

Time–temperature superposition method for predicting the permanence of paper by extrapolating accelerated ageing data to ambient conditions

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Abstract In this paper we present a time-temperature superposition method for predicting the permanence of paper by extrapolating accelerated paper ageing data to ambient conditions. The presented method includes a test for the presence of shift factors to superpose all of the raw accelerated ageing data over the temperature range studied to obtain a master curve, a numerical fit of the master curve for producing a master equation representing the kinetics of paper degradation, a critical examination of applying Arrhenius equation for explaining the relationship between the empirically determined shift factors and the accelerated ageing temperature, and a verification of the Arrhenius activation energy extrapolation assumption. Unlike the usual approach that extrapolates the Arrhenius relationship between lifetime and temperature, without corroborating evidence, to ambient temperatures, we test the Arrhenius activation energy extrapolation assumption by determining the influence of acidity on cellulose hydrolysis reactions, and have found that detection and identification of the acid-sensitive linkages in cellulose substances is an ultra-sensitive and reliable method to measure degradation of cellulose and

paper in what is normally the extrapolation region (ambient temperatures). Taking the examples of natural ageing data in literature from 18 bleached kraft dry-lap pulps for 22 years under ambient conditions and three handsheet samples for 22 years under controlled conditions, comparison of the predictions with natural ageing results has been addressed.

Keywords Accelerated tests · Ageing tests · Cellulose degradation · Time–temperature superposition · Kinetics · Durability · Paper properties

Introduction

There currently exist no reliable methods and techniques to predict directly the long-term ageing behaviour of paper. The prediction of paper permanence often requires extrapolation of accelerated ageing data (Roberson 1976; Gurnagul et al. 1993; Porck 2000). This is because many of the chemical and physical changes that take place in paper under natural ageing conditions occur too slowly to study easily; accelerated ageing conditions such as elevated temperatures are often used to speed up these changes. It therefore becomes necessary to demonstrate that the changes that occur during accelerated ageing are comparable to the changes that occur during

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natural ageing at ambient conditions (Erhardt and Mecklenburg 1995).

The concepts of chemical reaction kinetics are often applied to accelerated ageing experiments of paper to predict how long paper will last under natural ageing conditions. The most important methodology for extrapolations and predictions in paper ageing studies is based on the Arrhenius equation

$$k = A \exp\left(-\frac{E_a}{RT}\right), \quad (1)$$

where k is the reaction rate of the chemical degradation process under investigation, E_a the Arrhenius activation energy (J/mol) which is said to represent the effective activation energy for the overall chemical kinetic expression governing the degradation, R the gas constant (8.314 J/mol/K), T the absolute temperature and A the pre-exponential factor. By determining how many hours or days of accelerated paper ageing are needed at different ageing temperatures to obtain a certain measurement of paper degradation, a “temperature-vs.-time needed” plot (called Arrhenius plot) can be made. If a log-plot of the failure time ($1/k$) vs. the inverse absolute temperature is a straight line, the Arrhenius equation is said to be valid and activation energy is then determined from the slope of the plot using Eq. 1. This then will allow one to determine the paper degradation rate at any temperature. Following this approach, the permanence of paper is estimated by extrapolating accelerated ageing results to ambient conditions (Gurnagul et al. 1993; Porck 2000). The assumption is of course that the reactions occurring are chemical thus the applicability of the Arrhenius equation (1), while effects studied by mechanical properties such as tensile strength and folding endurance may not as a consequence follow a linear dependence (Browning and Wink 1968; Zou et al. 1994).

The key issue regarding the use of the Arrhenius methodology concerns the accuracy of the extrapolation (Wise et al. 1995), i.e. using elevated temperatures for accelerated ageing of paper, how much confidence can one have in the resulting predictions of paper permanence over long periods of natural ageing? Over the last

four decades there have been discussions about the suitability of the Arrhenius equation to paper ageing degradation kinetics, not only because of the complex nature of the paper degradation kinetics process and the likely changes in the rate-determining parameters, but also due to the extrapolation procedure which use only one experimental data point from each accelerated ageing temperature curve and eliminating most of the experimental points from analysis. On the other hand, a significant progress has been achieved in the development of improved methods for analyzing and extrapolating accelerated ageing data to ambient conditions. In particular, an improved Arrhenius approach that involves applying the time-temperature superposition (TTSP) method to derive shift factors and probe for Arrhenius behaviour has been successfully used for years in polymers to make predictions of thermal ageing at experimentally inaccessible times (Gillen and Clough 1989; Gillen et al. 2000; Gillen and Celina 2001; Wise et al. 1995).

