EFFECTS OF DIFFERENT CONSOLIDATION ADDITIVES ON AGEING BEHAVIOUR OF ARCHIVED DOCUMENT PAPER

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Consolidation additives are used in the restoration of old paper documents for partial recovery of the loss of structural strength by natural ageing, as well as for reducing their further deterioration, due to environmetal action. The study evaluates the effectiveness of some unconventional chitosan-based additives, comparatively with conventional consolidation additives based on cellulose ethers. The effectiveness of consolidation additives was investigated by their direct effects on the paper properties, as well as by accelerated thermal ageing behaviour of the consolidated paper samples. The results pointed out that chitosan acetate (CHa) and carboxymethylchitosan (CMCH) lead to a significant improvement of the paper strength properties (especially burst strength) and to the reduction of water absorption capacity, which results in a better preservation of the consolidation effect over time. The investigation of paper surface topography by the AFM technique evidenced better film forming properties and higher efficiency of the chitosan derivatives over time, compared to conventional treatments based on cellulose ethers.

Keywords: chitosan, carboxymethyl chitosan, cellulose ethers, paper restoration, paper ageing

INTRODUCTION

Natural ageing of paper documents from archives and libraries is responsible for a huge loss of documentary cultural heritage. The consequences of using aluminum sulphate as a common additive, respectively, of paper production under acid medium, have been ignored for many years. Today, the researchers' interest is directed towards an urgent and efficient solution to the problems related to the conservation and restoration of documentary heritage. The conservation and restoration of paper documents refer to the series of operations taken to extend their lifetime by protecting them against deteriorating factors, or by repairing the degradation they underwent. The final objective of the restoration-conservation operations is to save the physical and functional integrity of documents.

Most of the studies on restoration-conservation are dedicated to finding the most efficient deacidifying methods, acidity being the main danger for paper supports. However, paper deacidification does not recover the physical-mechanical properties lost by ageing. Therefore, it is imperative to find out better solutions for the consolidation of the deteriorated supports.

Most restorers prefer cellulose ethers, especially the Na salt of carboxymethylcellulose (CMC) and methylcellulose (MC), as consolidation materials. CMC is mostly used in Europe, while MC is favoured by the specialists from the USA. The cellulose derivatives impart good strength properties to the treated paper, but cannot protect it against humidity, as they are hydrophilic substances.[1]

Considering the particularly harmful effects of humidity during the natural ageing of paper, it appears imperative to find a solution that would be efficient from both points of view: in improving the physical-mechanical properties and in reducing the water absorbtion capacity of paper. Our previous studies[1,2] have shown that chitosan (CH) and carboxymethyl-chitosan (CMCH) impart good physical and mechanical properties to the treated paper, similar to those obtained when using cellulose ethers, but higher strength under the action of humidity.

The main purpose of this study has been to assess the effect of conventional additives based on cellulose ethers (CMC, MC), compared to those of unconventional chitosan-based additives (CH, CMCH). The assessment was mainly based on the measurement of the physical-mechanical properties of laboratory-made paper handsheets, both untreated and treated with different consolidation additives, before and after accelerated thermal aging. AFM investigation of the paper surface was used in this work as a tool to observe the differences in the 2D and 3D structures of the coating layer applied during the consolidation treatment.

EXPERIMENTAL

Materials

Paper samples: the consolidation treatment was carried out on paper handsheets obtained on a Rapid-Köthen apparatus, at a standard grammage of 64 ± 1 g/m^2; paperstock composition was a typical one for a modern printing paper manufacture, consisting of a mixture of hardwood and softwood pulps (70/30 w/w), 30% w/w natural calcium carbonate ($CaCO_3$), 1% alkyldimerketene emulsion as sizing agent (AKD) and 1% cationic starch.

Additives for restoration-conservation: cellulose ethers as conventional additives, currently used in restoration-conservation treatments – methyl cellulose (MC) and carboxymethyl cellulose (CMC) – products obtained from Kalle Nalo GmbH Company; unconventional additives – chitosan (CH), received from Vanson, Inc. Company, and carboxymethyl chitosan (CMCH), synthesized in the laboratory by chitosan etherification with monochloroacetic acid, following a patented method.[7]

Methods

Accelerated thermal aging at 105 ºC, for 6 days: initially, the lab paper sheets were subjected to an accelerated ageing treatment, selected to be equivalent to 50 years of natural ageing.[3,4] Through this ageing treatment, the lab paper sheets could be defined as old paper documents.

