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Evaluation the Effectiveness of CMC and Klucel-E Modified with TiO2 and ZnO Nanoparticles Used for Consolidation the Damaged Paper Maps

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Abstract

The main goal of this work is to study and evaluate the effectiveness of nano titanium dioxide and nano zinc oxide for enhancing the performances of Carboxymethyl cellulose CMC and Klucel-E used as consolidation materials for historical paper maps. Historical map samples dating back to 1817 & 1952 A.D were treated with CMC and Klucel-E loaded with TiO2 nanoparticles and ZnO nanoparticles. Some of the treated samples were submitted to investigation methods and others were submitted to the artificial thermal aging and then to investigation methods to monitor the changes of consolidation materials after accelerated aging test and to evaluate their effect on mechanical, physical and chemical properties of historical paper samples under effect of artificial heat ageing. Visual assessment, pH measurements, Attenuated Total Reflection infrared spectroscopy (FTIR- ATR) study and mechanical properties determination were undertaken, to see if any significant structural or chemical differences could be detected between “untreated”, “treated” and “treated aged” samples. The results showed that no dramatic changes in functional groups on the paper, as monitored by infrared spectroscopy, occurred in the samples before and after treatment; pH values, however, showed that the tested nanocomposites gave good results in decreasing the acidity of the treated paper. The nanocomposites also enhanced optical and mechanical properties of treated samples.

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Keywords: cellulose; nanoparticles; FTIR; artificial; mechanical properties.

1. Introduction

Conservation treatment is performed in order to preserve or restore artifacts. Therefore, only trained conservators who have experience in the appropriate material (such as paper, books art of works on paper, textiles, furniture, photographs, archeological objects, ethnographic objects and natural history specimens) should perform conservation treatments on ancient artifacts. The preservation of cultural heritage to future generations is one of the main duties of humanity. Un-fortunately natural, archaeological, historical and artistic materials are constantly subjected to the action of many detrimental actions due to environmental pollutants, wrong handling practices, natural disasters, accidental damage, or simply to neglect. Thus, in order to ensure the durability of the whole human cultural heritage, any further decay shall be minimized. The natural ageing of paper documents from archives and libraries is responsible for a huge loss of documentary cultural heritage. Furthermore, the oxidative degradation of cellulose is primarily induced by the presence of oxygen, but the presence of water plays an essential role in the hydrolytic degradation of cellulose. The consequences of using aluminum sulphate as a common additive 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 [1-4]. The final objective of the restoration and conservation operations is to save the physical and functional integrity of documents. Most of the studies on restoration and conservation are dedicated to finding the most efficient de-acidifying methods, acidity being the main danger for paper supports. However, paper de-acidification does not recover the physical-mechanical properties lost by ageing [5-7]. Protection of documents is a basic concept of archives conservation. Protection can be achieved in a variety of ways. One important archival protective technique is consolidation of weakened papers. Polymers have been in museums for as long as there have been museums. With the advent of synthetic polymers in the late 19th century, the number and types of polymers found in a museum increased, along with the number and types of associated problems. 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. 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. CMC is a linear polymeric derivative of natural cellulose, made water soluble because of the presence of carboxymethyl groups [8-13]. Also, The Klucel E is very promising in consolidation of wood without negative effects on its properties even after aging. Titanium dioxide nanoparticles (TiO2 –NPs) offer a range of physical and chemical properties that make it suitable for a wide spectrum of applications such as conservation paper art work where some studies reffesed to the role of TiO2 –NPs in the inherent protection of paper works of art to protect them against damaging effect of ultraviolet radiation, pollutant gasses, mold and bacteria [14]. Zinc oxide nanoparticles (ZnO-NPs) are one of the most efficient photocatalyst material, they

were found to versatile and considered to be the new potential next-generation material as self-protection, and biocidal or disinfecting agents [15-17] .The photocatalyst, ZnO, has been used in the degradation and complete mineralization of environmental pollutants [14]. Furthermore, ZnO nanoparticles are able to decompose and mineralize bio-recalcitrant organic pollutants in the form of CO2 and H2O [18]. This study aims to evaluate Carboxymethyl cellulose CMC and Klucel-E emulsion loaded with nano titanium dioxide and nano zinc oxide to possibly introduce a fairly unused method to the conservators' repertoire. It will hopefully aid in the choice of method when confronted with a paper maps object that needs an enforcemen.

2. Experimental

2.1. Sampling

Figure 1: shows the map (A) which was used in this experimental study. Stains, spots and yellowness on the paper surface can be clearly observed in addition to cuts and missing parts.

