

Changes in the Tensile Properties of Paper in Response to Fluctuating Relative Humidity – Relevance to Paper Conservation

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Since its invention nearly 2000 years ago paper has been one of the most useful and widely used materials for the storage and transmission of information. Many printed artifacts of great historical and cultural importance have been executed on a paper substrate. The care of such artifacts is based in part on knowledge gained from scientific research into the ways in which paper degrades. It is common practice to attempt to simulate the effects of ageing in model papers by holding samples at elevated temperatures. The work presented in this paper examines the effects of fluctuations in relative humidity during artificial ageing at elevated temperature on the tensile properties of paper. The results of this work suggest that fluctuating relative humidities have a greater effect on paper than stable humidities. This has important implications for the safe handling and transport of historic paper artefacts.

Introduction

Since its invention nearly 2000 years ago [1] paper has been one of the most useful materials known to man. Paper is the major structural component of many of the cultural and historic artifacts cared for by conservators in museums, galleries, libraries and archives. They include works of art on paper, posters, books, archival documents, ephemera and photographs on paper substrates. Many of these artifacts were produced by printing processes and include some of the earliest examples of printing such as the Korean printed Buddhist prayers dating from the 8th century AD known as the Mukujumkwang Dharani Sutra [2]. Some of these printed items are among our most important cultural artefacts such as the Gutenberg Bibles [3] and the prints of Rembrandt [4]. Many professionals in the cultural heritage sector are concerned with prolonging the life of paper artifacts including curators, librarians, archivists, collection managers and in particular paper conservators who devise and implement preservation policies and where appropriate carry out interventive treatments on paper objects.

There has been a large body of scientific research carried out over several decades into chemical changes in paper relevant to the concerns of conservators. Some examples are cited below. Workers in this field are interested in changes in paper resulting from conservation treatments or deterioration due to ageing and environmental factors. Chemical changes have been investigated by a variety of techniques [5].

These include pH measurements [6], FTIR spectroscopy [7] and measurement of the degree of polymerization (DP) of cellulose using viscometric methods [8]. Studies have often involved artificial ageing of paper samples using elevated temperatures [9, 10], controlled exposure to common gaseous pollutants known to be implicated in paper degradation [11] and elevated light levels [12].

As well as direct chemical analysis, macroscopic properties of paper have been investigated by conservation scientists, in particular mechanical properties. A wide variety of mechanical tests are used for analysis in the paper industry including finite span tensile, zero span tensile, fold endurance tests, burst and tear tests [13, 14]. In the context of paper conservation research the most frequently used tests are probably fold endurance, finite span tensile and zero span tensile tests [15]. The results of these tests have often been interpreted in terms of the chemical changes undergone by cellulose and other components of paper fibres during ageing [16].

One important factor which influences the properties and behavior of cellulosic fibers and which is of great importance in the context of conservation is ambient relative humidity. For example high relative humidity increases the risk of biodeterioration of cellulosic artifacts [17] whereas very low levels of relative humidity have been suggested as causing paper to become more brittle [18]. As well as extremes of relative humidity, fluctuations of relative humidity are also of concern. Some studies have indicated

that repeated cycling of relative humidity can accelerate the degradation of paper [19, 20]. The work reported here is concerned with investigating the potential effect of fluctuating relative humidity on the tensile properties of paper.

Experimental

The paper used for the experiments was Whatman No 1 Chromatography paper made from a high quality cotton linter pulp described by the manufacturers as consisting of pure cellulose. This particular paper was chosen for the experimental work because any changes noted as a result of experimental processing can largely be attributed to changes in cellulose itself. For this reason it is often used in conservation research [5]. The paper samples were subjected to differing conditions. Untreated specimens, labeled (0), were conditioned at a temperature of 20 °C and a relative humidity of 50% and were not exposed to any further treatment. Half the remaining specimens were subjected to an acid treatment by immersion and agitation in 1M hydrochloric acid for one hour, followed by soaking in still mains water for one hour coupled with a 10 minute wash in running mains water. This was done in order to simulate to a first approximation paper degraded by acid hydrolysis. This is recognized as one of the major modes of chemical deterioration of paper in museum, library and archival collections [21]. Specimens were then placed on clean blotting paper and air dried overnight. Specimens that were acid treated were labeled A, and those not treated with acid were labeled NA.