Accelerated thermal aging at 105 ºC, for 72 h: the effects of the consolidation treatments (with cellulose ethers or with chitosan derivatives) on the ageing behaviour were studied by applying the standard thermal ageing method (ISO 5630-1:1991).

The main steps of the experimental program are presented in Figure 1.

Paper sample analyses

Strength properties: tensile strength, expressed as breaking length, was measured on an Instron apparatus, according to TAPPI T494, and bursting strength was measured according to TAPPI T 403 om-02.

The sizing level of papers was evaluated by water absorption capacity ($Cobb_{60}$, g/m2), according to TAPPI T441 om-90.

Optical properties: opacity and brightness (ISO 2471) were measured on an L&W Elrepho 2000 spectrophotometer; *the yellow content* was calculated according to the formula: [5]

$$Y = [(A - B) / G] \cdot 100$$

where Y – yellow content; A – reflectance with amber filter; B – reflectance obtained with a blue filter; G – reflectance obtained with a green filter.

Paper surface characterization: to obtain additional information on the changes induced by thermal ageing on the paper surface characteristics, the handsheets were investigated by atomic force microscopy (AFM), using a SOLVER PRO M microscope. AFM utilization, a novelty in the research of paper ageing, provides the following information on the paper surface: 2D and 3D images, 2D profile images, data on surface roughness and surface histograms.

RESULTS AND DISCUSSION

Effects of thermal ageing on original handsheets

The changes in paper properties, resulting from thermal accelerated ageing, considered to be equivalent to 50 years of natural ageing, are presented in Table 1. The data show that paper underwent a deterioration process similar to that produced by natural ageing, involving pH decrease, increase of water absorption index, reduction of mechanical strength indexes, significant decrease of brightness and increase of the yellow content. It is worth mentioning that the pH of the aqueous extract did not decrease significantly, which is an effect determined by sizing under alkaline medium and by the high content of calcium carbonate.

Effectiveness of consolidation treatments

The consolidation additives were evaluated by their effectiveness in the restoration of paper in the first stage of ageing (6 days at 105 ºC), and also for preventing further ageing in the second stage (72 h at 105 ºC). The results are presented graphically for the reference sample (without consolidation) and for the samples treated with different additives, before and after the second accelerating ageing stage.

Water absorption capacity ($Cobb_{60}$)

Water absorption increases significantly after thermal ageing for both untreated samples and samples treated with cellulose ethers, the most notable increase being remarked for the CMC treated sample (Fig. 2). On the contrary, the paper samples treated with chitosan derivatives show a decrease of the water absorption index, which supports the hypothesis that the effect is mainly due to the presence of unreacted AKD in the samples treated with chitosan derivatives, being well-known that the AKD sizing reaction is favorized by the thermal treatment. This effect is not present in the CMC treatment, due to the high alkalinity which accelerates AKD hydrolysis.[6]

Tensile strength (breaking length)

The diagrams in Figure 3 show that, in all cases, the thermal treatment determines a slight decrease of breaking length, even if the decrease (below 1%) is not significant for the samples treated with chitosan derivatives.

Burst strength

Burst strength (Fig. 4) shows an important decrease in the cases of unconsolidated samples (about 30%) and a slight reduction for samples consolidated with cellulose ethers (8-15%). However, the chitosan and carboxymethylchitosan coatings appear as more resistant to ageing even if, as in the case of tensile strength, burst strength is not subjected to significant changes.

It may be remarked that the consolidation treatments with chitosan derivatives are efficient in improving the ageing resistance of paper, with respect to paper mechanical strength characteristics. Nevertheless, it should be underlined that the initial support properties – paper sized in a weakly alkaline medium, with a high content of calcium carbonate – assure a higher resistance to thermal ageing and a better efficiency of all consolidation treatments.

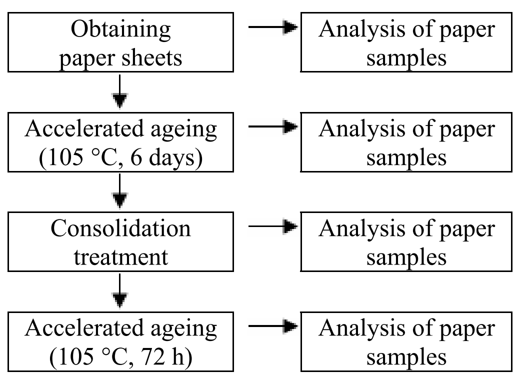

Figure 1: Experimental program for studying efficiency of consolidation treatments over time

