DEGRADATION OF CELLULOSE HANDSHEETS AS STUDIED BY BEGIN AND KAMINSKA METHOD

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The method of accelerated aging developed by Canadian Conservation Institute (CCI) and Library of Congress, and recently accepted by ASTM as a new standard (ASTM D 6819-02), intends to mimic the mechanical and chemical changes occurring in paper under natural conditions in a new way. [1] A wide array of existing methods and standards (see: [2]) does not take into account the factor evident to every reader opening an old book – its odour. In an aging experiment with free-hanging separate sheets of paper, the degradation products can be easily desorbed from the sheets, thus not affecting paper degradation any further – in contrast to real situation, where closed books or archive materials are tightly packed on shelves.

1. Reproducibility of the proposed test method

A series of samples used in the ASTM/ISR study was aged according to the ASTM D 6819-02 method and tested for the retention of their folding endurance, zero-span tensile strength and tear index. Results of measurements were compared with those published in the CCI report.[3] Tests have been performed at both recommended temperatures: at 90 °C for 14 days and at 100 °C for 5 days. Obtained results are consistent with the published data.[3] The values of double fold and tear index measured for samples aged at 100 °C are compared in Fig 1 and Fig. 2.

Noticed discrepancies can be attributed to the considerable measurement error, typical of mechanical properties of paper. Additionally, sealing of the used glass tubes is an important factor for the lab-to-lab repeatability.

2. Sealing of tubes

It has been found that recommended glass tubes do not allow to obtain a perfect seal at the aging conditions (Lab-line No. 308-9 and Kontes No. K736500-3515). Silicone rubber O-rings and Teflon resin gaskets used in the available hybridization tubes, although mechanically and chemically stable well above 100 °C, are considerably gas-permeable at the aging temperatures. The water loss from the tubes was observed by measuring the moisture content of the paper during aging (IR through-the-glass moisture-meter, Fibro). It was additionally confirmed by weighing the tubes after the prolonged times of aging. Flat, 2 mm thick disk, made of Viton fluoroelastomer (Du Pont Dow) were found to have satisfying sealing qualities. Additionally, to ensure tight sealing, the standard polypropylene screw caps were replaced with caps made of glass-fibre reinforced PPS (polyphenylsiloxan) (Bola H993-45, Germany) which were tightened on a tube with a dynamometric wrench at 18 Nm.

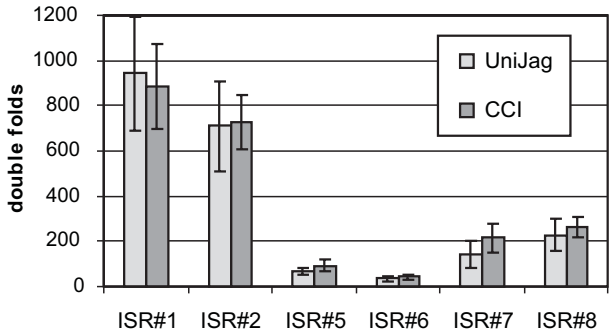

Figure 1: Folding endurance for ASTM/ISR samples measured at Jagiellonian University and CCI. Glass tube aging, 5 days, 100 °C.

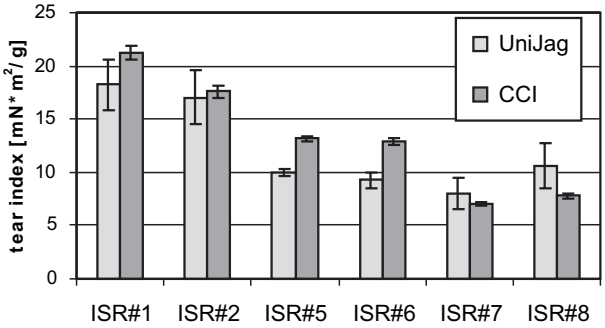

Figure 2: Tear index values for ASTM/ISR samples measured at Jagiellonian University and CCI. Glass tube aging, 5 days, 100 °C.

