CARBOXYMETHYL-CHITOSAN AS CONSOLIDATION AGENT FOR OLD DOCUMENTS ON PAPER SUPPORT

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Abstract

The present investigation discusses some aspects concerning the preparation, characterization and applications of carboxymethyl-chitosan (CMCH) as a consolidation agent in the restoration treatments of paper documents. Several physico-mechanical parameters (Cobb number, bursting strength, tensile strength) were investigated in order to distinguish the best consolidation agent in comparison with traditional and unconventional agents.

Keywords: paper conservation, chitosan, carboxymethyl-chitosan

1. Introduction

Paper is exposed to numerous deterioration processes, which may cause the irreversible degradation of important documents and works of art - the atmosphere humidity is one of these damaging factors.

The preservation and restoration of paper documents comprises the totality of operations necessary to be applied in order to extent the life time, by minimizing chemical and physical deterioration in order to prevent and reverse further damage and deterioration, as well as all the actions attempted in order to achieve the entire renovation of documents, artefacts or physical structures to their original conditions [1].

Consolidation is considered to be an important stage in restoration process of a document or a book and the main goal is to emphasize the resistance of paper support. Nowadays, different cellulose ethers are used in the consolidation treatment process of paper support, sodium chloride of carboxymethylcellulose (CMC) and methylcellulose (MC) are frequently used [2].

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The previous experiments have shown that cellulose derivatives are very efficient in paper consolidation especially by improving the mechanical strength (resistance properties), also by determining the increase of water penetration capacity. It has been proven that chitosan used as a consolidation agent of old paper support is a viable alternative for traditional consolidation agents [3].

The utilization of chitosan in papermaking and paper support consolidation is limited by its insolubility in water. For this reason, it is necessary chemically modified chitosan in order to confer solubility and amphoter characteristic.

The experiment on paper support consolidation presented in this paper was carried out using carboxymethylchitosan prepared by chemical modification of chitosan, which performances as a multifunctional additive used in papermaking have been evaluated previously [4].

2. Experimental

2.1. Materials

The support is a manual paper from the 19th century, without patrimony value, made from textile fibres, the sizing being made with gelatine. The old paper was cleaned with deionised water and deacidified by treatment with calcium hydroxide solution.

The following materials were used for consolidation and sizing:

- *traditional consolidation materials*: methylcellulose (MC) and carboxymethylcellulose (CMC). Their main characteristics are presented in Table 1.
- *unconventional consolidation materials*: chitosan (CH), carboxymethylchitosan (CMCH). This chitosan has used as solution in acetic acid for paper treatment, as well as to obtaining soluble CMCH.

Table 1. The physico-chemical characteristics of the methylcellulose (MC) and carboxymethylcellulose (CMC) and chitosan (CH).

Polymer	Substitution (degree)	Acetylation degree (%)	Molecular weight (g/mol)
MC	1.8	-	377.000
CMC	0.8	-	550.000
CH	-	20.8	415.000

2.2. Methods

Carboxymethyl-chitosan, a water soluble derivative of the chitosan (Figure 1) has been prepared under alkaline conditions using monochloracetic acid, using usual laboratory equipment.

Consolidation treatments were performed by applying with a brush the water solutions of chemicals on both sides of the paper. The total weight of the applied material (dry weight in g per square meter, g/m^2) was measured by weighting the sheets before and after each treatment and dividing the mass of material to sample surface.

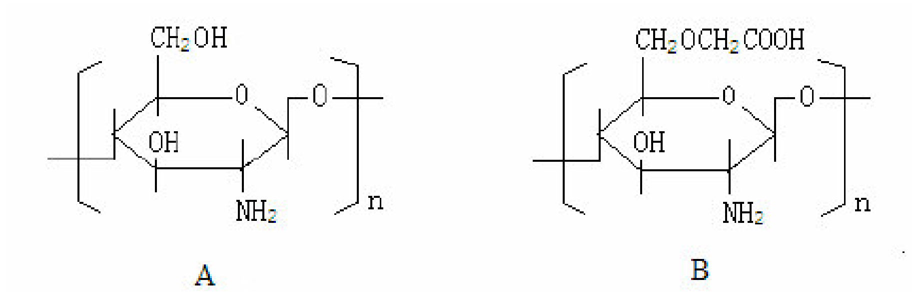


Figure 1. Chemical structure of chitosan (A) and O-carboxymethyl chitosan (B).

