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ASSESSMENT OF THE EFFECTIVENESS OF PAPER CONSOLIDATION TREATMENTS BY THERMOGRAVIMETRIC ANALYSIS

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Abstract

The article aims to investigate the effect of four compounds which can be used as possible consolidation agents for paper documents. The assessment of the efficiency of paper consolidation treatments using thermogravimetric analysis revealed no significant differences between the specific temperatures of the treated samples and those of the control samples. The paper consolidated by carboxymethyl chitosan (CMCH) behaves almost similarly to carboxymethyl cellulose, which is the most common material in classical consolidation treatments, more precisely in the main stage. The degradation occurs by reactions controlled by three-dimensional interface shifting (the contracting sphere model). The kinetic assessment of thermogravimetric data using the method proposed by Sergey Vyazovkin allowed us to calculate the lives of the samples (the time required for reaching a 50% mass loss when the samples are kept at a specific preservation temperature – T_{iso}). According to the specimen life values that were determined, samples stability decreases as follows: CMC paper > CH paper > CMCH paper > MC paper > control paper.

Keywords: TG, kinetics, consolidation agents, chitosan, paper

1. Introduction

Cultural and religious heritage has a high importance for human civilization, in general, and for each community, in particular [1, 2]. Among all these goods, the written ones seem to be of very high importance if we take into account the quantity and quality of information they transmit over generations. Paper is the most common support used with this aim and the issue of preservation and restoration of the documents is actual and very complex

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because there are many aspects that need to be considered and the optimum actions to be taken are difficult to fully comply with.

When assessing a preservation-restoration treatment, both the immediate and the long-term effects of treatments need to be known. The effects of a procedure are generally considered to be successful if they cause immediate paper properties improvement, i.e. if they increase paper resistance, chemical stability and pH, or if they improve its appearance. The chemical stabilization of paper is assessed by comparing the deterioration rate of the main properties of treated paper with the deterioration rate of the untreated paper properties during the accelerated ageing.

The effect of an unsuccessful restoration attempt consists of immediate paper properties deterioration, loss of resistance, decrease of the polymerization degree, increase of the oxidized groups content, paper ageing acceleration, alteration or destruction of the original structure components and materials in the object and aesthetic degradation.

If, hypothetically speaking, the procedure proves to be neither positive, nor negative, it is considered unjustified and unsuccessful, since it uselessly alters the original state of the object.

Paper life is described by notions of *durability and permanence*. Durability is defined as the ability of the paper to resist to the wear of handling operation. Durability depends on the physical characteristics of the materials that the paper is made of (fibres, filling materials, gluing agents, additives) and on the action of external factors (humidity, temperature, polluting agents, biological agents, etc.). Permanence is defined as the ability of paper to stay inert in time, from both the chemical and physical point of view. Paper permanence depends on the chemical resistance of its components and on the influence of external factors.

Within the preservation-restoration treatments applied to old paper supports, *consolidation* is a frequently used treatment. The purpose of this treatment is to increase support resistance. Document consolidation currently includes two stages:

- the *regluing* stage, when the document is covered by a gluing agent;
- the *actual consolidation* stage, when the document is partially or fully covered by different films or materials.

The consolidation agents used for old document restoration are natural polymers based on polysaccharides and their derivatives or based on polypeptides [3]. The consolidation agents commonly used are aqueous solutions of cellulose ethers (methyl cellulose, carboxymethyl cellulose, etc.). Recent studies have confirmed that consolidation treatments using particular chitosan derivatives increase the durability of treated paper by improving its mechanical properties and increasing its resistance to the action of biological agents [4, 5].

The purpose of our research is the assessment of the effectiveness of consolidation treatments using cellulose ethers and unconventional agents (chitosan and carboxymethyl chitosan), by various methods such as:

thermogravimetric analysis (TG), derivative thermogravimetric analysis (DTG) and differential thermal analysis (DTA).