For this study, two types of maps were acquired, to simplify, the types of maps will be called A, B

Map (A): It is a European paper map dating back to 1817 AD. It has a cardboard wrapping, 22 cm long and 18 cm wide. It represents 40 maps of the world, and 46 pictures of historical cities (see Figure 1). The map was obtained from one of the Az-bakeya library in Al-Ataba, Cairo. It suffers from severe dehydration as a result of exposure to direct sunlight. In addition to the presence of spots and yellowness, especially on the outskirts as well as underlining the pen contains more than three colors in addition to cuts and missing parts.

Map (B): It is an Egyptian African map dating back to 1952 AD, printed by the Department of Surveying and Mines, Giza. It represents a depiction of the natural and human phenomena that appear on the map in terms of the geographical distribution of cities. It was obtained from AlSayeda Aisha area (Friday Market). It is a paper

map with a cloth holder and carton and is 82 cm long and 26 cm wide. It suffers from severe dehydration due to exposure to direct sunlight. Also, it suffers from longitudinal cuts as a result of its frequent straightening, in addition to discoloration and brown spots. It includes more than four different colors (see Figure 2)

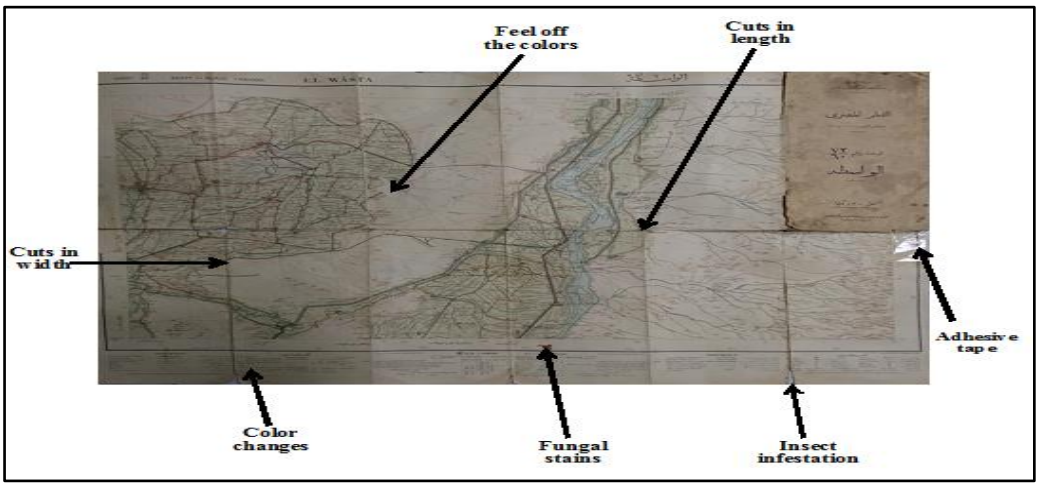


Figure 2: shows the map (B) used in this experimental study. Cuts in both length and width, fungal stains, insect infestation and discoloration can be observed.

2.2. Materials

2.2.1. Preparation of TiO_2 nanoparticles

A 25 ml of titanium isopropoxide (95%, Alfa, Aesar, Germany) is added drop wise at room temperature, to 125 ml of a 0.1 M nitric acid solution under vigorous stirring. A white precipitate is formed instantaneously. Immediately after the hydrolysis, the slurry is heated to 80°C and stirred vigorously for 8 hours in order to achieve the peptization (i.e. destruction of the agglomerates and redispersion into primary particles). Precipitate was obtained by centrifugation. Then, it was dried at 100 °C and calcined at 500°C for 2 hours.

2.2.2. Preparation of zinc oxide nanoparticles

The authors used zinc sulphate heptahydrate (M=287.49 g/mol, Sigma Aldrich), and zinc acetate (M=219.5 g/mol, Merk). Poly Vinyl Alcohol (PVA) (Sigma Aldrich) was used as the surface modificant. Distilled water was used as the solvent to the aqueous solution of zinc sulphate heptahydrate. Sodium hydroxide was added drop wise in a molar ratio of 1:2 under vigorous stirring, and the stirring action is continued for almost 18 hours and large amount of white precipitate was formed. This precipitate was filtered and washed with dis-tilled water and dried using a muffle furnace at a temperature of 100hC. Then it is ground to fine powders and finally the powder obtained was calcined at different temperatures such as 500hC, 700hC, 900hC. Here the particles are calcined at different temperatures in order to obtain just an idea about the relation connecting yield and temperature, as the calcination temperature increases the yield decreases.

2.2.3. Preparation of nanocomposites

Both of CMC and Klucel-E with a weight of 2 g were added to 100 ml of distilled water in four different flasks with stirring for 4 h until complete miscibility. During the stirring, the required amount of TiO2 & ZnO (0.1%, 0.3%) were added to the solution. The mixture was removed, the foam was skimmed off, and the solution was poured on leveled hydrophobic polystyrene petri dishes and dried for 48h at room temperatures to form the desired films. The films were finally removed from the trays (see Figure 3).