2.3. Analyses

Chitosan and Carboxymethyl-chitosan were characterized by:

- FTIR spectra of unmodified chitosan and CMCH samples, recorded in a KBr pellet, using a DIGILAB–EXCALIBUR FTS 2000 spectrometer; the spectra were registered in the range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1}, the scans were repeated 24 times;
- Ionic charge density was measured by colloidal titration with the Mutek PCD-02 apparatus and standard polymers (PDADMAC, NaPVS);
- Substitution degree of CMCH was measuring by adapting the sulphate method that is recommended for carboxymethylcellulose characterization [4].

Old paper samples, before and after different surface treatments were analyzed using:

- Sizing degree by Cobb method Tappi 441;
- Mechanical strength properties were evaluated by burst resistance (Tappi 403) and tensile strength (Tappi 494);
- Morphology of paper surface and in the bulk structure was studied by scanning electron microscopy – SEM (VEGA// Tescan with an accelerating voltage of 30 kV).

3. Results and discussion

3.1. Characterization of no conventional consolidating materials

3.1.1. FTIR spectroscopy

Both unmodified and modified chitosan samples were characterized using FTIR spectroscopy (Figure 2). The modifications observed in the FTIR spectra appear due to the changes of the chemical structure.

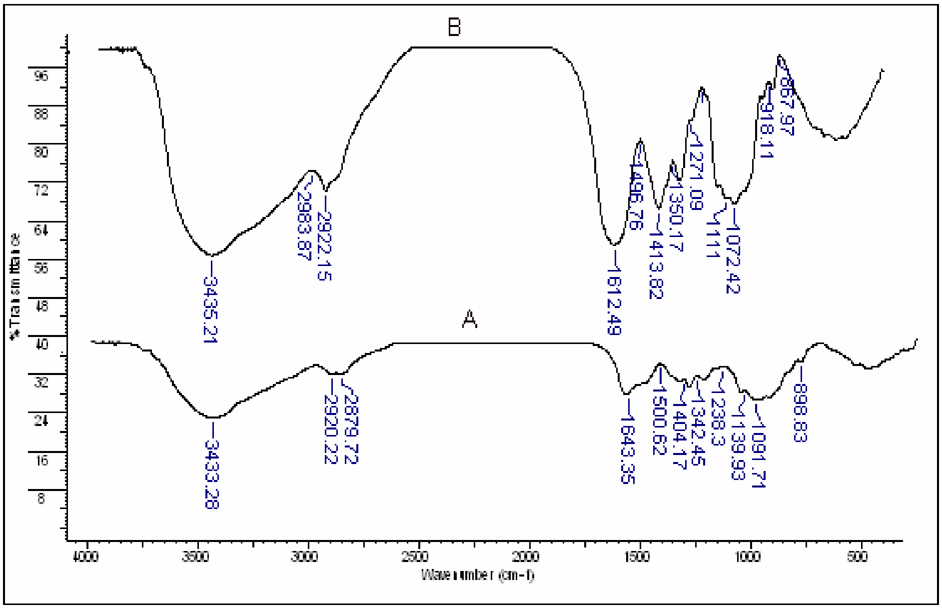


Figure 2. FTIR spectra of chitosan and carboxymethylchitosan.

- CMCH presents a more intensified FTIR adsorption bands in region of 1618 and 1414 cm^{-1} – bands specific for $–COO^-$ group and are according with the scientific results published before for CMCH [5].
- The presence of absorption bands at 3441 cm^{-1} which are specific for $–NH_2$ and –OH groups, as well as the band at 2922 cm^{-1} characteristic for $–CH_2$ group confirms that basic initial chemical structure of CTS (chitosan) was not modified during the synthesis and that $–NH_2$ group substitution is a partial one [6].
- The absorption band specific for –OH group appear at 3441cm^{-1}, at the same time, the absorption maximum specific for $–NH_2$ appear at 3100 cm^{-1}.

3.1.2. Ionic charge density

The electrostatic charge source of carboximethyl-chitosan is expressed by two groups from its chemical structure: carboxyl groups providing anionic charge and amino groups providing cationic charge.