Table 1
Paper handsheet properties, before and after accelerated ageing

Paper properties	pH	$Cobb_{60}$, g/m^2	Burst strength, $KPa/m^2/g$	Breaking length, m	Optical properties		
					Brightness, %	Opacity, %	Yellow content, %
Before accelerated ageing	7.96	18	1.44	3925	89	90	1.075
After accelerated ageing	7.81	43	1.41	3620	85	90.2	13.28

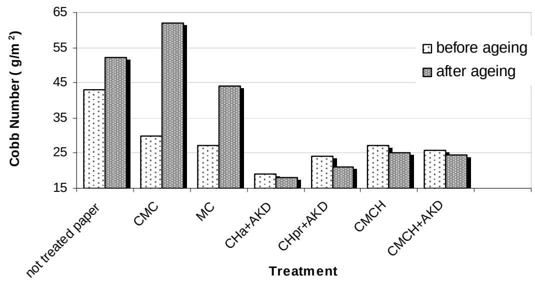

Figure 2: Water absorption index ($Cobb_{60}$), before and after thermal ageing, of untreated paper and of paper treated with various consolidation additives

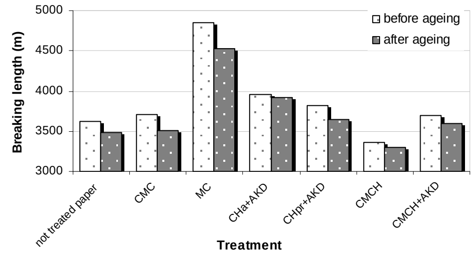

Figure 3: Breaking length, before and after thermal ageing, of untreated paper and of paper treated with various consolidation additives

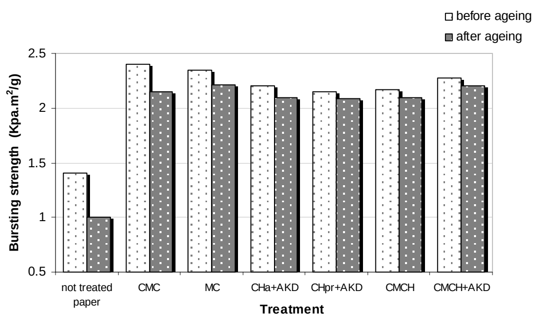

Figure 4: Burst strength, before and after thermal ageing, of untreated paper and of paper treated with various consolidation additives

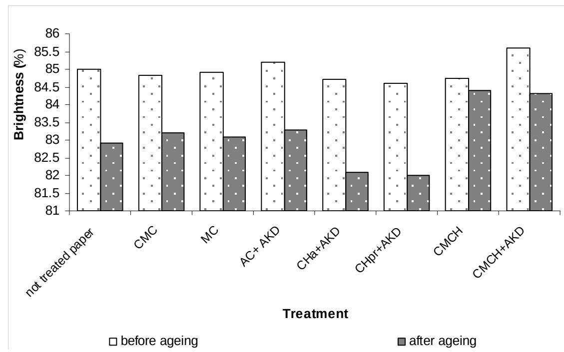

Figure 5: Brightness, before and after thermal ageing, of untreated paper and of paper treated with various consolidation additives

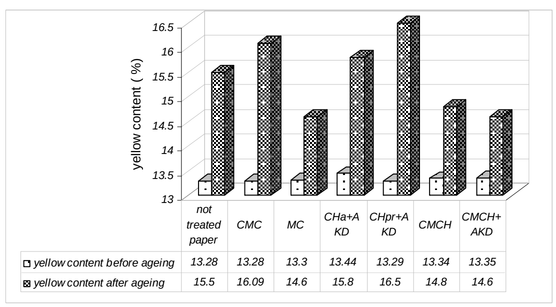

Figure 6: Yellow content, before and after thermal ageing, of paper treated with various materials, compared with untreated paper

Optical properties

A major decrease in brightness (Fig. 5) is observed for all samples, after the thermal treatment. Brightness reduction is more significant for the samples treated with chitosan acetate and chitosan propionate. The effect could be explained by the acid pH of the treatment solution, as well as by the lower brightness of the original chitosan films. Obviously, the yellow content increases (Fig. 6) after thermal ageing, the changes being correlated with the decrease in brightness. The highest stability of the optical properties is achieved by the consolidation with carboxymethyl chitosan.

Characterization of paper surface by Atomic Force Microscopy (AFM)

Figures 7 to 11 present the 2D images and 2D profiles of the paper samples' surface, studied by AFM, after thermal ageing. Both the 2D images and the 2D profiles of the paper surfaces show major differences among the samples under study.