3. RH inside the tube

An attempt was made to verify the actual aging conditions inside the tube, i.e the RH of air and the sample moisture content.

Since opening the sealed tube containing the tested sample will invariably lead to a sudden change of its moisture content, the only way to determine this content is by an *in-situ* measurement. Such a measurement could be carried out either with the use of a moisture sensor placed inside the tube during the aging test or by a moisture meter located outside the tube and capable of measuring the moisture content through the glass. The latter method has been applied (Fibro MCA 1410 Moisture Content Analyzer), and the RH of air inside the tube during aging at 90 °C was

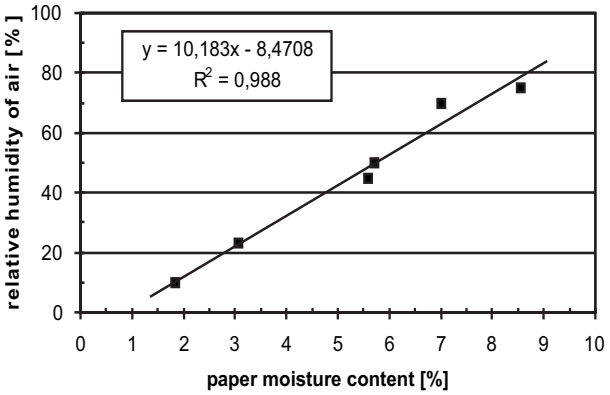

Figure 3: Relation between relative humidity of air and moisture content for paper P1 at 90 °C.

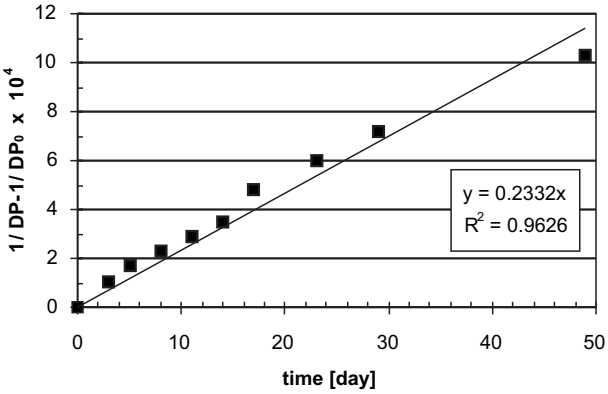

Figure 4: Kinetic curve of paper P1 degradation at 90 °C in sealed tubes.

established as 59% for a sample of the model paper P1.[4] This result shows that the conditions of aging in sealed tubes differ significantly from those established in the ASTM/ISR research program.[3]

Moisture content of paper P1 at various RH was measured in the climatic chamber at 90 °C. Using the obtained relation (shown in Figure 3) for the same temperature, the relative humidity in the glass tube with P1 paper was calculated from the IR moisture measurement for the sample. Additionally, under such conditions the total gas pressure inside the tube was determined not to exceed 2 atm.

4. Degradation rate

The P1 paper samples used for the studies of degradation rate were aged in sealed tubes at 90 °C. For each aging time, the degree of polimerization was measured (viscometrically) for samples from at least two different tubes. The kinetic curve (in the linearized coordination system) obtained for the samples aged with the new technique is presented in Figure 4. The rate constant of paper degradation was calculated according to the Ekenstam equation. The found value of the rate constant ($k = 2.3*10^{-5}$) correlates well with the results of our previous study, where P1 paper samples were aged in closed vessels containing saturated solutions of salts.[5] Using the relation between k and RH presented in the referred work, the rate constant for the conditions inside sealed tube with P1 paper could be estimated as $2.9*10^{-5}$.

In this work the discussed kinetic curve have been also related to other kinetic curves obtained for P1 paper aged under similar conditions (T, RH) but as free hung sheets in a climatic chamber.

5. References

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