Taking in consideration that the isoelectric point is situated at pH = 5.7, one can conclude that the CMCH numerical ratio for –COOH/-NH2 is over one. The ionic charge evolution during pH variation shows that the obtained polymer has amphoter character (Figure 3).

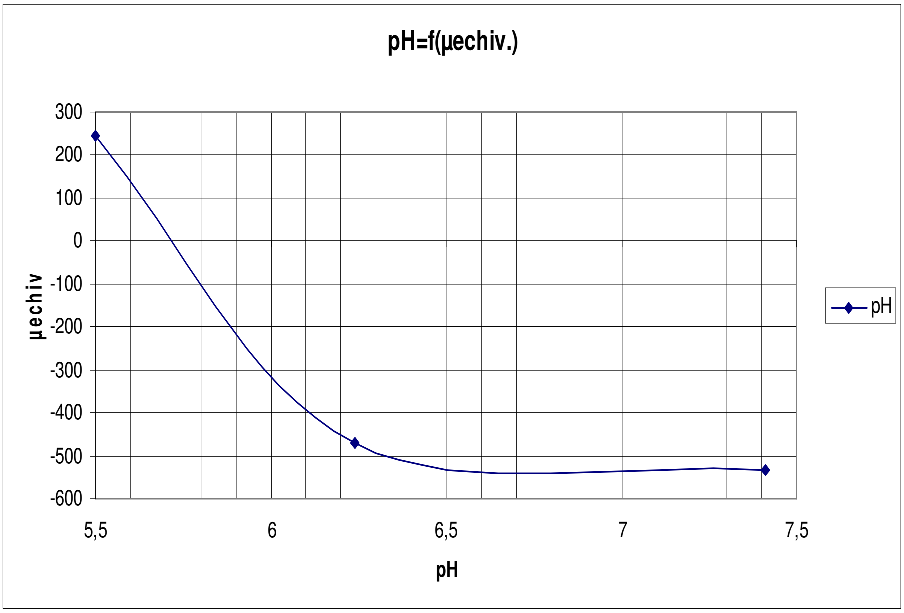


Figure 3. Effect of the pH variation on ionic charge modification.

3.1.3. Substitution degree of CMCH

The substitution degree was identified to be below one: 0.98. The main characteristics of chitosan are: acetilation degree - 20.8%, molecular weight - 415.000g/mol, cationic charge - 4500 µeq/g.

3.2. Physical-mechanical properties of the paper samples

3.2.1. Sizing degree – Cobb number (T441 om-90)

The graphical representation in Figure 4 shows that the treatments with cellulose derivatives, especially with CMS, determine the increase of water suction capacity. The only treatment which lead to the decrease of Cobb number is the one based on AC + AKD + Chitosan mixture.

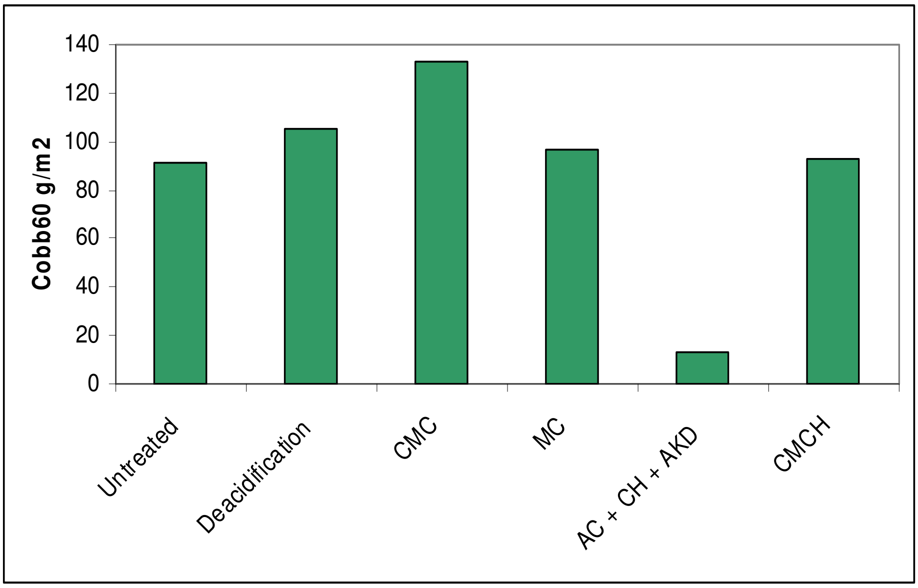


Figure 4. Evolution of Cobb number for treatments with different consolidation agents.

