DEGRADATION OF PAPER AS STUDIED BY FIBER LENGTH MEASUREMENTS AFTER HYDRODYNAMICAL TREATMENT

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1. Introduction

Comprehensive characterization of deteriorating papers is a prerequisite of selecting the best methods for their preservation. In this context, it is important to learn how macromolecular changes influence mechanical properties of paper.

Properties of cellulose chains determine the properties of cellulose fibers. A decrease in the degree of polymerization of cellulose lowers mechanical resistance of fibers, thus making them susceptible to shortening due to mechanical treatment. Consequently, mechanical properties of paper are also changed. A scheme of this cause-and-effect chain of the degradation process can be drawn:

Studies on the dependences DP = DP(t) and MP = MP(DP) exist in the literature, but description of a possible relation between fiber length and DP is hard to be found. Characterization of paper degradation through the studies of fiber length has several practical advantages:

a) a small amount of paper is necessary for the measurement (0.1 g sample, about 14 cm², would suffice);

b) paper samples covered with print, as well as those containing lignin, can be studied;

c) the measurements are fast.

2. Experimental

2.1 Samples

The experiments were carried out on a sample of model paper P1 (containing more than 95% of cellulose and obtained from TNO, Delft¹), previously subjected to accelerated aging². Some samples had been impregnated with aluminum sulphate prior to accelerated aging² in order to achieve an effect of degradation more advanced than that obtained for the non-impregnated samples after the same degradation period.

2.2 Equipment

Morphological properties of fibers were determined with a MorFi LB-01 fiber analyzer, produced by Techpap, France. The analysis is done on a fiber network, so that the measurement occurs in the natural unrestrained environment of fibers. This approach allows for a reliable statistical measurement of thousands of fibers at high speed and accurate determination of important characteristics of their shape.

2.3 Defibration procedure

The samples of degraded paper had to be defibered prior to a measurement in a simple domestic blender used as a disintegrator. Direct action of the blender knives, as well as the action of water whirl produced by the rotation of knives, were the defibering agents. In order to minimize the destructive action of knives, the defibering process (of total duration time equal to 3 minutes) was done in cycles: blender switched on for 5 seconds, then blender switched off for 10 seconds.

2.4 Fiber length measurements

The length of fibers was measured automatically in the MorFi apparatus by a computer analysis of images of the suspension flowing through a flat cell observed by a digital CCD video-camera. The analysis of morphological properties of fibers performed by MorFi LB-01 provided arithmetical average length of fibers (the value most sensitive to the effect of shortening of degraded fibers during their mechanical treatment), expressed by the equation

\[ FL = \frac{\sum z_i \cdot l_i}{\sum z_i} \]

where \( z_i \) is the number of fibers in a given class of length, and \( l_i \) is the mean length of fibers in the given class. Additionally, a determination of the degree of cellulose polymerization (DP), for all samples tested by MorFi LB-01, has been done viscometrically, in accordance with the SCAN-CM 15:88 standard.

2.5 SEM measurements

Another method of defibering of samples consisted in a gentle shaking of paper sample in a small bottle partly...
filled with water. After defibration, suspensions composed of separate fibres were obtained. From these suspensions small handsheets (1 cm² in diameter) were made. The length of fibres could be measured from the photographs of handsheets, made by Scanning Electron Microscope.

3. Results and Discussion

The dependence of both measured quantities – degree of cellulose polymerization (DP) and average fibre length (FL) – on time has been shown in Figure 1. Both curves are similar and running approximately in parallel, thus confirming existence of correlation between polymerization degree and fiber length.

However, this correlation was established only for paper samples containing cellulose with polymerization degree below 450, as illustrated by Figure 2.

It has to be stressed that a decrease in the arithmetical average length of fibers is an effect of weak mechanical treatment of sample, being the result of water whirl only (results of action of the blender knives was regarded as negligible). This decrease is due to the presence of sensitive places in the structure of degraded fibers. These places are distinguished by a very weak mechanical strength. It can be postulated that for DP values below 450 the number of weak points in fibers is so great that even a delicate mechanical treatment can break off the fibers.

When a dependence of average length of fibers on the polymerization degree of cellulose is drawn for all samples impregnated with aluminum (Figure 3), an existence of a logarithmic relation can be supposed. Such a hypothesis has been forwarded by Akcetin and Verschraege⁴. However, more experimental data in the region of lower DP values are necessary in order to obtain a more unequivocal confirmation of this supposition.

A comparison has been made between the values of fiber length obtained from SEM photographs and those measured with MorFi LB-01. Both values were of the same order of magnitude. The differences fall within the interval of (+10 – 33)% of the value obtained from MorFi LB-01. If the action of knives was a critical source of shortening of fibers, then the values of fiber length obtained from the analyzer would be significantly lower.

4. Conclusions

Determination of properties of cellulose fibers can be useful in paper degradation studies. However, essential decrease in arithmetical average length of fibers, correlated linearly with the decrease in cellulose DP values was observed only for paper samples aged for a long time, or under conditions increasing the rate of hydrolysis of cellulose chains. It is proposed that measurements of arithmetical average length of cellulose fibers can be used as an indicator of paper condition in books and printings, because for this kind of measurement only a small piece of paper is needed – as compared with other methods used in conservation practice.
5. References

4. D. Akcetin, L. Verschraege, Relation between the degree of polymerization, the fiber strength, and the breaking elongation, Textilis 1974, 10, 16.