The paper samples treated with CMC are considerably affected by ageing, the surface profile showing high roughness, nearly five times higher than that of the paper treated with chitosan acetate (Fig. 8). The AFM images of the paper samples treated with chitosan acetate show a more uniform surface morphology, indicating a better preservation effect of the consolidation treatment. Therefore, this effect is also supported by the changes in the physical-mechanical properties of these paper samples (Figs. 2-6).

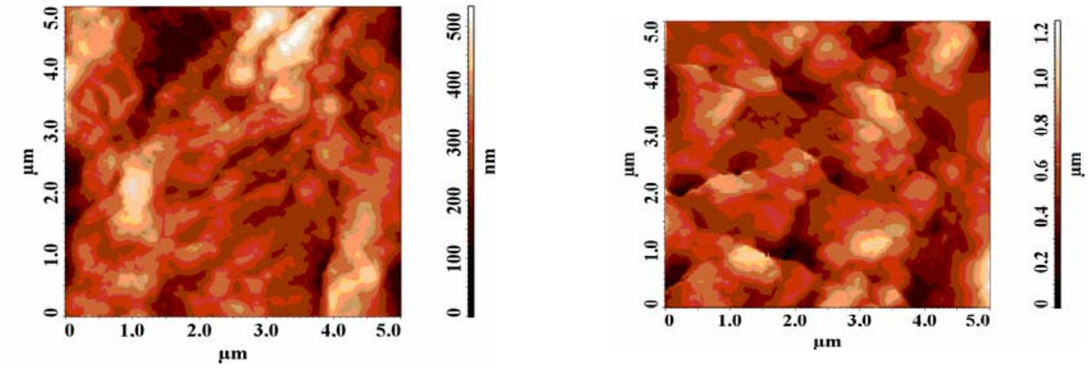

Figure 7: 2D image of the reference sample (left), compared with the CMC-treated paper (right)

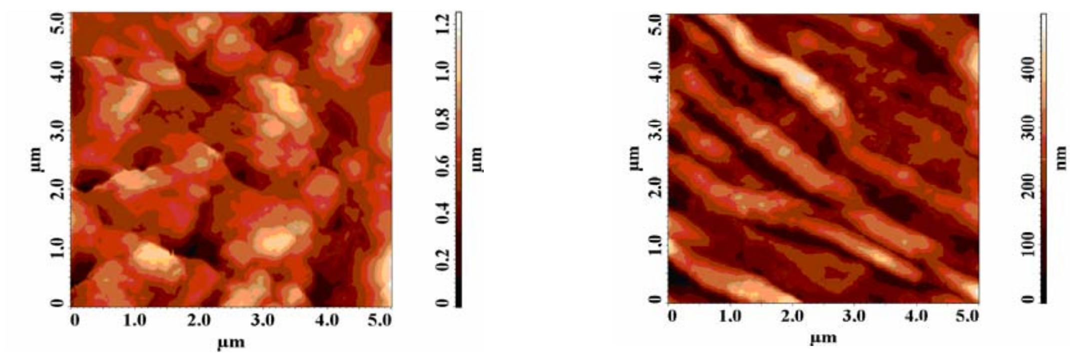

Figure 8: 2D image of the CMC-treated paper (left), compared with the CH-acetate treated paper (right)

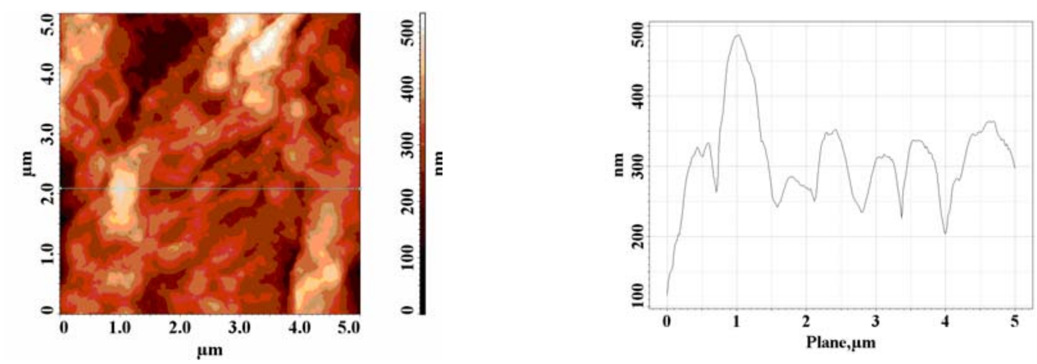

Figure 9: 2D image of the reference sample surface – view of the tested area (left); 2D profile (right)