Figure 3: shows the Preparation steps of nanocomposites.

2.3. Accelerated heat ageing.

The accelerated ageing experiments were per-formed on experimental maps samples. The ageing method was selected for the purpose of imitating an average deterioration observed for historical maps, at artificial or accelerated ageing methods. The sample is exposed in a climate chamber to extreme conditions in the terms of temperature and humidity for a certain period of time, during which the changes in the material are measured. Artificial ageing tests are often used to determine the permanence of paper, i.e. its rate of degradation, as well as to predict the long-term effect of a conservation treatment. Accelerated ageing regime was used comprising of Heat ageing. The treated and untreated paper samples were artificially thermally aged at 105°C for 7 days [15, 16] in united detector technology (UDT) – USA Model: 268 UVA Optimized/low profile sensor heads serial number: 3B142 traceability: NST-USA.

2.4. Measurements

2.4.1. Strength properties

Tensile strength expressed as breaking length and elongation, were measured according to TAPPI T494 by

using LLOYD LR10K, England, The mean values of tensile strength and stretch were calculated from 5 measurements with a precision in the ± 10% range.

2.4.2. Colorimetric measurements

Color changes induced by protective nanocomposites and samples degradation were evaluated by spectrophotometer Optimatch 3100® from the SDL Company. The dimension of the measured area of each sample equals to (1X1) cm2. The colors are given in CIE Lab coordinates, L* corresponding to the brightness (100 = white, 0 = black), a* to the red–green coordinate (positive sign = red, negative sign = green), and b* to the yellow–blue coordinate (positive sign = yellow, negative sign = blue). The total color difference ΔE* between two color stimuli $\Delta E^* = \{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2\}^{1/2}$ [14].

2.4.3. Fourier transformed infrared spectroscopy

The changes of molecular structure occurring in the treated samples upon aging procedures were monitored by BRUKER'S VERTEX 70 – Attenuated total reflection infrared spectroscopy (ATR -FTIR spectrometer) in the 650 – 4000cm-1 range with resolution of $4cm^{-1}$. The vibrational bands that appear in the infrared spectra provide information about the chemical functional groups of a sample which leads to study the changes in characterization of the materials.

2.4.4. Scanning Electron Microscopy

The microstructure of treated samples and treated aged samples were observed by JEOL JSM-5800 LV Scanning Electron Microscope ISIS-Oxford "high vacuum". This examination was performed to evaluate the distribution and behavior of the consolidation nanocomposites on the treated samples and treated aged samples.

3. Results and discussion

3.1. Mechanical Properties

In order to estimate the effect of consolidation on mechanical properties of paper maps, the tensile properties, which are tensile strength (kN/m) and elongation (%) were measured. Tables (1&2) show the effect of CMC (2%), CMC- TiO_2 nanocomposites, CMC- ZnO nanocomposites, Klucel-E (2%), Klucel-E- TiO_2 nanocomposites and Klucel-E- ZnO nanocomposites on mechanical properties of historical paper maps. The results showed that the breaking length of paper sheet dipped in CMC or Klucel-E solution increases by increasing the concentration of consolidation materials before and after aging, whether by spraying or brushing. This can be attributed to the increase of the inter fiber bonding of the paper sheets [17, 18]. From these mentioned results, it could be seen that treatment with 1% CMC or 1% Klucel-E solution gives maximum mechanical properties. The results in table (1) showed that the treated paper by spraying with 2% CMC loaded with 0.3% TiO_2 –NPs or 0.3% ZnO –NPs were of higher values 170.5 & 185.8 Nm/g respectively.

Table 1: showed the effect of CMC, CMC-TiO_2 nanocomposites, and CMC- ZnO nanocomposites on Tensile strength & Elongation of paper maps samples

Samples		Tensile strength (kN/m)				Elongation (%)			
		By spraying		By brush		by spraying		By brush	
		value	% Change	value	% Change	value	% Change	value	% Change
Control		**12.9**	--	**13.9**	--	**5.3**	--	**5.4**	--
CMC									
0.1% CMC	B. G.*	15.9	23.3	18.6	33.8	5.9	11.3	6.9	27.7
	A. G.**	10.4	-19.4	15.2	9.4	3.3	-37.7	5.9	9.3
0.3% CMC	B. G.	15.9	23.3	19.3	38.8	7.5	41.5	7.5	38.9
	A. G.	13.9	7.8	13.8	-0.7	2.9	-45.3	2.1	-61.1
0.5% CMC	B. G.	17.5	35.7	20.4	46.8	7.6	43.4	6.4	18.5
	A. G.	13.9	7.8	12.3	-11.5	4.8	-9.5	0.9	-83.3
1% CMC	B. G.	18.9	46.5	22.5	61.9	7.9	49.1	7.7	42.6
	A. G.	10.8	-16.3	10.8	-22.3	4.5	-15.0	3.4	-37.0
CMC- TiO_2 nanocomposites									
2% CMC +	A. G.	24.9	93.0	26.7	92.1	6.9	30.2	5.3	-1.9
0.1% TiO_2	B. G.	17.9	38.8	22.3	60.4	4.5	-15.0	3.6	-33.3
2% CMC +	A. G.	34.9	170.5	34.7	149.6	7.2	35.8	4.6	-14.8
0.3% TiO_2	B. G.	13.4	3.9	13.8	-0.7	3.9	-26.4	3.0	-44.4
CMC- ZnO nanocomposites									
2% CMC +	B. G.	28.4	120.2	26.9	108.5	6.9	30.2	5.7	5.6
0.1% ZnO	A. G.	18.5	43.4	12.2	-12.2	3.4	-35.8	4.5	-16.6
2% CMC +	B. G.	36.8	185.8	32.9	136.7	8.9	67.9	7.3	35.2
0.3% ZnO	A. G.	17.9	-82.1	19.5	40.3	1.4	-47.2	3.8	-29.6