In this paper, we will show that the TTSP method is also a better approach to examine the Arrhenius equation for its validity in predicting the permanence of paper by extrapolating accelerated ageing data to ambient conditions. The structure of this paper is as follows. In Section “The TTSP method”, we present a brief introduction about the TTSP method and its origin. In Section “The prediction of paper permanence by the TTSP method”, we describe how the TTSP method is being applied to predict the permanence of paper through an example. In Section “Verification of the Arrhenius activation energy E_a ”, we describe how the acid-sensitive linkage detection and identification method is being used to measure degradation of paper in what is normally the extrapolation region and to verify the validity of the Arrhenius activation energy extrapolation assumption. In Section “Comparison of natural ageing results with predictions”, taking the examples of natural ageing results available in literature, comparison of the predictions with natural ageing results is addressed. In Section “Discussions”, both open problems and merits in applying the TTSP method for predicting the permanence of paper are discussed. The concluding remarks are presented in Section “Conclusions”.

The TTSP method

TTSP is a well-known methodology that frequently used to describe the mechanical and electrical relaxation behaviour of polymers. The essential idea in the TTSP method is the assumption that the higher ageing temperature accelerates the changes in certain parameter/property of material microstructure in a uniform way such that the monitored parameter/property values obtained at short times and high temperatures can be used to predict parameter/property values at long times and low temperatures. The TTSP principle is generally attributed to the early work of Leaderman in 1940s in a study of viscoelastic behaviour in polymers and polymer fluids (Leaderman 1943).

Consider that a dynamic property of a material is influenced by both the test temperature and the time of the dynamic loading. According to the principles of the TTSP method, both time and temperature are equivalent, i.e. the material parameter values obtained for short times at a given temperature is identical with that measured for longer times at a lower temperature, except that the curves are shifted on a logarithmic time axis. The curves of the measured material parameter vs. logarithmic loading time at different temperatures can be superimposed by proper scale changes on the time axis. The shift distance along the logarithmic time axis is called the time–temperature shift factor a_T and is given by

$$a_T = t_{\text{ref}}/t_T, \quad (2)$$

where t_{ref} is the test time at a reference temperature T_{ref} , and t_T is the time required to give the same response at the test temperature T . The value of the shift factor a_T depends not only on the reference temperature but also on the material properties. For every reference temperature chosen, a fully superimposed curve could be formed, which is called the master curve. If a smooth master curve can be produced, extrapolations to temperatures lower than the experimental temperatures become possible. Accelerated ageing data that do not superpose can certainly not be extrapolated to lower tem-

peratures with confidence (Gillen and Clough 1989) and causes of these dispersions need to be separately investigated.

The shift factors of a master curve have some relationship with the temperature. Generally, the Arrhenius equation is acknowledged with a reasonably good accuracy to determine the shift factor (Gillen and Clough 1989; Gillen et al. 2000; Gillen and Celina 2001; Wise et al. 1995). Combining Eqs. 2 and 1 gives

$$a_T = \exp \left[\frac{E_a}{R} \left(\frac{1}{T_{\text{ref}}} - \frac{1}{T} \right) \right], \quad (3)$$

where both T and T_{ref} are absolute temperatures. If Eq. 3 can be shown to be valid, i.e. a plot of the logarithm of the empirically determined shift factor values vs. the reciprocal absolute temperature produces a straight line; this then will allow us to calculate a shift factor for any desired temperature. Once the shift factors of a paper are determined, they can be used to shift and extrapolate the accelerated ageing data to ambient temperatures.

The prediction of paper permanence by the TTSP method

Determination of master curve and master equation

The best way to help explain how the TTSP method is being applied to predict the permanence of paper is through an example. The accelerated ageing data of bleached bisulfite pulp (BBSP) samples, reported by Zou et al. (1996a), are adopted as an illustrative example for quantitative determination of master curve and master equation. According to the authors' description in Zou et al. (1996a), the BBSP samples are those of bleached softwood bisulfite pulp originating from various Canadian mills and formed into standard handsheets (60 g/m²). In this accelerated ageing study the paper strips were suspended in completely sealed glass jars. Accelerated aging experiments were conducted at temperatures ranging from 60 to 100°C and a relative humidity of 75% (a saturated NaCl solution was placed in the jar

to obtain a desired relative humidity). After accelerated ageing treatment, the samples were conditioned at 23°C and 50% RH for at least 24 h, and then tested. The intrinsic viscosity values of the paper samples were determined using the SCAN method (Scandinavian Pulp, Paper and Board Testing Standard 1962). The average degree of polymerization (DP) was calculated from the intrinsic viscosity values.