Differential thermal analysis (DTA) and differential scanning calorimetry (DSC) were used to investigate the thermal decomposition of cellulose and to assess the stability of different document pastes and papers. Dynamic mechanical thermal analysis (DTMA) was also used to study paper ageing. The use of these paper permanence assessment methods seems to have a good potential on evaluating the effect of different preservation procedures [6, 7].

2. Experimental Part

2.1. Materials and methods

64 ± 1 (g/m^2) laboratory-manufactured paper sheets were used for the consolidation treatments. The fibrous composition of the paper sheets was the typical composition used to obtain writing/printing paper, namely a 70/30 (w/w) mixture of bleached hardwood and softwood pulp and an admixture of 30% (w/w) filling material – natural $CaCO_3$. Sheet gluing was done in a neutral environment with alkyl-dimercetene emulsion.

Aqueous solutions of methyl cellulose, carboxymethyl cellulose, carboxymethyl chitosan and chitosan solution in acetic acid were used as consolidation materials.

Chitosan, prepared by alkali deacetylation of chitin, is a polymer of 2-amino-2-deoxy-D-glucose units and 2-acetylamino-2-deoxy-D-glucose units [8].

Carboxymethyl chitosan (CMCTS) was synthesized by the Department of Paper Engineering of the Faculty of Industrial Chemistry, "Gh. Asachi" Technical University. The CMCH obtaining method and its description was based on previous studies [9].

The consolidation treatments were performed using the classical method of brush covering.

2.2. Thermogravimetric analysis

We conducted a research on the thermal stability of a series of paper samples within the 25-700°C temperature range. The paper samples were as follows: control paper, methyl cellulose consolidated paper (MC), carboxylmethyl cellulose consolidated paper (CMC), chitosan consolidated paper (CH) and carboxymethyl chitosan consolidated paper (CMCH). The samples were subjected to thermal and thermodifferential destruction using a TGA/SDTA 851 Mettler Toledo analyzer.

The paper samples, weighing 3-4 mg each, were heated at three different heating rates, namely 5 °C/min, 10 °C/min and 15 °C/min, in an air atmosphere provided by a synthetic air bottle (99.998% purity), up to a temperature of 700°C.

3. Results and discussion

The TG, DTG and DTA curves recorded for the paper samples enabled us to set the main thermogravimetric characteristics: T_i = the initial temperature at which the thermal degradation starts, T_m = the temperature at which the degradation rate reaches its peak, T_f = the temperature at which the degradation process ends in each stage, W% = percent losses in mass during each stage are reported in Table 1.

Figure 1 shows the thermal degradation curves of chitosan (CH) and carboxymethyl chitosan (CMCH).

The analysis of the results shown in Table 1 reveals that the degradation process includes three stages. During the first stage, the water adsorbed by the paper samples is lost, as the process is endothermic. During the following stages, the decomposition is accompanied by the sample oxidation since the process occurs in air. The related thermal effects are obviously exothermal.

The thermogravimetric characteristics in Table 1 show good a thermal stability for both the chitosan consolidated samples (CH) and for those consolidated with carboxymethyl chitosan (CMCH), as thermal decomposition starts at temperatures exceeding 312°C. The obtained results support the literature data according to which the thermal decomposition of chitosan in inert atmosphere starts at 280°C and occurs by its depolymerization until acetamide is formed [10, 11].

As one may note, in the third stage, the thermal decomposition process ends within the 421°C - 471°C temperature range, and is the consequence of the release of volatile hydrocarbons resulting from the thermal decomposition of the cellulosic material components (cellulose, hemicellulose and partially lignin).

The mass losses W% occurring in the first stage are very small (below 2%), they vary between 54% and 63% during the second stage and between 13% and 21% during the third stage.

The specific temperatures do not change considerably in the treated samples as compared to the control samples, and if we consider the mean temperature we may say that the used unconventional additive, i.e. carboxymethyl chitosan (CMCH) is more resistant than unaltered chitosan (CH), and has a very light destabilizing effect as compared to the control sample, which is almost identical to that of carboxymethyl cellulose (CMC).

