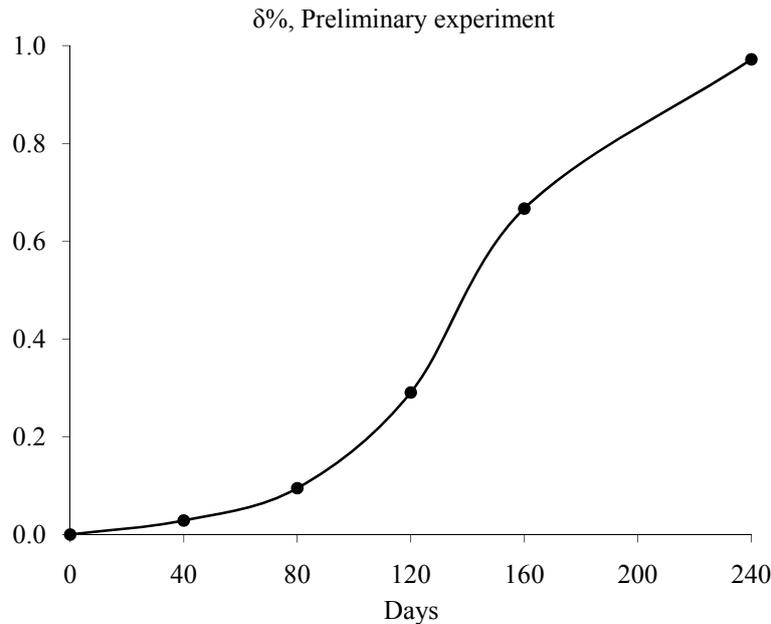
Figure 7. Plot of δ% against time, preliminary experiment

MECHANICAL AND OPTICAL PROPERTIES

The linear model is the most commonly used mathematical model for the description of the mechanical and optical properties of paper: $P = P_o \pm k\,t$, (Browning and Wink, 1968; Gray, 1969, 1977; Walker, 1977; Williams et al., 1977; Roberson, 1981; Tang, 1981; Fellers et al., 1989), where P_o and P are the values of the property P at times 0 and t and k = constant. Given that under the conditions that this model is valid (ventilated ovens), δ% is proportional to time (equation 3), it is implied that $P = P_o \pm c$ δ% (c = constant) or else that the change of the property in study is proportional to δ%. Such a relationship seems reasonable and wherever it has been applied, even if it has not been explicitly stated, led to acceptable results. We thus set: $\Delta P = c$ δ%, which means that the property under study is related to time by the formula:

$$P = P_o \pm C\,(2^{k\,t} - 1),\ C = \text{constant} \tag{15}$$

We used the statistical package SPSS v. 8 for Windows to fit the experimental results to equation 15. The results are shown in table 4 and figures 8a-8f that follow. From the values of the regression coefficients, it is evident that the model works quite well.

t	Folding Endurance exper.	Folding Endurance pred.	Tensile Strength exper.	Tensile Strength pred.	Stretch at Break exper.	Stretch at Break pred.	Tensile Energy Absorption exper.	Tensile Energy Absorption pred.	L* exper.	L* pred.	b* exper.	b* pred.
0	1.31	1.33	1770	1793	2.60	2.66	37.54	38.25	97.63	97.61	2.10	2.19
30	1.31	1.32	1813	1792	2.72	2.64	39.03	37.80	96.18	96.29	3.22	3.01
60	1.31	1.29	1795	1788	2.58	2.60	35.95	36.65	94.56	94.49	4.11	4.20
90	1.22	1.20	1760	1765	2.48	2.48	33.92	33.66	92.20	92.02	5.79	5.92
120	0.91	0.92	1661	1660	2.09	2.09	25.85	25.95	88.43	88.65	8.56	8.43
150	0.04	0.04	1161	1161	0.89	0.89	6.07	6.05	84.11	84.04	12.02	12.05
P_o	1.33		1793		2.66		38.25		97.61		2.19	
k	0.0557		0.0749		0.0545		0.0456		0.0151		0.0179	
C	-39.36×10^{-4}		-26.34×10^{-2}		-61.09×10^{-4}		-28.44×10^{-2}		-3.587		1.820	