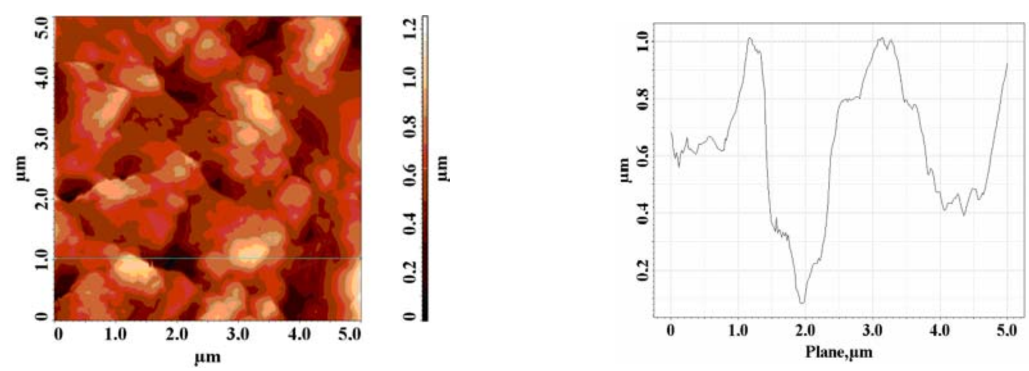

Figure 10: 2D image of the CMC treated paper surface – view of the tested area (left); 2D profile (right)

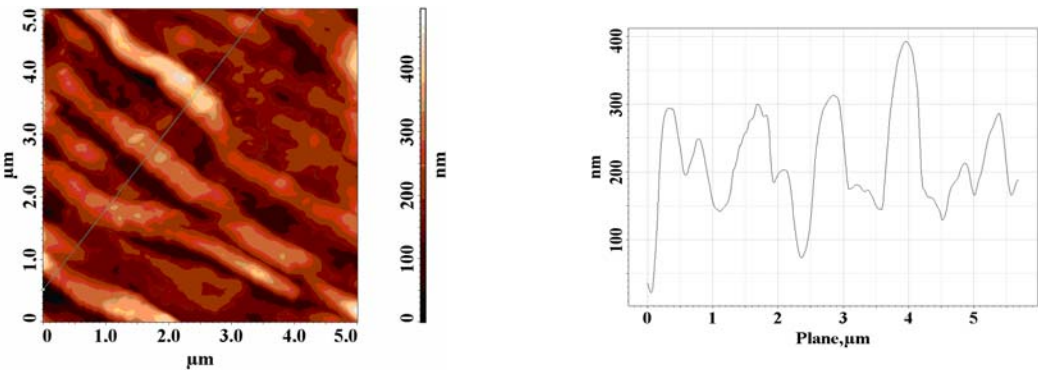

Figure 11: 2D image of the CH-acetate treated paper surface – view of the tested area (left); 2D profile (right)

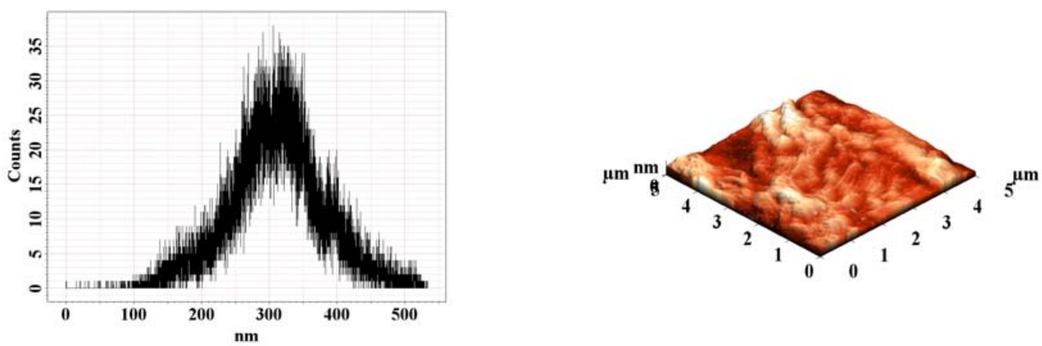

Figure 12: Histogram (left) and 3D image (right) of the reference paper surface (without consolidation)