Thus, at heating rates of 10 K/min and 15 K/min, the specific temperature variation decreased by 5°C for the CMCH treated papers, whereas the same mean decrease was of 24°C in CH treated papers. From this point of view, CMCH behaves almost similar to the most common material used in classical consolidation treatments, i.e. carboxymethyl cellulose (whose specific temperature decreases on the average with 5°C), but has the additional advantage of antimicrobial protection.

Table 1. Thermogravimetric characteristics.

Thermo-gravimetric data	Heating rates (°C/min)	Control paper			MC paper			CMC paper			CH paper			CMCH paper		
		Step 1	Step 2	Step 3	Step 1	Step 2	Step 3	Step 1	Step 2	Step 3	Step 1	Step 2	Step 3	Step 1	Step 2	Step 3
DTA data	5	Endo	Exo	Exo	Endo	Exo	Exo	Endo	Exo	Exo	Endo	Exo	Exo	Endo	Exo	Exo
T_i (°C)			269.9	399.9		281.2	394.1		266.0	377.1		291.5	372.5		266.7	380.0
T_m (°C)			**325**	**433**		**314.8**	**431.8**		**313.8**	**424.7**		**317.6**	**413.5**		**312.5**	**420.8**
T_f (°C)			328.7	443.6		330.0	443.6		334.6	435.2		333.9	420.7		334.5	435.6
W (%)			56.85	16.41		59.12	15.22		54.58	19.28		59.40	16.71		55.42	20.93
DTA data	10	Endo	Exo	Exo	Endo	Exo	Exo	Endo	Exo	Exo	Endo	Exo	Exo	Endo	Exo	Exo
T_i (°C)		40.19	290.9	402.5		280.1	404.1		290.0	391.3		302.8	393.4		271.3	394.5
T_m (°C)		**54.57**	**326.7**	**439.7**		**327.6**	**439.9**		**326.5**	**439.9**		**332.3**	**421.1**		**329.2**	**435.8**
T_f (°C)		102.3	345.2	457.0		344.3	454.2		344.3	455.7		350.0	434.6		344.0	450.9
W (%)		1.92	58.26	15.76		61.12	15.21		54.72	19,05		60.59	14.78		57.18	19.32
DTA data	15	Endo	Exo	Exo	Endo	Exo	Exo	Endo	Exo	Exo	Endo	Exo	Exo	Endo	Exo	Exo
T_i (°C)			289.3	405.4	50.92	292.9	419.4		284.8	405.9		294.2	406.1	44.04	286.8	394.4
T_m (°C)			**334.8**	**445.8**	**61.64**	**337.1**	**454.8**		**329.9**	**440.5**		**339.2**	**416.4**	**61.95**	**331.7**	**439.8**
T_f (°C)			354.3	458.1	95.82	354.2	470.9		349.4	461.9		359.2	436.8	111.9	352.6	458.3
W (%)			57.48	15.50	2.33	62.66	12.62		56.58	19.78		60.30	15.85	1.82	57.12	19.67