Table 4. Experimental and predicted values of basic mechanical and optical properties. Values of the constants of equation 15.
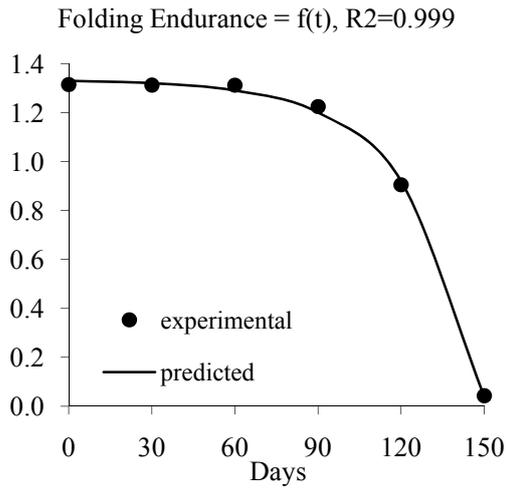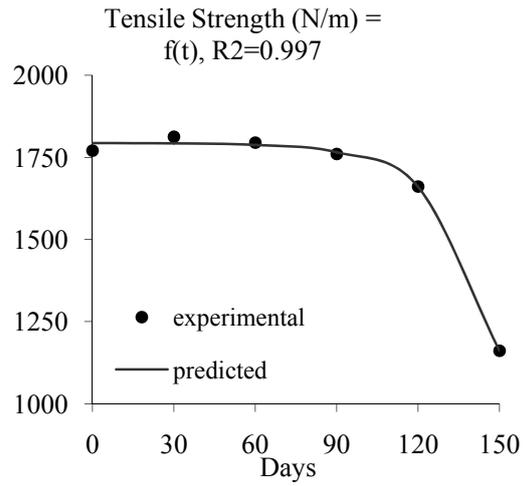
Folding Endurance = f(t), R2=0.999

Figure 8a. Plot of Folding Endurance against time

Tensile Strength (N/m) = f(t), R2=0.997

Figure 8b. Plot of Tensile Strength against time

Stretch at Break % = f(t), R2=0.996
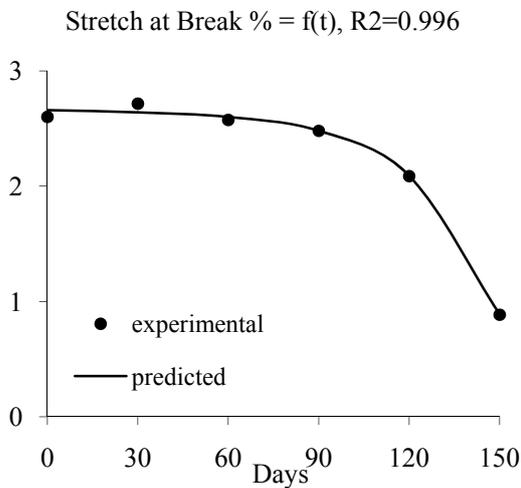
Figure 8c. Plot of Stretch at Break against time

Tensile Energy Absorption (N/m2) = f(t), R2=0.997
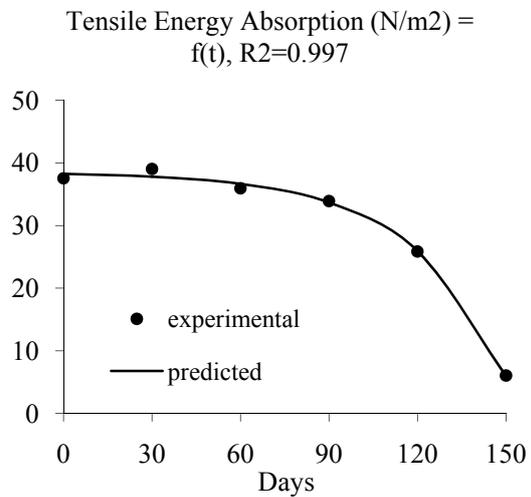
Figure 8d. Plot of Tensile Energy Absorption against time

L* = f(t), R2=0.999

Figure 8e. Plot of L* against time

b* = f(t), R2=0.999
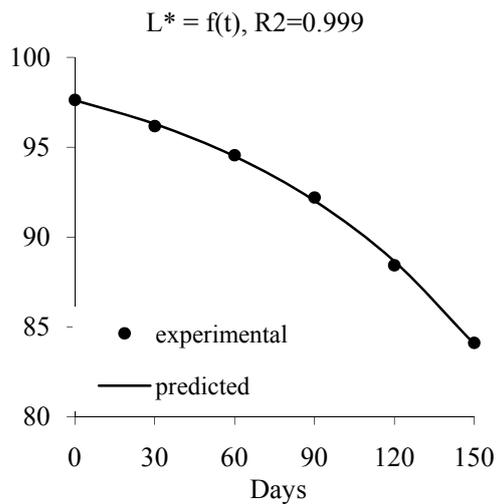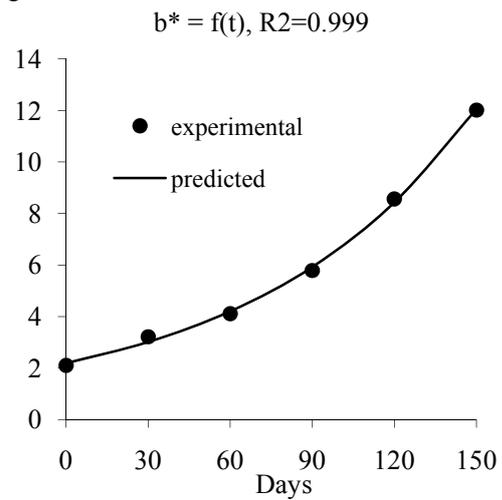
Figure 8f. Plot of b* against time