B.G.* = before ageing, A.G. ** = after ageing

Table 2: showed the effect of **KLU**-E, **KLU**-E -TiO_2 nanocomposites, and **KLU**-E – ZnO nanocomposites on Tensile strength & Elongation of paper maps samples

Samples		Tensile strength (kN/m)				Elongation (%)			
		By spraying		By brush		by spraying		By brush	
		value	% Change	value	% Change	value	% Change	value	% Change
control		**12.9**	--	**13.9**	--	**5.3**	--	**5.4**	--
KLU-E									
0.1% KLU-E	B. G.	12.2	-5.4	12.4	-10.8	5.5	3.8	5.7	5.6
	A. G.	9.6	-25.6	11.2	-19.4	4.8	-9.4	4.8	-9.4
0.3% KLU-E	B. G.	14.5	12.4	14.6	5.0	6.3	18.9	6.8	25.9
	A. G.	13.6	5.4	7.8	-43.9	3.5	-37.7	2.0	-62.9
0.5% KLU-E	B. G.	16.5	27.9	16.7	20.1	3.8	-28.3	5.7	5.6
	A. G.	14.3	10.9	14.3	2.9	3.3	-37.3	4.8	-11.9
1% KLU-E	B. G.	17.2	33.3	17.9	28.8	7.8	47.2	7.9	46.3
	A. G.	15.6	20.9	14.6	5.0	4.5	-15.0	9.2	-49.2
KLU-E - TiO_2 nanocomposites									
2% KLU-E +	A. G.	20.8	61.2	18.2	30.9	7.5	41.5	5.7	5.6
0.1 % TiO_2	B. G.	19.9	54.3	10.5	-24.5	4.8	-9.4	4.7	-12.9
2% KLU-E +	A. G.	28.9	124.0	28.9	107.9	6.7	26.4	7.5	38.9
0.3% TiO_2	B. G.	25.5	97.7	18.9	36.0	4.9	-7.5	4.7	-12.9
KLU-E - ZnO nanocomposites									
2% KLU-E +	B. G.	22.8	76.7	22.8	64.0	6.8	28.3	5.9	9.3
0.1% ZnO	A. G.	12.6	-2.3	16.4	18.0	4.3	-18.8	4.8	-3.9
2% KLU-E +	B. G.	28.3	119.4	29.8	114.4	6.8	28.3	5.5	1.9
0.3% ZnO	A. G.	15.2	17.8	16.9	21.6	3.3	-37.7	4.8	-11.9

After ageing, the results showed that the highest increase in tensile strength (kN/m) and elongation (%) were for the treated samples with 2% CMC loaded with 0.1% TiO_2 –NPs by brush method. In the same context the results obtained after ageing showed that, the higher value was obtained from treated papers with 2% CMC loaded with 0.1% ZnO –NPs by spraying. It was found in table (2) that adding 0.3% TiO_2 –NPs or 0.3% ZnO –NPs to 2% Klucel-E solution gave the highest increase in tensile strength and elongation % before and after ageing when these solutions were applied by spraying.

3.2. Color change

Colorimetric test was used first for the determination of the natural paper color parameters. The following step was the investigation of the color changes induced by the treatment of the paper with the tested emulsions. Finally, this technique was used for the assessment of the treated color changes that intervened during the artificial accelerated aging tests. Based on color parameters measurements, the total color change ΔE values were calculated. These values indicate the registered color differences between the natural and the treated or treated/aged paper samples. The color changes that might intervene following the treatment of paper with chemical products have to be reduced to a maximum extend in order to alter as little as possible as compared to the untreated samples. According to lictures, the ΔE value must be < 5[6].