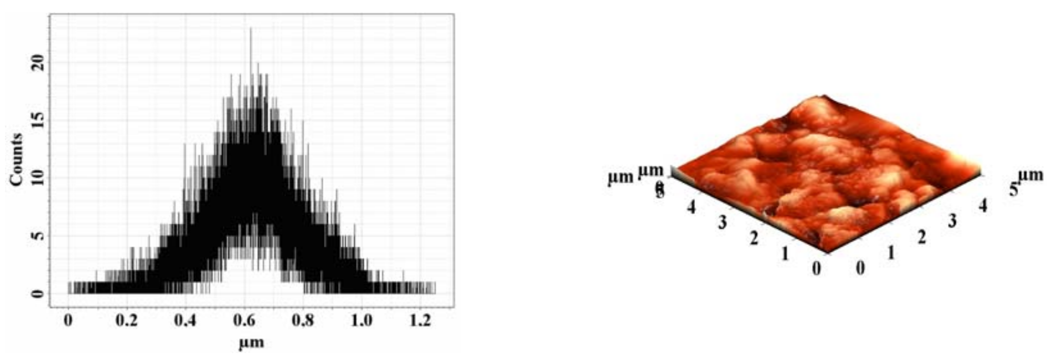

Figure 13: Histogram (left) and 3D image (right) of the paper surface, consolidated by CMC treatment

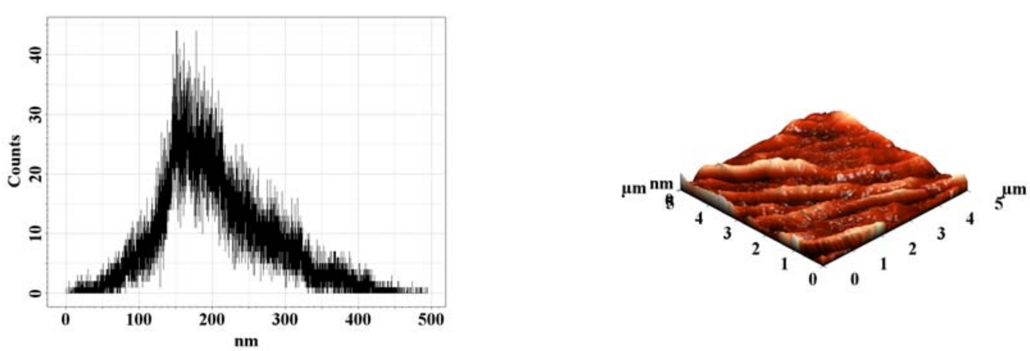

Figure 14: Histogram (left) and 3D image (right) of the paper surface consolidated by CH acetate treatment

The histograms and the 3D images presented in Figures 9 to14 illustrate the structural differences in the surfaces of the paper sheets treated with CMC and chitosan acetate, respectively. Surface roughness, calculated for the studied samples, takes the following values: reference sample – 53.9442 nm, CMC-treated sample – 127.065 nm, and chitosan acetate-treated sample – 57.0709 nm. The roughness values, the histograms and the 3D images prove that the chitosan acetate film, applied as a consolidation treatment, is not only resistant to degradation through thermal treatments, but also that the initial coating was much more uniform, compared to the CMC one.

CONCLUSIONS

The analysis of the changes resulting from accelerated thermal ageing of consolidated and unconsolidated (reference) paper samples led to the following concluding remarks:

- Water absorption capacity ($Cobb_{60}$) increases considerably (up to 106%) for unconsolidated paper samples and for the samples treated with cellulose ethers.
- The chitosan derivatives are more efficient as additives for consolidation treatment, if considering water absorption capacity and the preservation of the mechanical strength of paper after thermal ageing.
- Paper brightness shows an important decrease for all the studied paper samples, the highest decrease being observed for the samples treated with chitosan acetate and propionate. The highest impact of the chitosan derivatives is due to the lower pH of the chitosan solution, compared to that of cellulose ethers.
- AFM investigations evidenced by roughness values, histograms and 3D images of the paper surface prove not only that the chitosan acetate film, applied during the consolidation treatment, is resistant to degradation through thermal treatment, but also that the initial coating is more uniform, compared to that achieved by the CMC treatment.
- The information obtained by these investigations support the conclusions of previous studies regarding the better efficiency of the consolidation treatments with chitosan derivates over time, compared to conventional treatments based on cellulose ethers.
- AFM appears as a promising technique for establishing the degradation level of the paper material and the efficiency of consolidation and deacidifying treatments.

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