DISCUSSION

The model that is presented here applies to experimental setups that do not allow for the renewal of the ageing atmosphere. It has been demonstrated to be valid in the case of pure cotton cellulose ageing in sealed vessels. We believe that it would also be valid for certain kinds of paper and for other experimental setups (mainly for ageing in oil), but this remains to be proved. It is remarkable that other researchers using similar experimental setups rarely encounter the deviations from linearity that are reported here. Until further research is done, we can only offer the following speculations to explain this fact:

(a) It takes relatively long periods of ageing for the acceleration to become evident, if stable cellulose is used. In the case of unstable celluloses, the acceleration effect would contribute very little to the overall rate. Very interesting data that support this speculation were found in the work of Baransky et al. (2000). Remarkable differences are reported between the two different papers that were used as samples. The plot of $1/DP_t - 1/DP_o$ is linear for paper P_1 (cellulose from coniferous trees), but deviates from linearity for Paper P_2 (cotton linters cellulose which is more stable). Instead, DP appears to be a linear function of time. If the data for paper P_2 were plotted in terms of $1/DP_t - 1/DP_o$ or $\delta\%$, a similar plot to ours with an upward trend would result.

(b) The pH of the paper is a critical factor that affects its stability. Low pH results in highly unstable papers that degrade very fast, thus masking the results of autocatalysis.

(c) The details of the experimental setup are very important. The sealing of the vessels must be perfect, in order to have the complete effect of acceleration.

Browning and Wink (1968) used sealed glass tubes for the ageing of samples. They reported deviations of folding endurance versus time from linearity for several of their samples. However, these deviations were not attributed to the accumulation of degradation products, since they appeared under ventilated conditions also.

Emsley and Stevens (1994) reviewed the kinetics of cellulose degradation in oil. The presented data conform to the linear model with few exceptions of upward curvatures at higher temperatures (140°C) and longer times. The authors speculate that these deviations could be attributed to the accumulation of water produced by paper degradation.

Zou et al. (1996) used sealed vessels in a very similar experimental setup to ours and did not encounter any deviations from linearity.

The stronger evidence supporting our findings was published by Shahani et al (1989) and Shahani (1995). It was found that the plots of folding endurance deviated from linearity if the ageing took place in stacks or sealed bags. The plots also indicated an acceleration of the reaction rate. Shahani speculates that the process is autocatalytic. The acidic volatile products are supposed to be absorbed by the paper matrix and catalyze the depolymerization of cellulose. Since the concentration of the acidic species increases with time, it is reasonable that the rate would increase with time also.

Our model is based on this simple but intuitive concept. We have presented concrete evidence that the volatile degradation products are acidic in nature and that their concentration in the NaCl solution increases with the time of ageing. This is a confirmation of the soundness of assumption no 5, which is a crucial step for the formulation of the model.

As to the identity of the volatile acidic species and the mechanism of their production, few things are known. We know that the products of paper ageing include water, CO and CO_2 but also formic and acetic acid (Shahani, 1995; Emsley and Stevens 1994). The mechanism of the production of volatile acids could include the breaking of the $C^5 - C^6$ bond of C^6 oxidized cellulose or the opening and the subsequent fragmentation of the glucopyranose ring. The fragments could undergo further oxidation, so that finally a mixture of low molecular weight species including several volatile acids would be produced.

The fact that the model is valid for values of $\delta\%$ less than 0.7 does not reduce its significance. This limiting value of $\delta\%$ is reached after about 150 days of ageing under our experimental conditions. At the end of this time interval, the folding endurance of the paper samples has dropped to zero, tensile energy absorption to the 1/6 and tensile strength to about the 2/3 of their original values. Since it is mainly folding endurance and to a lesser extent tensile energy absorption and not tensile strength that determine the usability of paper (Barrow et al., 1959; Wilson et al., 1981; Brandis, 1994; Bansa et al., 1997), our model is applicable for the whole span of the useful life of paper.

One final remark, concerning the numerical value of the constant k_2 of equation 11. k_2 can be calculated from the $\delta\%$ data (equations 6 and 13):

$k_2 = \ln2\ k = \ln2 \times 33.75 \times 10^{-3} = 0.0234$

It can also be calculated from the paper pH data (equations 11 and 14):

$k_2 = m/\log(e) = 0.0198/\log(e) = 0.0456$

The disagreement between the two values of constant k_2 is not a fault of the model, but is due to the empirical definition of the pH of paper[1].