3.2.2. Bursting strength (T403)

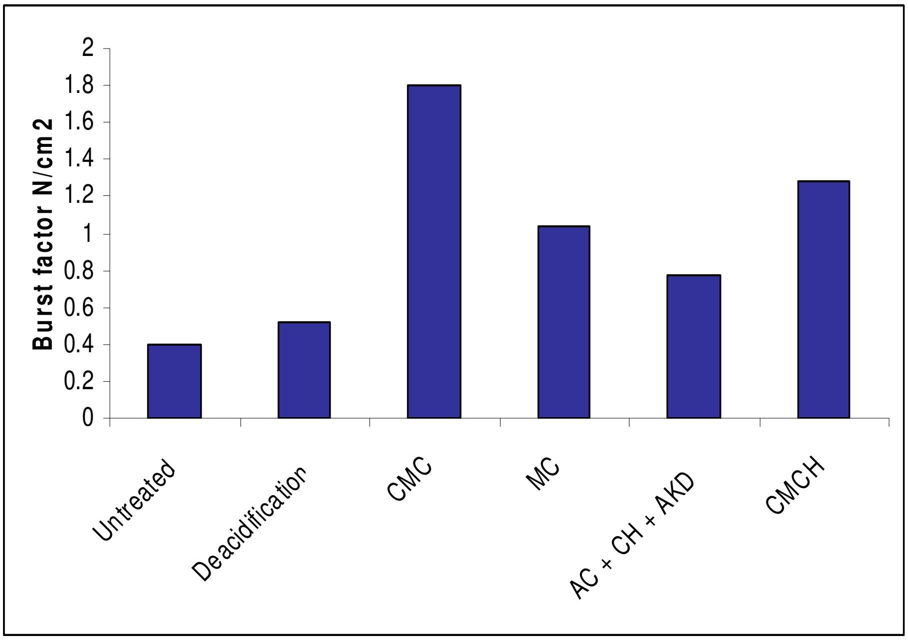


Figure 5. Evolution of bursting strength index for treatments with different consolidation agents.

Analyzing the graphical representation from the Figure 5, one can see that the bursting strength index reach the maximum value in case of CMC treatment. This fact appears due to the increase of paper weight, in this way determining a substantial improvement of bursting strength. The other treatments also have a good consolidation effect; meanwhile, the CMCH treatment offers a satisfactory result.

3.2.3. Tensile strength (T494)

The comparative variation of tensile length is illustrated in Figure 6. Analyzing the case of MC and AC + AKD + CH, several appropriate values can be observed. In the case of CMC treatment, the tensile strength is increased by four times. The second best improve of tensile strength is achieved in the case of CMCH treatment.