NA and A samples were heat and humidity treated in WK3-180/40 Weiss Gallenkamp environmental test cabinets for periods of 9 or 20 days either under constant relative humidity (K) or cycled relative humidity (CY) conditions. The constant conditions were a temperature of 80 °C and 65% relative humidity. The humidity and temperature probes in this cabinet recorded that the actual relative humidity varied by $\pm 1\%$ from the set point and that the temperature varied between 78.5 °C and 82 °C. The conditions in the cabinet used for cycled conditions were set as follows. The relative humidity was cycled between 30 and 80% and the temperature was held constant at 80°C. The full cycle was: 3.5hr at 80% relative humidity, 0.5hr linear ramp

down to 30% relative humidity, 3.5hr at 30% relative humidity, 0.5hr linear ramp up to 80% relative humidity. Three cycles were completed every 24 hours. The cabinet running the CY tests accurately followed the programmed set-points for temperature and humidity, but developed a fault after four days that led to the complete evaporation of the water used for the conditioning. For a period of 6.5hr, the specimens remained at 80 °C, but RH readings fell to 0%. A second batch of specimens, labeled 2B, was introduced to both cabinets for 9 days of ageing after this fault was rectified. No discernible differences have been noticed between the specimens from the cycling cabinet introduced before and after the fault. All mechanical testing was executed in a controlled environment room. The temperature and relative humidity were controlled using a combination of an air conditioning unit, a humidifier and a dehumidifier. During the testing relative humidity was maintained at a value of $50\% \pm 2\%$. During testing temperatures varied between 25.0 °C and 28.1 °C. All specimens were conditioned in the controlled environment room for at least 24 hours prior to testing.

Finite Span Tensile Tests

These were carried using an Instron 4411 tensile testing machine fitted with a 500 N load cell. Paper specimens were tested using the protocol outlined in British Standard 4415:1985 Part 1 as a basis [22]. Paper specimens were cut to the following size: length 250 mm, width 25 mm. Strips were only prepared with their long axis in the machine direction of the paper. This was because the paper width, in the cross direction as supplied was shorter than the length required by BS4415 for test specimens. The key measurements recorded relating to BS4415 were maximum load per width (Nmm⁻¹) and slope (Nmm⁻¹). In addition tensile energy absorption (Nmm⁻¹) was also recorded. In order to ensure accurate calculation of these values by the Instron software the width of each specimen was measured to the nearest 0.5 mm. This was done in order to eliminate any errors due to small variations in the width of the specimens as cut. Specimens were held by pneumatic grips for the test. The gauge length was 200 mm. Specimens were tested in tension until failure. The rate of application of tensile force was selected by un-

dertaking initial trials in order to select loading rates which caused failure in an average time of 20 seconds \pm 5 seconds. The rate chosen as a result of these tests was 10 mm/minute. For each sample group a number of specimens were tested. The results of any specimens that failed within 10 mm of the grips were rejected as specified by BS4415. Additionally any specimens that failed at visible flaws resulting from pre-testing processing were also rejected. In all sample groups with one exception (see below) at least ten specimens were tested which did not have to be rejected under the above criteria. Mean values and standard deviations for sample group measurements were recorded.

Scanning Electron Microscopy

A Hitachi S-2600N scanning electron microscope was used in variable pressure mode to inspect specimens of paper used for the finite span and zero span tensile tests. Images were captured using a backscattered electron detector.

Results

Finite span

The results for the untreated sample mean and sample standard deviation, were as follows (Table 1).

The results for 9 day samples, means and sample standard deviations, were as follows (Table 2)

The results for the 20 day samples, means and sample standard deviations, were as follows (Table 3).