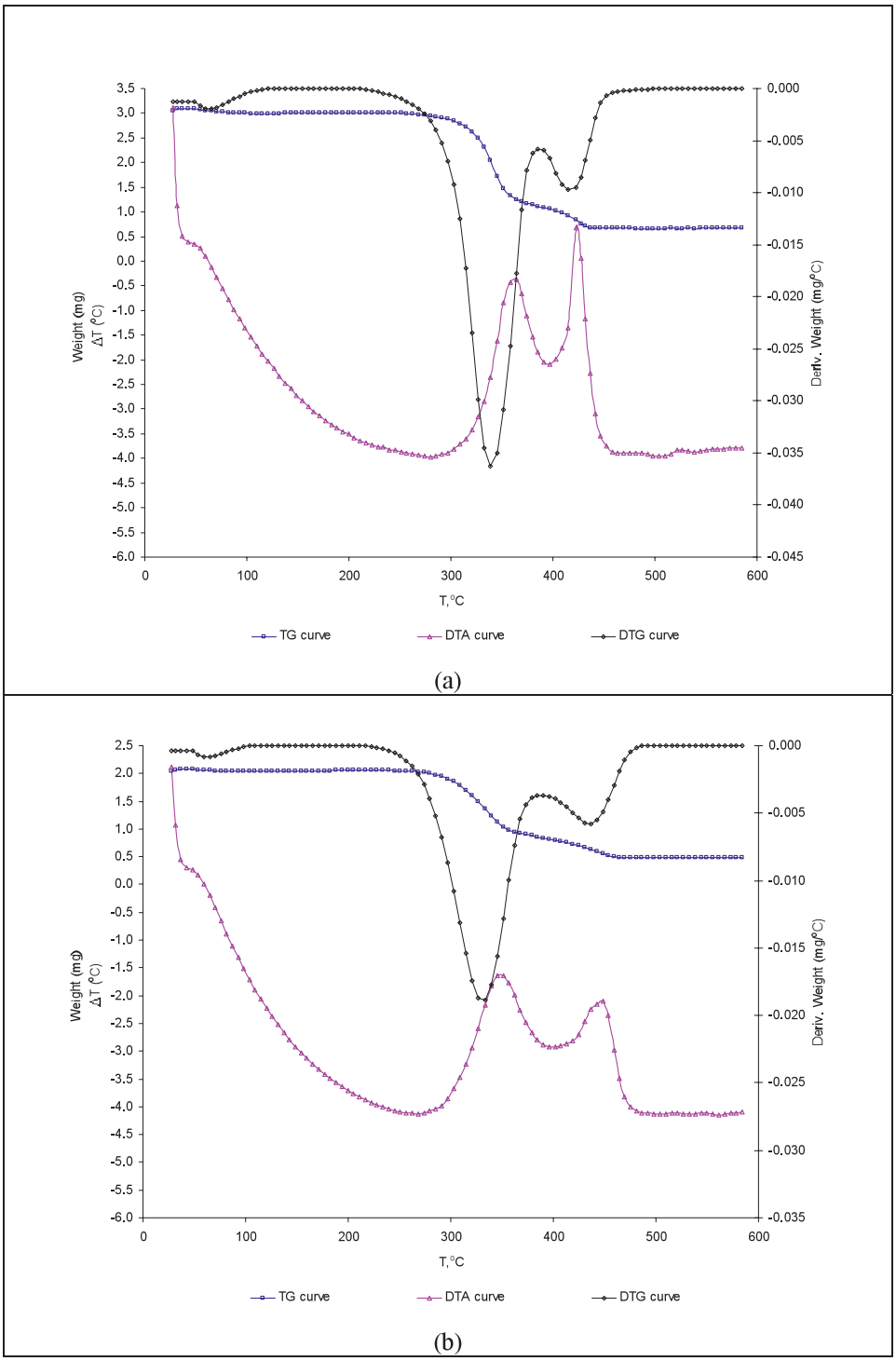

Figure 1. Thermal degradation curves TG (at 15 °C/min) in synthetic air: a) chitosan, b) carboxymethyl chitosan.

The ASTM E-698 standardized method was employed for the highest degradation rate [12]. The activation energy was determined using the following relation:

$$\ln \frac{\beta}{T_m^2} = \ln \frac{AR}{E_a} - \frac{E_a}{R} \cdot \frac{1}{T_m} \quad (1)$$

where β is the heating rate (5, 10 and 15°C/min), R is the gas constant per mole, E_a is the apparent activation energy and A is the pre-exponential factor. Table 2 shows the kinetic parameters, obtained by means of the above method, for the thermal decomposition in air atmosphere.

Table 2. Apparent activation energy values calculated using the ASTM E-698 standardized method for the Control, MC, CH, CMCH and CMC samples (β = 5, 10, 15°C/min).