Zou et al. (1996a) originally reported their paper ageing data in the form of DP vs. accelerated ageing time. Figure 1 shows their data re-plotted as the retained DP divided by its unaged value (DP/DP_0) vs. the log of the ageing time under a series of isothermal ageing temperatures, ranging from 60 to 100°C. To apply the TTSP method to determine the master curve over the ageing temperature range, we first select the lowest experimental temperature (60°C for the data shown in Fig. 1) as the reference temperature. For each data set at an elevated temperature, we then multiply the experimental time at this ageing temperature by a shift factor that is chosen empirically to produce the best overall superposition with the data under the reference temperature. The results of applying this shifting procedure to the data of Fig. 1 are shown in Fig. 2, where the x -axis gives the superposed time results at the lowest experimental temperature of 60°C and the values of empirical shift factors used to superpose the data are indicated in the figure. It is obvious that a master curve (the solid line in

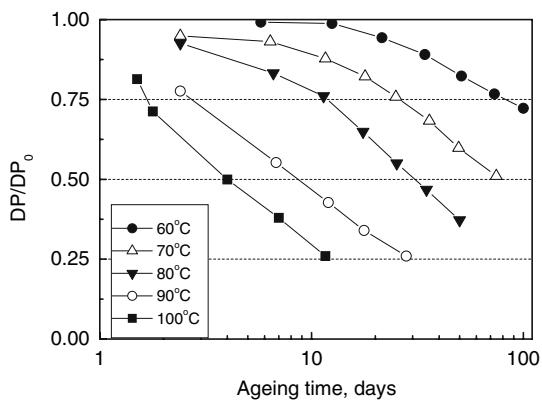


Fig. 1 Re-plot of accelerated ageing data of Zou et al. (1996a) for the bleach bisulfite pulp (BBSP) paper with a relative humidity of 75%

Fig. 2) can be obtained from the curves of individual data set at different ageing temperatures according to the above TTSP shifting procedure, and good superposition therefore exists for accelerated ageing data of Zou et al. (1996a).

The master curve can be further fitted by non-linear regression technique to produce a master equation representing the kinetics of paper degradation. One form of the master equation can be written as

$$\frac{DP}{DP_0} = \frac{1}{1 + DP_0 * kt_{ref}} \quad (4)$$

This is equivalent to the well-known and widely used Ekenstam equation in the form (Ekenstam 1936; Emsley and Stevens 1994; Zou et al. 1996a)

$$\frac{1}{DP} - \frac{1}{DP_0} = kt_{ref} \quad (4a)$$

Another form of the master equation can be written as

$$\frac{DP}{DP_0} = \left(1 - \frac{k_0}{k}\right) + \frac{k_0}{k} e^{-kt_{ref}} \quad (5)$$

This is equivalent to the cellulose and paper degradation kinetic equation proposed by Ding and Wang (2005) in the form of

$$1 - \frac{DP}{DP_0} = \frac{k_0}{k} (1 - e^{-kt_{ref}}) \quad (5a)$$

Here k is the reaction rate constant and k_0 is the ageing rate coefficient. Equation 5a had been applied to explain the accelerated ageing data of kraft paper by several experiments carried out at different conditions over a wide ageing temperature range from 60 to 160°C. Non-linear regression analysis of the superposed data set in Fig. 2 yields $k = 1.14 \times 10^{-3} \text{ year}^{-1}$ and $DP_0 = 1,336$ for master equation (4) and $k = 1.6686 \text{ year}^{-1}$ and $k_0 = 1.2848 \text{ year}^{-1}$ for master equation (5). All non-linear regression analyses were performed using Origin 6.0 software and a minimum chi-square (Chi^2) algorithm to obtain best-fit parameters for Eqs. 4 and 5.

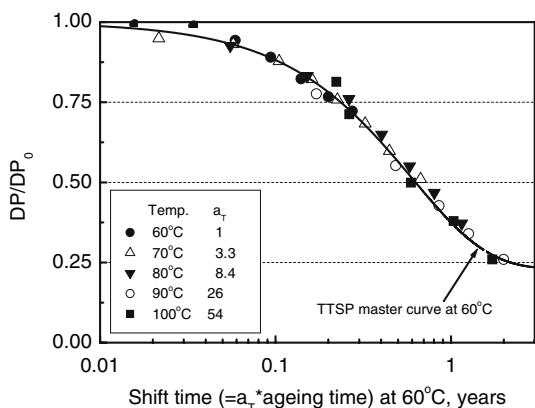


Fig. 2 Time–temperature superposition of the BBSP ageing data from Fig. 1 at 60°C using the shift factors as shown on the figure