Sample groups which were not pretreated with acid showed little change in slope (Fig. 1), maximum load per width (Fig. 2) and tensile energy absorption (Fig. 3) before and after aging, both in constant and cycling RH conditions, for 9 and 20 days. Compared to the untreated and acid treated unaged sample groups, acid treated groups – constant and cycled RH – showed a slight decrease in values of strength and tensile energy absorption after 9 days aging and an increase in stiffness after 9 days. After 20 days aging the stiffness of the constant RH group showed little change but the strength and tensile energy absorption showed a marked decrease. In the case of the cycled acid treated specimens, after 20 days aging, every single specimen tested (in total 18) failed at the grips. Under BS4415 such results would not normally be re-

Table 1 Finite span test results for untreated paper

Slope Nmm ⁻¹	Maximum load/width Nmm ⁻¹	Tensile energy absorption Nmm ⁻¹
28.1 \pm 1.0	2.41 \pm 0.07	0.025 \pm 0.003

Table 2 Finite span test results for samples aged for 9 days

Sample group	Slope Nmm ⁻¹	Maximum load/width Nmm ⁻¹	Tensile energy absorption Nmm ⁻¹
Non-acid constant RH	29.8 \pm 0.9	2.40 \pm 0.08	0.023 \pm 0.003
Non-acid cycled RH	28.9 \pm 0.9	2.45 \pm 0.07	0.024 \pm 0.003
Acid treated constant RH	23.4 \pm 1.6	1.99 \pm 0.17	0.021 \pm 0.006
Acid treated cycled RH	24.1 \pm 1.1	2.09 \pm 0.13	0.023 \pm 0.004

Table 3 Finite span test results for samples aged for 20 days

Sample group	Slope Nmm ⁻¹	Maximum load/width Nmm ⁻¹	Tensile energy absorption Nmm ⁻¹
Non-acid constant RH	30.7 \pm 1.3	2.51 \pm 0.06	0.022 \pm 0.002
Non-acid cycled RH	28.3 \pm 1.3	2.50 \pm 0.11	0.024 \pm 0.003
Acid treated constant RH	25.2 \pm 1.3	1.67 \pm 0.19	0.009 \pm 0.004
Acid treated cycled RH	24.4 \pm 1.3	1.07 \pm 0.18	0.002 \pm 0.001

corded. However it does seem reasonable to regard the behavior of this sample group as being of interest. An error in the testing procedure (such as specimen misalignment or a fault in the tensile tester) is unlikely to have caused this consistent failure at the grips as for all other sample groups tested both before and after this group during the same working day, the majority of the specimens failed at distances greater than 0.5 cm from the grips. As well as the maximum load and slope values recorded under BS4415, tensile energy absorption values were also noted. The mean tensile energy absorption for 20 day acid treated, relative humidity cycled group was the lowest recorded for any of the sample groups suggesting that this sample was the most brittle and as a result stress concentration lead to failure at the grips for all 18 specimens.

This contention is supported by examination of load elongation curves for the different sam-

ple groups. The untreated specimens showed behavior typical of a machine made paper with an initial linear elastic region followed by a non-linear plastic region until failure (Fig. 4). Non-acid treated sample groups (both constant and cycled relative humidity) showed similar behavior after 20 days ageing. However acid treated samples did show a change in behavior. In both cases the amount of plastic deformation decreased, with the greatest decrease being for the cycled sample group (Fig. 5). This correlates with the reduction in both maximum load and tensile energy absorption values recorded for these samples. The reduction in tensile energy absorption for these samples appears to be largely due to the loss of the plastic region of deformation.