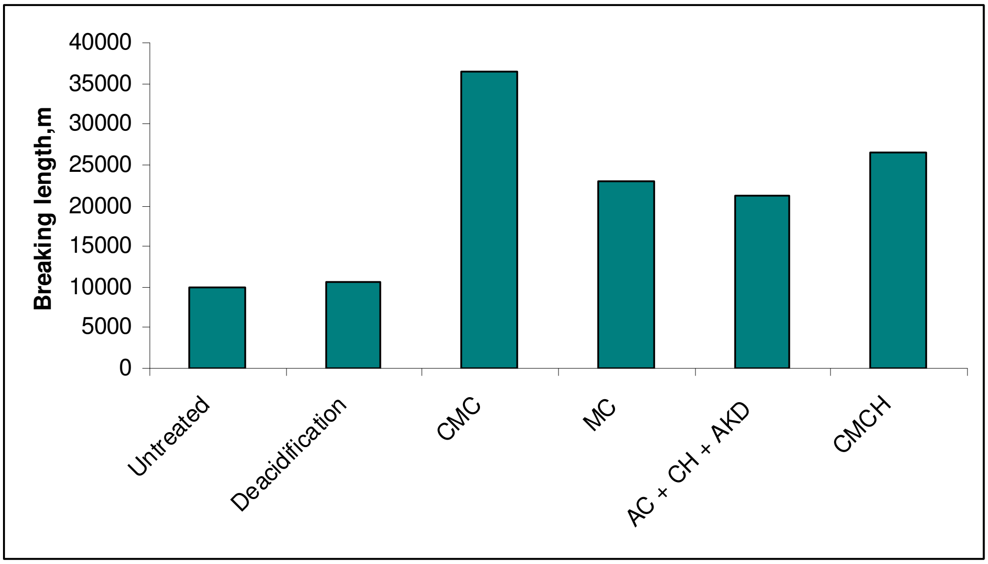


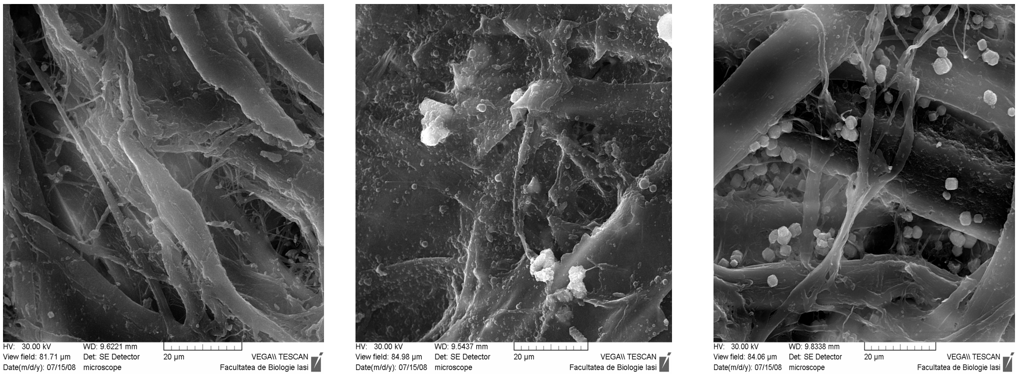
Figure 6. Variation of breaking length (transversal direction) for treatments with different consolidation agents.

Even thought the tensile strength in case of CMCH treatment is not the best one, it is value is very close to the maximum (obtained in case of CMC). In papermaking and in paper utilization as well as in time preservation all physico-mechanical parameters are acting together: the medium value of tensile and bursting strength and are compensated by an appropriate value of Cobb value (the Cobb number is lower then in the case of CMC).

3.3. Scanning electron microscopy of paper samples

The morphological structure was investigated for all consolidation agents on paper material. Figure 7 presents the microphotographs (with an investigated area of 80 μm) of the CMC (Figure 7B) treated and CMCH (Figure 7C) treated papers. Cellulose fibres can be easily seen and between these fibres, several microspheres can be distinguished. The main difference in case of CMC and CMCH agents on paper consist in the size of the aforementioned microspheres: the CMCH microagregates are larger, that is why it seems to be more dense/agglomerated.

The microspheres are fulfilling the interfiber space, in this way this additive is influencing the physico-mechanical properties, determining its improvement.



A B C

Figure 7. SEM images of: untreated (A), CMC treated (B) and CMCH treated (C) paper; (X1800 resolution).

4. Conclusions

Starting with conventional treatments for paper consolidation, which are based on cellulose derivatives, new formulas based on complex combinations between cellulose and sizing synthetic agents can be developed for consolidation of paper based documents.

The unconventional agents, chemically modified or combined with other consolidation agents can lead to the improvement of physico-mechanical characteristics in this way contributing to an efficient paper based documents preservation. The utilization of chitosan, carboxymethyl-chitosan and alkildimercetenes confers real advantages in comparison with traditional techniques.

The best consolidation agents used in this experiment are CMC and CMCH. CMC is conferring physico-mechanic stability; at the same time according to the whole experimental data CMCH is not just improving the tensile and bursting strength but also maintain the same water suction capacity.

Another specific characteristic of CMCH is its antifungal properties [7], its application still needs to be tested in the case of pulp and paper materials.

The whole experiment is considered to fulfil the basic research for the paper based documents. Still, several domains need to be investigated: the compatibility with other paper components and writing and ornamental materials, the reaction in the environmental degradation and during accelerated aging treatment.

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