Determination of the Arrhenius activation energy E_a

Figure 3 shows that the empirical shift factors used to produce good superposition of accelerated ageing data in Fig. 2 are consistent with the Arrhenius equation (3), and the analysis yields an apparent activation energy of $E_a = 104$ kJ/mol, determined from the slope of the straight line through the results, with 95% confidence limits on the mean of 99 and 109 kJ/mol. Such an Arrhenius behaviour ($E_a = 104$ kJ/mol) can be further confirmed when the log of the time to equivalent degradation (TED) is plotted vs. the

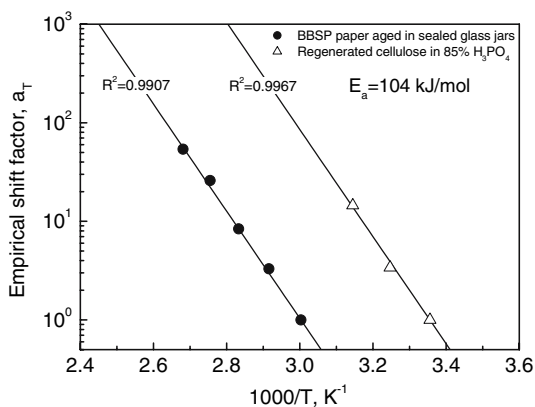


Fig. 3 Arrhenius plots of empirical values of the shift factor a_T used to superpose accelerated ageing data for the BBSP from Fig. 2 and for the regenerated cellulose in 85% phosphoric acid from Fig. 6

inverse of the ageing temperature, as shown in Fig. 4. Clearly, over the temperature range studied, the times required for the retained degree of polymerization DP/DP_0 to reach 0.75, 0.5 and 0.25 are consistent with the Arrhenius relationship. The slope of the straight line through the $DP/DP_0 = 0.5$ data in Fig. 4 gives $E_a = 104$ kJ/mol; the plots for $DP/DP_0 = 0.75$ and 0.25 data are also with the same slope (therefore the same E_a). It is interesting to note that for the BBSP samples the apparent activation energy of $E_a = 104$ kJ/mol found by the TTSP method is exactly the same figure found by the usual kinetic analysis of the ageing process (Zou et al. 1996a). This figure for energy of activation is also in good agreement with the reported activation energy of about 111 ± 6 kJ/mol for Kraft paper in literature (Emsley and Stevens 1994).

The prediction of paper permanence at ambient conditions

Knowing master equation (4) or (5) and the correspondent fitting parameters at the lowest experimental temperature 60°C ($a_{T=60^\circ\text{C}} = 1$), the retained degree of polymerization at ambient temperature conditions ($T < 60^\circ\text{C}$, $a_T < 1$) can therefore be predicted by combining Eqs. 4 or 5 with Eq. 2. Substituting Eq. 2 into Eqs. 4 and 5, we have

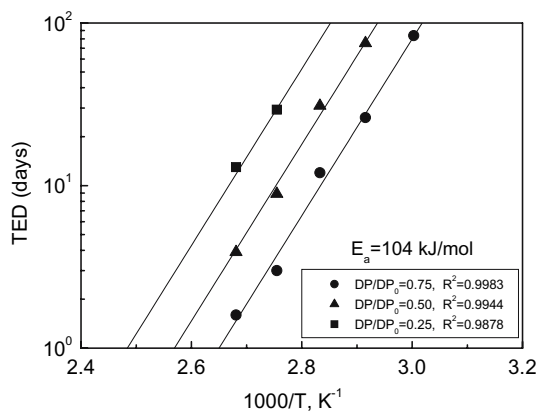


Fig. 4 Arrhenius plots for the accelerated ageing data of the BBSP paper from Fig. 1. The log of the time to equivalent degradation (TED) is plotted vs. the inverse of the ageing temperature

$$\frac{DP}{DP_0} = \frac{1}{1 + 1.523a_T t_T} \quad (6)$$

$$\frac{DP}{DP_0} = 0.23 + 0.77e^{-1.6686a_T t_T}, \quad (7)$$

where a_T is the shift factor at the ageing temperature T and its value can be determined by Eq. 3 with $T_{\text{ref}} = 60^\circ\text{C}$, and t_T is the ageing time by years at the temperature T .