Fig. 1
Graph of slope vs. ageing duration for finite span tests

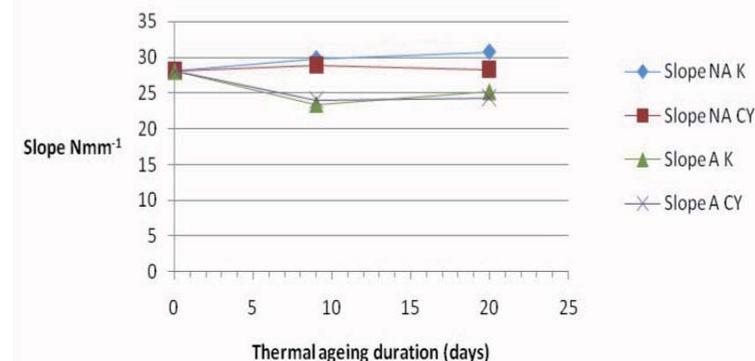
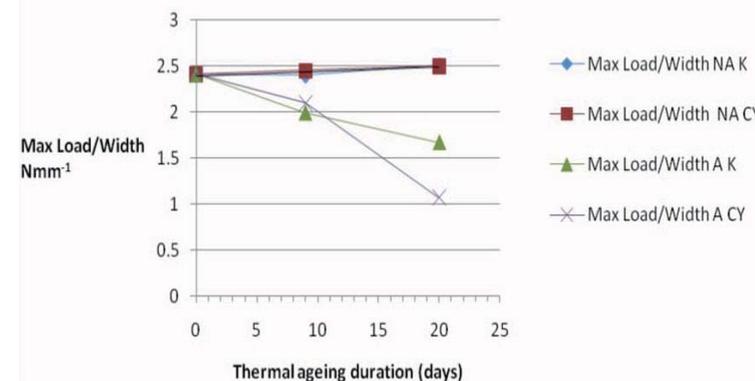


Fig. 2
Graph of maximum load/width vs. ageing duration for finite span tests



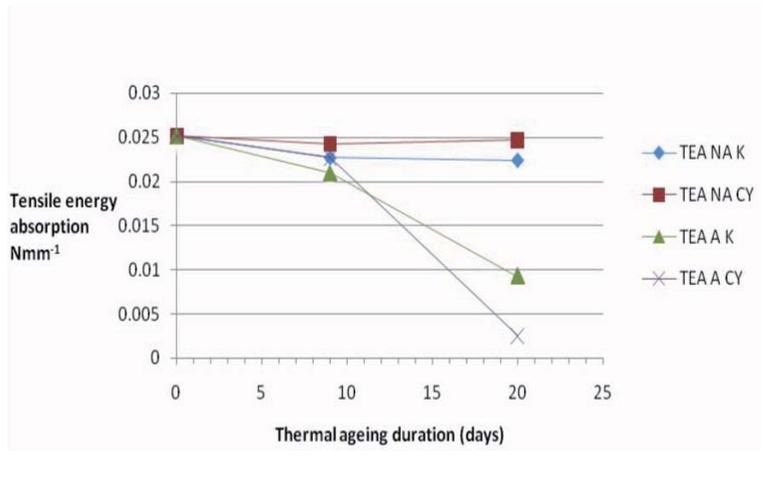


Fig. 3
Graph of tensile energy absorption vs. ageing duration for finite span tests

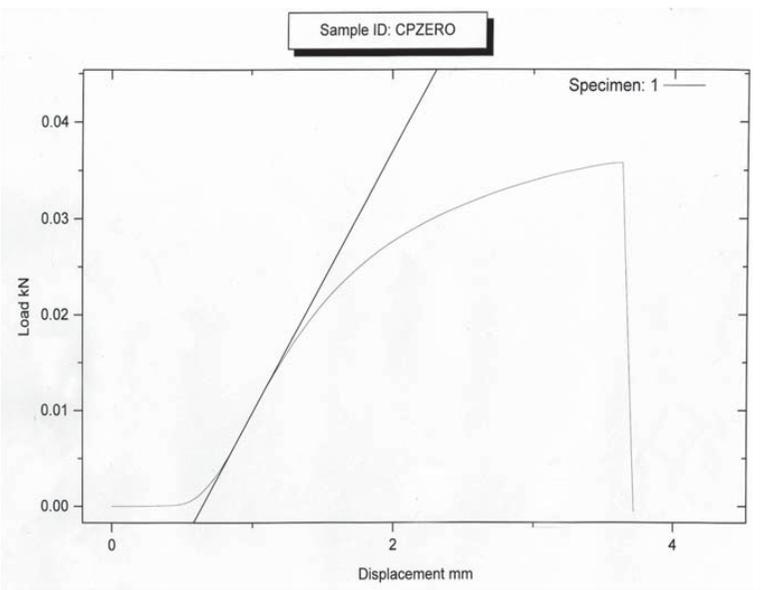


Fig. 4
Example of a load extension curve for an untreated, unaged sample of paper recorded during a finite span tensile test