CONCLUSIONS

The model we propose here resulted from the study of pure cotton cellulose. We believe that similar behavior must be exhibited by historical (especially rag) paper for long ageing times in sealed vessels, but more research is needed to verify this speculation. If our model describes more precisely the ageing of paper kept in libraries and archives, we have to reconsider many tenets that are currently widely accepted. Our model predicts a low rate in the beginning of ageing that increases with time and brings about an abrupt breakdown of paper. The linear model predicts a constant rate of ageing. In the very early stages of ageing, both models must give similar results. Thus, it seems that the linear model overestimates the useful life of paper. If this notion is correct, the time margin left for taking measures for the preservation of our written heritage is less than we thought.

Considering that the volatile products of paper ageing are acidic and that they accelerate the process of ageing, it seems reasonable that ventilation of the storage areas is a crucial preservation factor. The presence of materials that absorb and neutralize these acidic substances could contribute to their removal from the atmosphere of the repositories.

We believe that the simple act of browsing through a book, apart from being a potential source of damage, could also have a positive influence if done carefully,

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[1] Paper is not a solution, so pH cannot be defined for it. Instead, an arbitrary definition of paper pH has been introduced as an indication of its acidity, specifying that it equals the pH of the extract of a certain quantity of paper in a volume of water. The exact quantities of paper and water depend on the standard used, and for ISO 6588 are: 2 g of paper in 100 ml of water. Consequently, the pH figures of paper have no absolute value but should be interpreted relatively and the numerical value of k_2 calculated from the pH figures should not be taken at face value.

since it aids its ventilation and removes part of the volatile acidic products of paper ageing, thereby contributing to its preservation. Thus, the tenet that "access (usage) is an enemy of preservation" might also need reconsidering.

APPENDIX

Derivation of equation 2

Suppose

ν = number of cellulose molecules

DP = number average DP

γ = total number of glucose molecules

N = total number of glycosidic bonds

Than

DP – 1 = average number of glycosidic bonds per cellulose molecule

N = ν (DP – 1) = total number of glycosidic bonds and

ν DP = γ = total number of glucose molecules

Since ν DP = $\gamma \Rightarrow \dfrac{1}{DP} = \dfrac{\nu}{\gamma}$

$$100\left(\frac{1}{DP_t} - \frac{1}{DP_o}\right) = 100\left(\frac{\nu_t}{\gamma} - \frac{\nu_o}{\gamma}\right) = 100\left(\frac{\nu_t - \nu_o}{\gamma}\right) =$$

$$100\left(\frac{\text{number of new cellulose molecules}}{\gamma}\right) = 100\left(\frac{\text{number of broken glucosidic bonds}}{\gamma}\right) =$$

(and since for large DP_o: $N_o = \nu_o (DP_o - 1) \approx \nu_o \, DP_o = \gamma$)

$$= 100\left(\frac{\text{number of broken glucosidic bonds}}{N_o}\right) = 100\left(\frac{\text{number of broken glucosidic bonds}}{\text{initial number of glucosidic bonds}}\right)$$

Therefore: % broken bonds = $\delta\%$ = $100\left(\dfrac{1}{DP_t} - \dfrac{1}{DP_o}\right)$

ABSTRACT

In this paper, we propose a new kinetic model that describes the depolymerization of pure cotton cellulose, applicable to ageing experiments in sealed vessels. By recording the pH of the salt solutions used for controlling the relative humidity inside the vessels, we demonstrate that volatile acidic species are produced during the ageing of pure cellulose. Based on the proposition that the acids produced must have an autocatalytic effect on the depolymerization of cellulose, we theoretically developed equations describing the time dependence of the percentage of the broken glycosidic bonds, the folding endurance, tensile strength, tensile energy absorption, stretch at break and the L* and b* coordinates of the CIEL*a*b* color system. The experimentally determined values of these pure cellulose paper properties were fit into the model equations by use of a computer statistical package. The very high values of the regression coefficients indicate that the model equations work quite well. The experimental data and the model equations indicate that for long ageing times (up to 150 days at 80ºC), the deterioration of the sample properties accelerates and finally brings about an abrupt breakdown of the samples. Under the light of these findings, we believe that the useful life of the historical paper stored in archives and libraries is less than predicted by the existing models, and steps for its preservation should be taken immediately. As an additional preservation measure, we propose the

ventilation of the storage areas so that the volatile acidic products of paper deterioration that accelerate its ageing are removed.

KEY WORDS

Cellulose ageing, model, sealed vessels, degree of polymerization, mechanical properties, optical properties

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