Table 3: showed ΔE and Lab values of treated samples by CMC and CMC - ZnO and TiO_2 nanocomposites before and after thermal ageing

Samples	Application method	Δb^*	Δa^*	Δl^*	ΔE^*	Observations
1% CMC						
B.G.	brush	0.28	-1.99	-5.63	5.98	Perceptible difference in ΔE was obtained between untreated, treated and treated aged samples.
A.G.		2.17	1.29	-3.75	4.52	
B.G.	spraying	6.63	2.49	-3.07	7.72	
A.G.		4.64	0.14	-4.24	6.29	
2% CMC + 0.1% TiO_2						
B.G.	brush	-0.75	-0.15	-1.85	2.00	ΔE < 5, i.e., acceptable changes were obtained between untreated and treated samples. After ageing slight changes resulted and the surface tended to be more darkened.
A.G.		0.27	0.04	-6.37	6.38	
B.G.	spraying	3.80	1.35	1.93	4.47	
A.G.		6.10	2.85	-0.62	6.76	
2% CMC + 0.1% ZnO						
B.G.	brush	-1.35	-2.82	-10.75	11.20	Observable color change was obtained in case of brush treatment. This difference decreased after thermal ageing. On the other hand, opposite results were obtained in case of spraying treatment.
A.G.		2.36	1.30	-4.20	4.99	
B.G.	spraying	3.90	1.67	1.75	4.59	
A.G.		6.91	3.67	-3.12	8.42	
2% CMC + 0.3% TiO_2						
B.G.	brush	-0.97	-0.30	-0.26	1.05	Good results were obtained when the map surfaces were treated with 2% CMC+ 0.3% TiO_2 nanoparticles or + 0.3% ZnO nanoparticles using brush and spraying methods where there were no noticeable changes in the color before and after thermal ageing.
A.G.		1.85	-0.25	-10.50	2.66	
B.G.	spraying	3.44	-0.85	-5.65	2.67	
A.G.		5.32	1.76	2.53	2.53	
2% CMC + 0.3% ZnO						
B.G.	brush	1.18	-1.23	-2.59	1.10	
A.G.		-0.63	-1.57	-1.57	2.52	
B.G.	spraying	4.54	-0.64	-4.22	1.23	
A.G.		6.88	2.64	1.07	2.45	

According to sham and his colleagues 2004 [19, 20], ΔE scale in stone materials conservation is as follow: • $\Delta E < 0.2$: not perceptible difference• $0.2 < \Delta E < 0.5$: very small difference• $0.5 < \Delta E < 2$: small difference• $2 < \Delta E < 3$: fairly perceptible difference• $3 < \Delta E < 6$: perceptible difference• $6 < \Delta E < 12$: strong difference• $\Delta E > 12$: different colours. Color change such as ΔE and Lab values of treated samples by CMC and CMC - ZnO and TiO_2 nano composities before and after thermal ageing are presented in Table 3. ΔL values proved that when the surfaces of these maps were moistened with 1% CMC using brush and spray methods they darkened, but after aging, the darkness of the surfaces decreased especially in case of using brush method. **ΔE** values ranged between 4.52 and 7.72 so, slight difference in total color change was obtained between untreated, treated and treated aged samples. On the other hand, the best results were obtained when the surface of the map was treated with CMC+ 0.3% TiO_2 – nanoparticles or + 0.3% ZnO nanoparticles using brush and spraying methods before and after thermal ageing. Results in table 4 showed that paper samples treated with KLU- E + 0.3% ZnO nanocomposites before and after aging have acceptable ΔE values where it ranges between 2.68 and 3.30 for treated samples by spraying. Other treated samples with KLU-E and KLU-E-TiO_2 are not fitting in these limits i.e., treated samples with KLU-E have ΔE values between 6.04 and 8.75 depending on application methods. These values indicate that CMC induced chromatic variations resulting from its thermal oxidative decomposition.

The results in Tables 3& 4 showed that color variations of paper samples treated with KLU- E loaded by nanoparticles decreased after the thermal aging where ΔE values were 5.14, 6.90 and 3.30 for treated samples with KLU- E loaded by 0.1% ZnO ,0.3% TiO_2 and 0.3% ZnO respectively and fitted the acceptable ΔE values. On contrary, consolidation of samples with CMC + 0.1% ZnO produced different colors where ΔE became 11.20 after thermal aging.