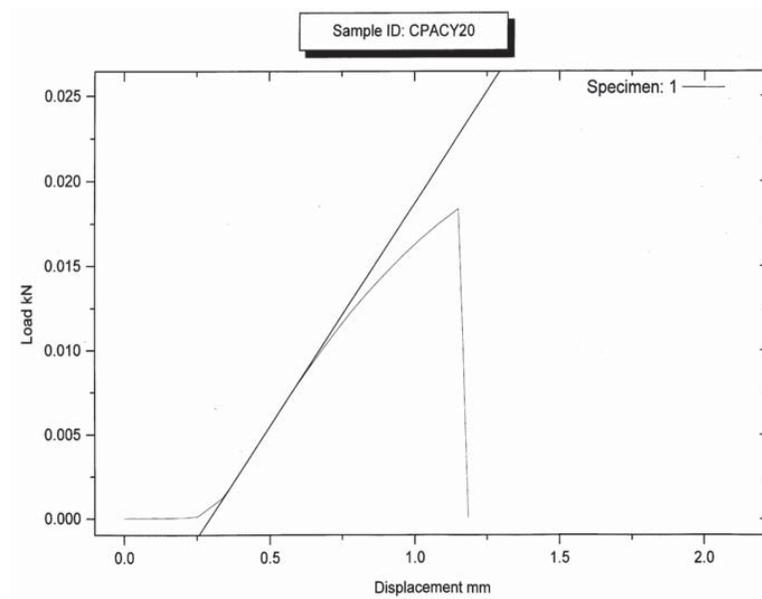
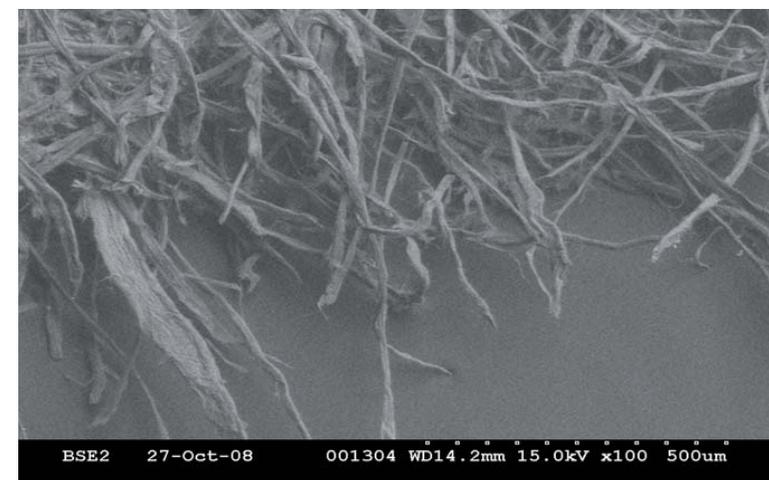


Fig. 5
Example of a load extension curve recorded during a finite span tensile test for an acid treated sample of paper aged under fluctuating relative humidity for 20 days

Scanning Electron Microscopy

Figure 6 shows a typical example of the break of an untreated specimen of paper following a finite span tensile test. The image clearly shows that fiber pull-out has occurred during failure of the specimen. In comparison figure 7 shows an example of the break at the end of an acid treated relative humidity cycled for 20 days specimen where there is little or no fiber pull-out and failure has instead been accompanied by the fracture of the individual fibers.