It is now necessary to ask the following question. What measure of confidence can be placed in the predicted paper permanence calculated by extrapolation of a model over a data range for which the model was not developed? It should be pointed out that the accuracy of predicted paper permanence depends on the reliability of the activation energy. Variability in predictions based on uncertainty in the figure for energy of activation cannot be avoided in any method for prediction of paper permanence by extrapolating accelerated ageing data to ambient conditions. The use of a single activation energy figure in predictions embodies two assumptions. One is that the Arrhenius activation energy E_a of paper remains constant in the extrapolation temperature region (over the experimental temperature range). Another is that the activation energies (therefore the ageing rates) of all paper samples are affected equally by relative humidity and by moisture content.

If an activation energy E_a of 104 kJ/mol is assumed for all BBSP paper samples at ambient conditions, it becomes possible to predict the retained degree of polymerization at ambient conditions in terms of master equations (6) or (7). According to Eq. 3, the extrapolated shift factor a_T will be $a_{T=23^\circ\text{C}} = 0.0091$ at $T = 23^\circ\text{C}$, which implies that with same relative humidity of 75%, the ageing rate of BBSP paper will be 110 times as fast at 60°C as at 23°C , or the time required to reach a given level of degree of polymerization at 23°C will be 110 times that required at 60°C . If we further assume that the deviation of the activation energy $E_a = 104$ kJ/mol is $\pm 5\%$, then $E_a = 104 \pm 5$ kJ/mol and $a_{T=23^\circ\text{C}} = 0.0073$ and 0.0114 for the lower and upper values. These correspond to factors of 137 and 87 for the relative ageing rates at 60 and 23°C . Numerical computation can also

show that both master equations (6) and (7) provide very similar prediction for the permanence of BBSP paper at 23°C with a relative humidity of 75% over a broader time range of 200 years, but when the age of paper is beyond 60 years, the figure obtained by Eq. 6 is slightly larger than that by Eq. 7.

Admittedly, these are approximation. The figure of $E_a = 104$ kJ/mol determined over accelerated ageing temperature range may not be applicable to all paper samples at ambient conditions. Because the chemical mechanisms leading to ageing of paper may change with temperature and, thus, that the activation energy may change in the extrapolation ambient temperature region. Thermal ageing study of polychloroprene rubber materials has already found temperature-dependent activation energies that are the evidence of non-Arrhenius behaviour (Gillen et al. 2005). Improved prediction of paper permanence thus requires extrapolation from the lowest experimental temperature 60°C to ambient temperature 23°C to be justified. Ultra-sensitive techniques are required to measure processes directly related to the reactions responsible for macroscopic degradation of paper at or near ambient temperatures. This will be addressed in detail in next section.

Verification of the Arrhenius activation energy E_a

On the basis of the known chemical reactions of cellulose, it has been recognized that both hydrolytic and oxidative processes may occur in the ageing of paper (Smith 1969; Arney and Jacobs 1979; Arney and Novak 1982). The hydrolytic degradation of the cellulose molecules is the most common reaction, and the rate of the hydrolytic process is determined by the temperature, the acidity (pH value) and the moisture content in the paper. The oxidative degradation of the cellulose is primarily induced by the presence of oxygen in the environmental air. So, one possibility of developing ultra-sensitive techniques is to measure oxygen consumption rates at accelerated ageing temperatures to establish the necessary correlation, and at low temperatures (down to ambient temperatures) to determine their

temperature-dependence in the extrapolation region. For thermally aged elastomers under air-oven ageing conditions, it has been reported that oxygen consumption measurements fit these requirements, since they can be very sensitive and oxidation reactions were found to dominate the deterioration of mechanical properties (Wise et al. 1995). This oxygen uptake technique, however, remains to be verified experimentally for the ageing of paper. Furthermore, since most accelerated ageing experiments of paper are conducted in completely sealed vessels, it becomes necessary to develop an alternative technique except oxygen uptake measurement to test the validity of the activation energy E_a extrapolation.

Another possibility of developing ultra-sensitive techniques is to determine the influence of acidity on cellulose hydrolysis reactions in the ageing of paper. The following experimental evidences of paper ageing are relevant. First, it has been recognized for nearly a century that acidity is a major factor contributing to the degradation of cellulose containing materials and acids catalyze the hydrolysis. Second, experiments have shown that cotton cellulose regenerated from cuprammonium and cupriethylenediamine solution contains randomly distributed linkages which are approximately 10,000 times more sensitive to acids than the normal glucosidic linkages (Sharpley 1954). Third, further experiments with samples of cellulose regenerated in various ways also confirm that the presence of such acid-sensitive linkages appears to be a general phenomenon, and the process by which they are formed does not seem to be associated with any specific chemical reaction (Michie et al. 1961). Fourth, experiments have shown that homogeneous hydrolysis of regenerated cellulose in 85% phosphoric acid (H_3PO_4) at 25°C can be best represented by a single rate of reaction obeying first-order kinetics, and the activation energy for the homogeneous hydrolysis is of the same order of magnitude as that found for the hydrolysis of the β -glucosidic linkages (Daruwalla and Narsian 1966). As a consequence of the above, it is reasonable to believe that detection and identification of acid-sensitive linkages in cellulose substances is an ultra-sensitive method to measure degradation of paper in what is normally

the extrapolation region, and to test the validity of the activation energy E_a extrapolation.