Table 4: showed ΔE and Lab values of treated samples by CMC and CMC - ZnO and TiO_2 nanocomposites before and after thermal ageing

Samples	Application method	Δb^*	Δa^*	Δl^*	ΔE^*	Observations
1% KLU-E						
B.G.	brush	-1.43	0.03	-3.59	3.86	
A.G.		-2.80	-1.54	-5.13	6.04	ΔE values ranged from 3.86 to 8.75 indicating the presence of perceptible difference in color between untreated, treated and treated aged samples. ΔL values proved that all maps samples darkened when treated using brush and spray methods but after aging, the darkness decreased in case of using brush method and increased using spraying method.
B.G.	spraying	-1.15	0.60	-8.65	8.75	
A.G.		3.67	0.89	-6.57	7.58	
2% KLU-E + 0.1% ZnO						
B.G.	brush	-4.06	-2.58	-6.56	8.13	
A.G.		0.54	-2.47	-6.66	7.12	
B.G.	spraying	2.16	0.79	-6.04	6.46	
A.G.		5.03	0.42	-0.98	5.14	
2% KLU-E + 0.3% TiO_2						
B.G.	brush	-2.75	-10.43	-5.09	5.96	
A.G.		-2.18	-0.04	-12.16	6.35	
B.G.	spraying	0.56	-1.10	-8.42	8.51	
A.G.		-1.78	4.09	-5.27	6.90	
2% KLU-E + 0.3% ZnO						
B.G.	brush	-3.41	-1.03	-1.81	4.00	The best results were obtained when the map samples were treated with 2% KLU-E + 0.3% ZnO.
A.G.		-4.37	-1.54	-12.23	3.08	
B.G.	spraying	2.32	-1.13	-0.74	2.68	
A.G.		3.44	2.63	-8.23	3.30	

3.3. FTIR

The infrared spectra of the treated samples with CMC& KLU-E before and after thermal aging showed that the stability of these consolidants didn't depend on the application method. No remarkable changes were shown between treated samples by brush or spraying. Figures 4 and 5 show the IR spectra of the untreated, treated and aged treated paper maps. It is evident that all spectra have similar peaks such as a wide band at ≈ 3451cm^{-1} which is corresponding to bonded O-H stretching band of cellulose. The presence of short peaks around 2900 cm^{-1} are due C-H stretching of aliphatic group. Band corresponding to Water deformation plus C=O conjugated stretching of some oxidized cellulose appears around 1640 cm^{-1}. The characteristic vibration bond at 1156 cm^{-1} can be assigned to C-O-C vibration of ether groups. Vibrational mode peak at 1026 cm^{-1} can be assigned to the C-O stretching bond vibration. In the spectra of treated paper, the intensity and broadness of O-H stretching band of cellulose increases due to the presence of hydroxyl groups in the structure of the treated materials [20-24]. After ageing, no major changes in the treated paper samples are observed, except a slight decrease in the broadening of O-H stretching band confirming the breakdown some of the hydrogen bonds in addition to slight increase in the broadening and intensity of the band around 1640 cm^{-1} resulting from partial oxidation of various C-OH groups in glucopyranose rings of cellulose to C=O groups. Many researchers reported the thermal oxidation process of hydroxyl groups of cellulose molecules to the carbonyl and carboxyl groups [25-30]. More carbonyl groups may be formed as a result of further oxidation of C□OH groups of cellulose and there has been the removal of the association CH stretching [31-32].