Fig. 6
Scanning electron micrograph of an untreated specimen of paper fractured in a finite span tensile test



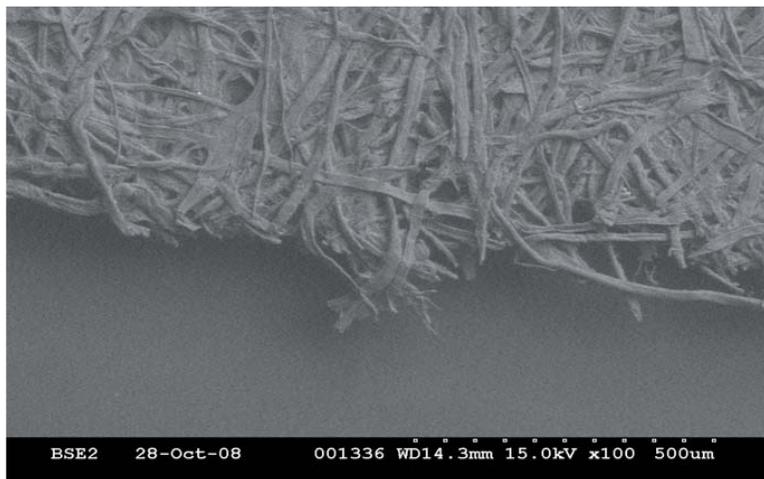


Fig. 7
Scanning electron
micrograph of an acid
treated, aged for 20 days
specimen fractured in a
finite span tensile test

Conclusion

The results presented above support the view that paper which has already suffered some degree of degradation via acid hydrolysis is more vulnerable to further deterioration as a result of artificial ageing than undegraded paper. Additionally accelerated thermal ageing under cycling relative humidity conditions appears to enhance the rate at which brittleness of paper increases as demonstrated by the results for tensile energy absorption.

Decreases in zero span paper strength after several thousand cycles of fluctuating relative humidity at room temperature have been reported by Bogaard and Whitmore [20]. They suggest that changes in relative humidity create very high local stresses within the fibers that accelerate the hydrolysis of cellulose by mechano-chemical processes. The rupture of chemical bonds as a result of the influence of mechanical stress has been observed in a number of polymers [23].

Another possible factor to consider is that cycling relative humidity could be promoting an increase in the crystalline fraction within the cellulose fibers. It has long been recognized that native cellulose is partially crystalline. The cellulose molecules are arranged in fibrils within the fiber cell wall which have both amorphous and crystalline regions. There are two native (i.e. naturally occurring) polymorphs, cellulose I_{α} and cellulose

I_{β} . Cellulose I_{α} has a triclinic unit cell and is the dominant form in lower plants and bacterial celluloses. Cellulose I_{β} has a monoclinic unit cell and is dominant in the higher plants [24, 25]. It is known from studies of paper pulping processes that the relatively extreme conditions involved (temperature, changes in moisture content etc) can increase the ordering of cellulose [26]. Given the potentially large number of cycles of fluctuating relative humidity that cultural artifacts made of paper may experience in many collections (where strict environmental controls may not be in place) an ordering effect may be observable over a long period of time. Unpublished research by the authors found that the largest crystallite size, measured by X-ray diffraction and the highest crystallinity index, measured by FTIR spectrometry was detected for the acid treated sample cycled at fluctuating relative humidity for 20 days. This would support the proposition that the possibility for increased ordering exists as a result of fluctuating relative humidity values for paper fibers which have undergone some degree of acid hydrolysis. It has been suggested that this can happen because cellulose chains in the amorphous regions have greater freedom to move into a more crystalline arrangement when shortened by acid hydrolysis [27]. In this study this seems to have occurred under conditions not as extreme as those employed in paper pulping

processes. Increased crystallinity in paper fibers is known to increase the brittleness of the paper itself [28]. Brittleness in paper is a major concern of paper conservators as it increases risks to artifacts during handling and transport. Contemporary conservation practice is increasingly centered on making historic collections more accessible to individual researchers and, via exhibitions, the wider public. In order to reduce the development of brittleness our findings emphasize the desirability of avoiding large fluctuations in relative humidity during archival storage and exhibition of historic paper artifacts.

Further research will be undertaken to investigate the hypothesis that cycling humidity increases the crystallinity of degraded cellulose in

paper and the effects of cycling humidities at the temperatures at which paper artefacts are conventionally stored and exhibited.

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