Figure 5 shows the DP of regenerated cellulose divided by its unaged value (DP/DP_0) vs. time in 85% phosphoric acid at different temperatures of 25, 35 and 45°C. The original experimental results were reported by Daruwalla and Narsian (1966) in the form of $(2/PW_t - 2/PW_0)$ vs. time (where PW_t and PW_0 are the viscosity average molecular weights at time t and time zero, respectively). It is noticed by the original authors that regeneration of cellulose from a solution of cotton in phosphoric acid was carried out in an inert atmosphere of nitrogen, and the regenerated cellulose samples were conditioned at 65% RH and used in never-dried condition for subsequent hydrolysis experiments. Cuprammonium fluidity of the hydrolyzed samples was determined at 25°C according to ASTM standard (1961: Apparent fluidity of dispersions of cellulose fibres, part 10:230). In the present plot in Fig. 5, the DP was calculated as multiplying the intrinsic viscosity $[\eta]$ by 190 (ASTM D1795-90 1990), and $[\eta]$ was related to the viscosity average molecular weight PW by the well-known Mark-Houwink-Sakurada (MHS) equation: $[\eta] = K[PW]^\alpha$, where α and K are MHS constants, and ASTM D4243-86 (1986) quotes values of $\alpha = 1$ and $K = 0.0075$. The MHS equation can be found in any standard polymer textbook (for example, Billmeyer 1984). The

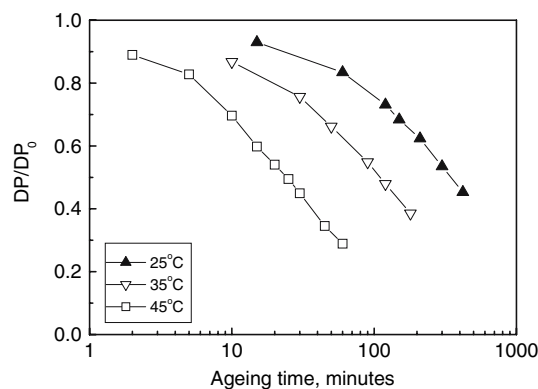


Fig. 5 DP of regenerated cellulose divided by its unaged value (DP/DP_0) vs. ageing time in 85% phosphoric acid at the indicated temperatures. Data is after Daruwalla and Narsian (1966)

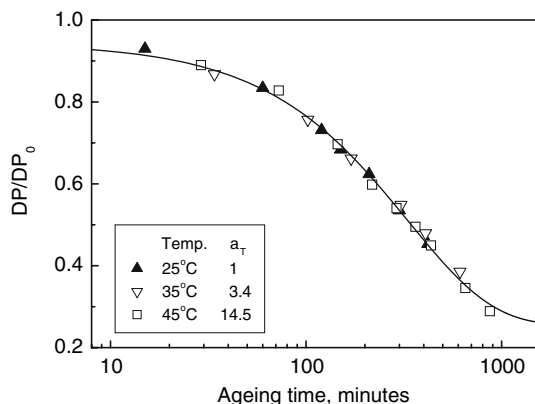


Fig. 6 Time–temperature superposition of the DP/DP_0 data from Fig. 5 at a reference temperature of 25°C

superposition of the DP/DP_0 data over the range 25–45°C is shown in Fig. 6 for $T_{ref} = 25^\circ\text{C}$. The associated empirical values of a_T are shown as triangles in Fig. 3. Clearly, these data are well described by an Arrhenius relationship with $E_a = 104$ kJ/mol as well; and the value of 104 kJ/mol for the regenerated cellulose in 85% phosphoric acid at ambient temperatures of 25–45°C is in exact agreement with the activation energy value determined for the BBSP aged in sealed glass jars at accelerated temperatures of 60–100 °C. This gives further support and confidence to predict paper permanence by extrapolating accelerated ageing data to ambient conditions.