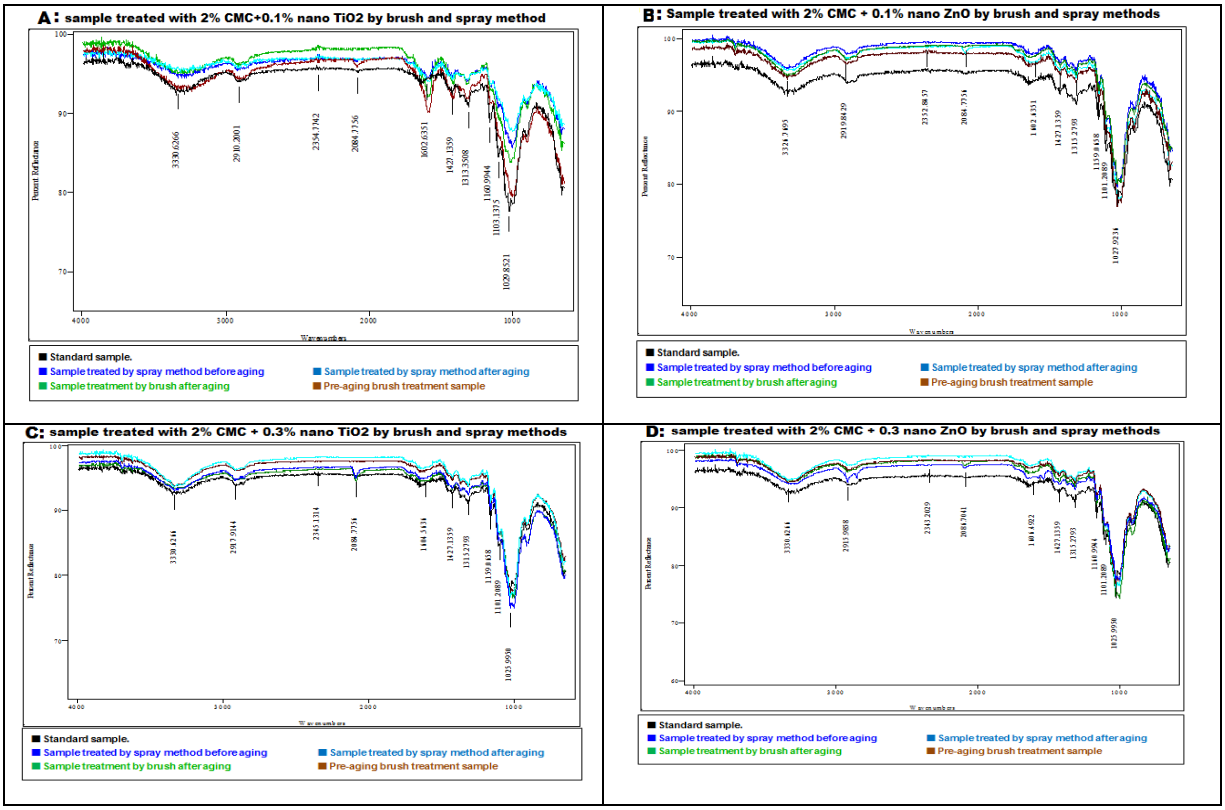


Figure 4 (A—D): FTIR spectra of treated paper map samples with 2% CMC + TiO_2 or + ZnO nanoparticles applied by brush and spraying method before and after ageing

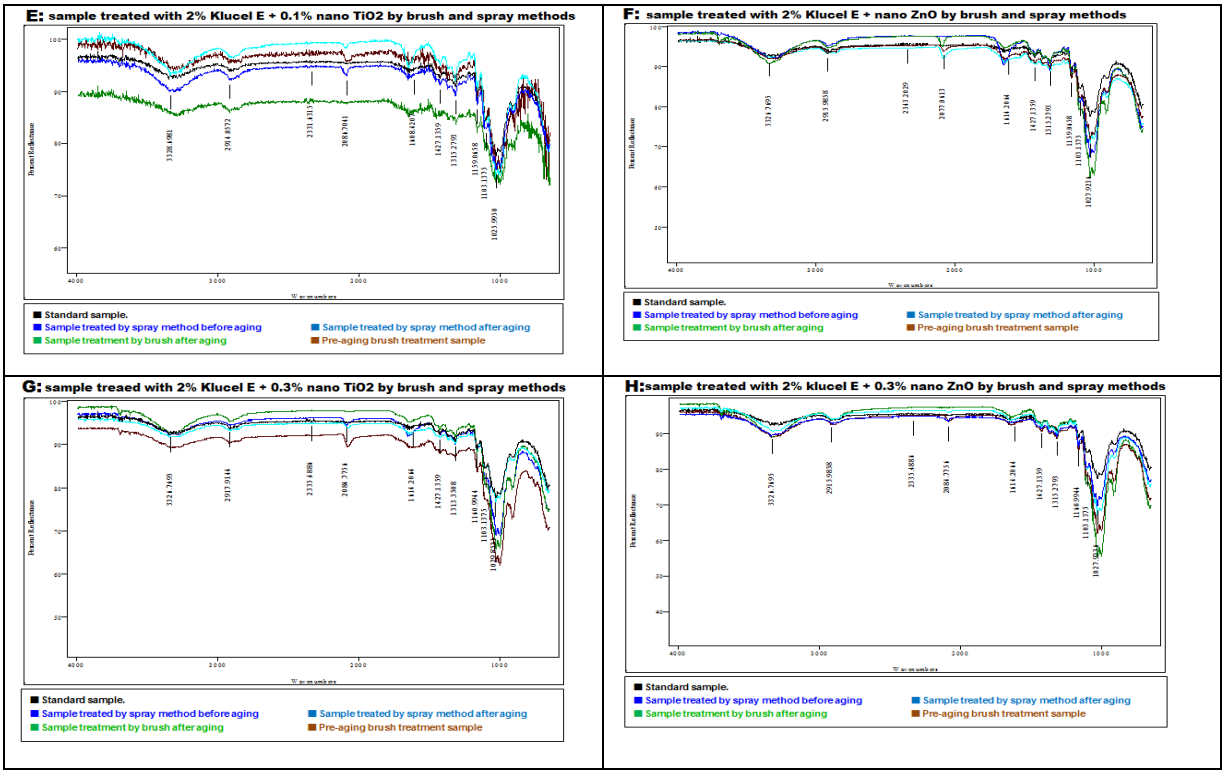


Figure 5 (E—H): FTIR spectra of treated paper map samples with 2% Klucel E +TiO_2 or + ZnO nanoparticles applied by brush and spraying method before and after ageing