Sample	Step	n[a]	E_a(kJ/mol)[b]	lnA[c]	r^2 [d]
Control paper	2	1	125.99	20.34	0.975
	3	1	211.63	31.25	0.991
MC	2	1	122.72	19.51	0.994
	3	1	142.45	23.59	0.974
CH	2	1	128.79	20.62	0.936
	3	1	213.22	32.49	0.569
CMCH	2	1	115.30	18.23	0.842
	3	1	150.37	20.10	0.897
CMC	2	1	140.66	23.59	0.979
	3	1	158.33	21.78	0.999

Note: [a] reaction order, [b] apparent activation energy, [c] pre-exponential factor, [d] correlation coefficient

The comparative analysis of the apparent activation energy values specific to the main degradation stage supports the previous thermogravimetric data. We found close activation energy values for the Control, MC and CH samples; values lower with about 10 kJ/mol for the CMCH treated paper and values higher with about 15 kJ/mol in the carboxymethyl cellulose CMC consolidated paper. The apparent activation energy values of the last degradation stage were around 212 kJ/mol for the control and chitosan CH consolidated samples and 150 kJ/mol in the other samples.

For the second stage (the most important one) we also performed the kinetic calculations by means of the method proposed by Sergey Vyazovkin (Kintool V2.5 software - TAOsoft 1993) [13-15]. The dependence of the apparent activation energy and of the pre-exponential factor on the reacted fraction, were calculated. As can be seen from Figure 2 the values of the activation energy ranged in the same domain of values.

The formal models of the decomposition processes giving the best fit with the experimental data were also determined (Table 3).