Comparison of natural ageing results with predictions

Let us now attempt to reconcile the above TTSP extrapolation method with specific experimental data of natural ageing. Unfortunately, very few data of natural ageing of paper are available in literature. In this work, natural ageing results from 18 bleached kraft dry-lap pulps aged for 22 years under ambient conditions and three handsheet samples aged for 22 years under controlled conditions, originally reported by Zou et al. (1996b), are adopted as an illustrative example for quantitative comparison. According to the authors' description (Zou et al. 1996b), the average moisture content and the average pH in

naturally aged kraft pulps are $5.99 \pm 0.37\%$ and 4.43 ± 0.66 , respectively. The moisture content was measured and the pH values of all the pulp samples were determined at 23°C and 50% RH. They assumed that both moisture content and pH value were constant over storage period, and all bleached kraft pulps were naturally aged for 22 years under ambient conditions ($T = 23 \pm 3^\circ\text{C}$ and $\text{RH} = 50 \pm 20\%$, estimated) and all handsheet samples were naturally aged for 22 years under a constant temperature of $23 \pm 1^\circ\text{C}$ and constant RH of $50 \pm 2\%$. The activation energy for bleached kraft pulps that was experimentally determined by Zou et al. (1996b) is $E_a = 109$ kJ/mol.

We first calculate extrapolated shift factors at ambient temperature conditions by assuming that $E_a = 109$ kJ/mol is applicable to all paper samples. The results are given in Table 1.

We then determine the value of the retained degree of polymerization after t_T years at $T = 23 \pm 3^\circ\text{C}$ from Eq. 7 as

$$\frac{DP}{DP_0} = 0.23 + 0.77e^{-0.0077t_{T=20^\circ\text{C}}} \quad (\text{for } T = 20^\circ\text{C}) \quad (8a)$$

$$\frac{DP}{DP_0} = 0.23 + 0.77e^{-0.0122t_{T=23^\circ\text{C}}} \quad (\text{for } T = 23^\circ\text{C}) \quad (8b)$$

$$\frac{DP}{DP_0} = 0.23 + 0.77e^{-0.0190t_{T=26^\circ\text{C}}} \quad (\text{for } T = 26^\circ\text{C}) \quad (8c)$$

We finally use natural ageing results of Zou et al. (1996b) to test prediction Eq. 8. Comparison of the predictions according to Eq. 8 with natural ageing results is shown in Fig. 7 and Table 2. All results are reported as means \pm SD.

Table 1 Extrapolated shift factors at ambient temperature conditions using Eq. 3 and $T_{ref} = 60^\circ\text{C}$ ($a_{T=60^\circ\text{C}} = 1$)

a_T	$E_a = 104$ kJ/mol	$E_a = 109$ kJ/mol	$E_a = 115$ kJ/mol
$T = 20^\circ\text{C}$	0.0059	0.0046	0.0034
$T = 23^\circ\text{C}$	0.0093	0.0073	0.0057
$T = 26^\circ\text{C}$	0.0140	0.0114	0.0089

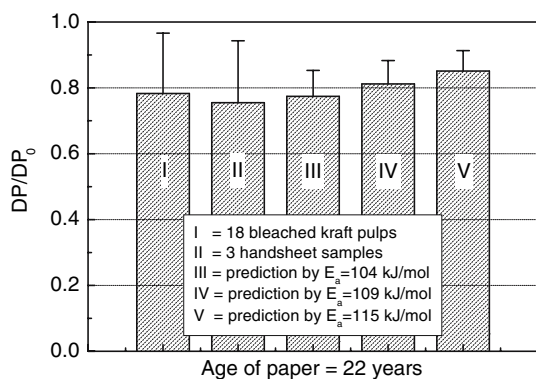


Fig. 7 Comparison of the predictions for 22 years with natural ageing results of eighteen bleached kraft pulps under ambient conditions and three handsheet samples under controlled conditions. Natural ageing data is after Zou et al. (1996b)

Table 2 Predictions of the retained degree of polymerization of paper after 22 years and comparison with natural ageing results of 18 bleached kraft pulps and of three handsheet samples

$\frac{DP}{DP_0}$	Mean value	SD
18 bleached kraft pulps	0.783	0.183
Three handsheet samples	0.755	0.188
Prediction by $E_a = 104$ kJ/mol	0.774	0.079
Prediction by $E_a = 109$ kJ/mol	0.812	0.071
Prediction by $E_a = 115$ kJ/mol	0.851	0.062

The natural ageing data is after Zou et al. (1996b)

Considering that the figure of $E_a = 109$ kJ/mol may not be applicable to all bleached kraft pulps under ambient conditions and all handsheet samples under controlled conditions. It may be necessary to introduce corresponding deviations of the activation energy from the figure $E_a = 109$ kJ/mol. If the deviation is $\pm 5\%$, then $E_a = 109 \pm 5.45$ kJ/mol. After repeated calculations as described above, the corresponding changes in extrapolated shift factors at ambient temperature conditions are given in Table 1, and the resulted changes in predictions are given in Fig. 7 and Table 2.

With the paucity and relatively large standard deviation of natural ageing data, it is difficult to simply say whether the model predicts well or not. However, it is remarkable that the model prediction gives values that are in the bulk part of

natural ageing data. Because the natural ageing behaviour of paper under ambient conditions is complicated and could be affected by the average temperature as well as relative humidity of storage (possibly also by temperature as well as humidity cycling), exposure to light, the presence of atmospheric contaminants and other factors that cannot be anticipated in a predictive test, an exact figure for life expectancy of paper or handsheet cannot be given in any event (Browning and Wink 1968). By considering the statistical error involved in determining the activation energy as well, the agreement between the predictions and natural ageing data appears to be justified in principle (in terms of the mean value of all natural ageing data).

Furthermore, it may be interesting to note that the investigation conducted by Erhardt and Mecklenburg (1995), who have found that the ageing process of cellulose under the conditions studied at 60–90°C and 30–80% RH is mainly RH dependent, and lowering the RH from 50 to 30% may slow the rate of cellulose hydrolysis by a factor of three to five times. According to these findings, it is not surprising to see the large standard deviation in natural ageing data of Zou et al. (1996b), because the estimated RH changes from 30 to 70%.

Discussions

To the best of the authors' knowledge, this work probably is the first application of the TTSP method for analyzing and extrapolating accelerated paper ageing data to ambient conditions. Some open problems in applying the TTSP method for predicting the natural ageing behaviour of paper are seen as follows. First, most accelerated paper ageing data available in practice may not always be comparable because the test temperature and initial conditions like moisture content of the samples differ among them. In some cases the test temperature may vary through the duration of the test. Also, due to material variability and experimental error, each data set at a particular test temperature may not correspond with each other. All these can lead to non-superposition of the overall shift factor over the

ageing temperature studied. It is important to know that TTSP violations may not be just exceptions but, in fact, quite common. If the TTSP method does not always work, it cannot be assumed *a priori*, and the option of using the TTSP method to arrive at a smooth master curve is also no longer available. Second, the TTSP method is developed for thermal ageing only. It is well-recognized that the relative humidity, the moisture content and acidity of paper also have a significant impact on paper ageing process. We have not yet included contributions of variable RH, moisture content and other factors to paper ageing in the present predictions, but it may be necessary to extend the TTSP method to develop a time–temperature–moisture–acidity superposition procedure in including moisture and acidity effects on paper ageing.

On the other hand, the TTSP method has a number of merits and features which distinguish it from existing paper durability analysis methods. First, unlike the normal Arrhenius analysis procedure that may use only one processed data point from each curve, the TTSP method uses all of the raw accelerated ageing data. Second, unlike the arbitrary definition of paper degradation rate by assuming the first-order or second-order reaction kinetics, the TTSP method does not pre-requisite the kinetic analysis of cellulose and paper degradation. Third, unlike the usual approach that extrapolates the Arrhenius relationship between lifetime and temperature, without corroborating evidence, to ambient temperatures; the present TTSP method provides evidence in support of the Arrhenius activation energy extrapolation.

Conclusions

From the results obtained in the present study the following conclusions are drawn:

- (1) The TTSP method can be applied in the studies of cellulose and paper ageing.
- (2) A general approach for more confidently correlating accelerated ageing results of papers with ageing under ambient conditions using the Arrhenius methodology has been presented. Unlike the usual approach

that extrapolates the Arrhenius relationship between lifetime and temperature, without corroborating evidence, to ambient temperatures; evidence in support of the Arrhenius activation energy extrapolation is presented in the present approach. We have shown that the Arrhenius activation energy E_a extrapolation assumption can be tested by detecting and identifying the acid-sensitive linkages in cellulose substances, which is an ultra-sensitive and reliable method to measure degradation of cellulose and paper in what is normally the extrapolation region (ambient temperatures).

- (3) A quantitative comparison of the predicted paper permanence with natural ageing results in literature has been made. The results show that the model gives values that are in the bulk part of natural ageing data. By considering the statistical error involved in determining the activation energy, the agreement between the predictions and natural ageing data appears to be justified in principle.

All these results shall give papermakers and end-users more support and confidence in extrapolating accelerated ageing data to predict the permanence of paper.

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