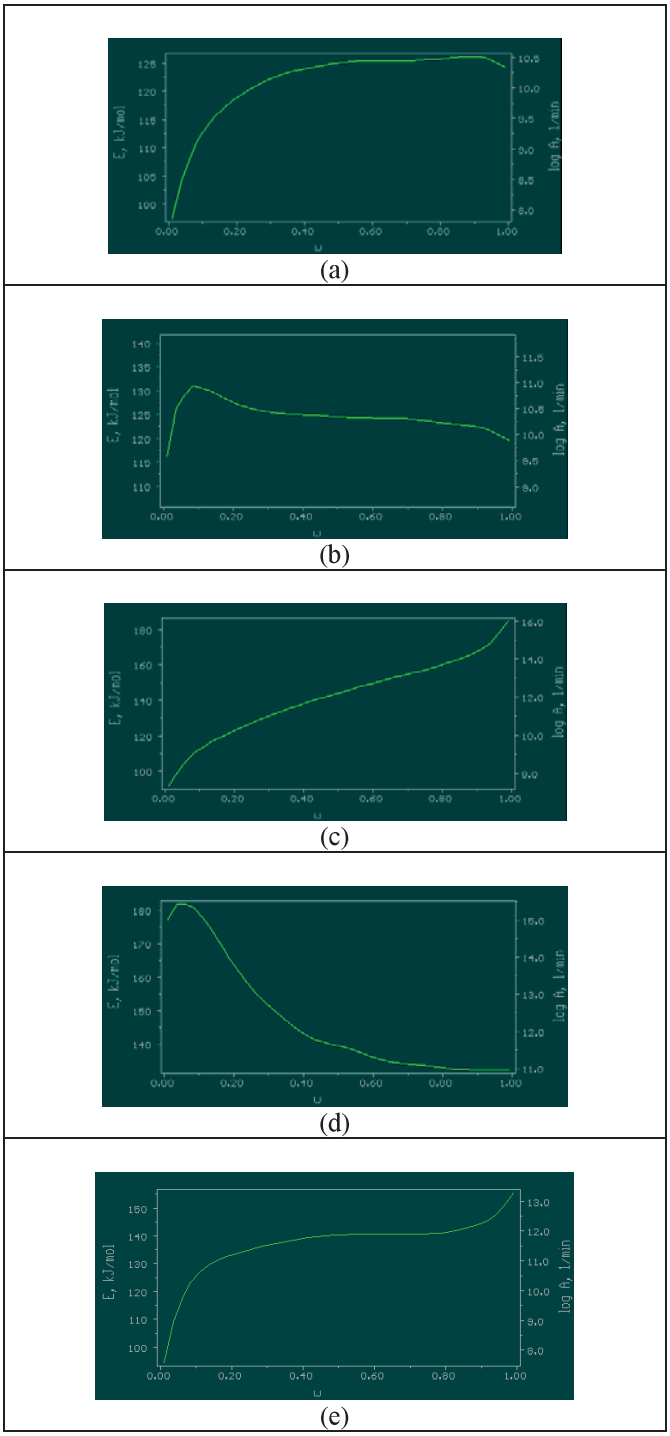

Figure 2. Variation of the apparent activation energy and of the pre-exponential factor vs. the reacted fraction for the second step: (a) control paper, (b) MC paper, (c) CMC paper, (d) CH paper and (e) CMCH paper.

Table 3. Models of the decomposition processes.

Kinetic parameters	Control paper	MC paper	CMC paper	CH paper	CMCH paper
f(α)	$\alpha^{1/2}$ power law	$\alpha^{1/2}$ power law	$3[1-(1-w)^{1/3}]$ contracting sphere	$2[1-(1-\alpha)^{1/2}]$ contracting cylinder	$3[1-(1-w)^{1/3}]$ contracting sphere

The method was also used to predict the behaviour in time of the analysed paper samples (Table 4). Therefore, we calculated the lifetime of the samples as being the time when the mass loss weight reaches 50% at a certain preserving temperature (t_{iso}).

Table 4. Lifetime prediction for the second stage of thermal degradation.

Lifetime prediction (Years)	Control paper	MC paper	CMC paper	CH paper	CMCH paper
t_{iso} (50%) at 17°C	$1.4 \cdot 10^6$	$1.65 \cdot 10^6$	$7 \cdot 10^7$	$5 \cdot 10^7$	$3 \cdot 10^7$
t_{iso} (50%) at 20°C	$8.5 \cdot 10^5$	10^6	$3.8 \cdot 10^7$	$2.5 \cdot 10^7$	$1.75 \cdot 10^7$
t_{iso} (50%) at 23°C	$5 \cdot 10^5$	$6.5 \cdot 10^5$	$2.3 \cdot 10^7$	$1.5 \cdot 10^7$	$1.1 \cdot 10^7$

The obtained values are much larger than expected [7]. It is true that the paper samples were different from our previous study but this can't explain so large differences. On the other hand, they are between the values obtained in nitrogen atmosphere and in air. Taking into account that the TG curves present the third stage (the oxidation) the only reasonable explanation regards the composition of the synthetic air – it seems that it contained less oxygen than normal. However, according to the results the stability order decreases as follows: CMC paper > CH paper > CMCH paper > MC paper > control paper.

4. Conclusions

The assessment of a paper conservation procedure may be seen as a comparative study of the permanence of treated and untreated paper. Therefore, the permanence study methodology may be applied to assess a preservation treatment.

The research revealed that the main thermogravimetric characteristics of the processed samples are not very different from those of the control samples. The paper consolidated by carboxymethyl chitosan (CMCH) behaves almost similarly to the most common material employed in classical consolidation treatments, i.e. carboxymethyl cellulose. Nevertheless, the former has the advantage of the antimicrobial protection it provides [16]. In the main stage, the degradation of these two samples occurs by reactions controlled by three-dimensional interface shifting (the contracting sphere model). The comparative analysis of the apparent activation energy values of the main degradation stage supports the thermogravimetric data. The kinetic assessment of thermogravimetric data using the method proposed by Sergey Vyazovkin allowed us to calculate the lives of the samples (the time required for reaching a

50% mass loss when the samples are kept at a specific preservation temperature – T_{iso}). According to the specimen life values that were determined, samples stability decreases as follows: CMC paper > CH paper > CMCH paper > MC paper > control paper

Thermogravimetric analysis proved to be a useful analysis tool for the assessment of the permanence of papers treated with various consolidation agents.

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