3.4. SEM

From SEM photomicrographs (see figures 6 & 7), it is clear that the untreated fibers are completely separated from each other, whereas in case of polymer treated samples, full fibers can be noticed which may be due to the formation of the fiber bundles between cellulose fibers and polymer matrix. These fiber bundles increased by increasing the polymer concentration. Also, some aggregates of the polymer can be noticed on treated samples which is a good evidence for the success of the polymer treatment process. Furthermore, SEM images, reported in Figure 6, clearly show that the nanocomposite treatment is homogenously distributed over the samples surfaces. The adhesion of small clusters of ZnO & TiO_2 nanoparticles to cellulose fibers is clearly seen. The distribution of Klucel E plus ZnO or TiO_2 nanoparticles on map surfaces was assessed with SEM (Figure 7): white spots due to the presence of ZnO and TiO_2 nanoparticles are homogenously distributed over the surface. The comparison between maps acquired on treated and untreated samples clearly shows that the presence of ZnO or TiO_2 is mainly ascribed to the applied treatment. It is worth noting that the spray method does not limit the spreading of particles over the surface. For the micrograph related to the samples treated with the polymers and after aging thermally, it can be observed, that the cotton surface showed smooth fibers, soft grain and the fibers interfered with each other.

Untreated sample

2% CMC plus 0.1% TiO_2

2% CMC plus 0.1% ZnO

2% CMC plus 0.3% TiO_2

2% CMC plus 0.3% ZnO

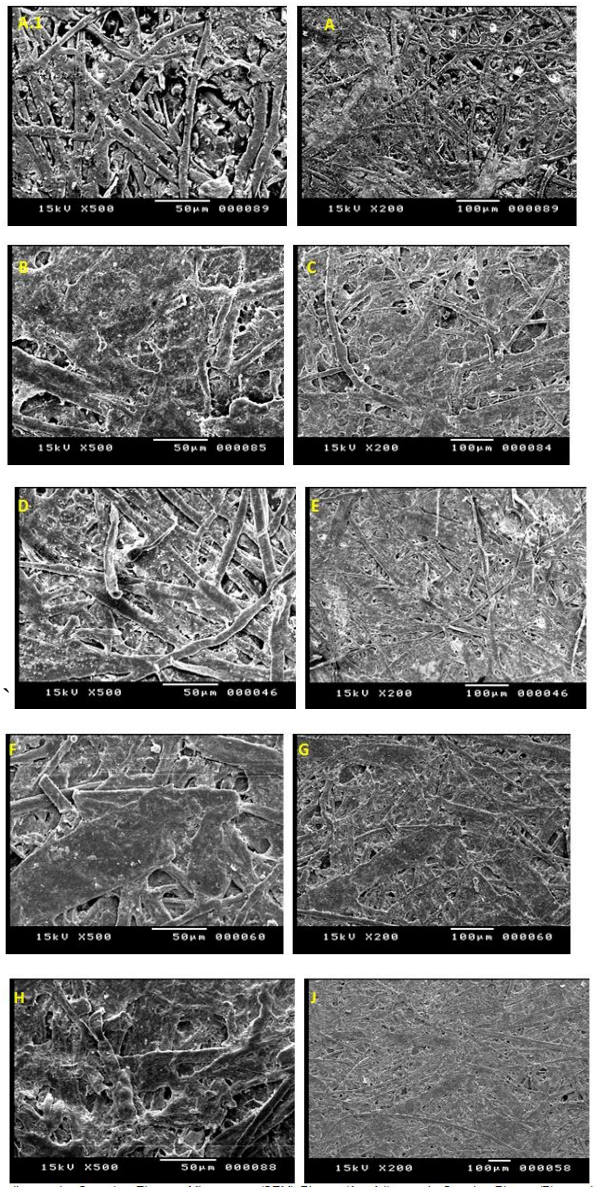
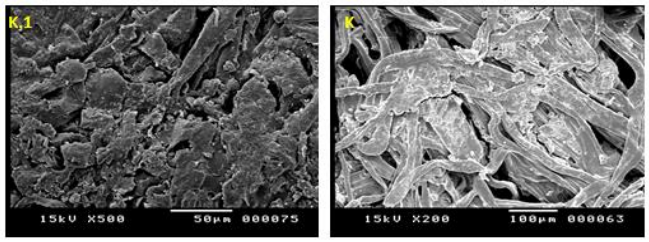
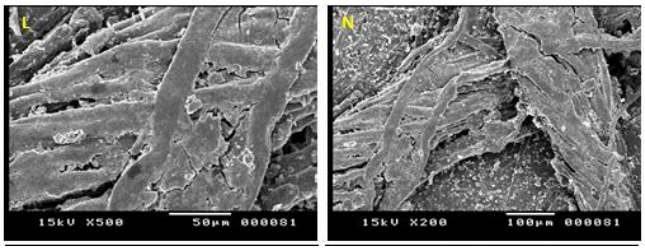


Figure 6: SEM photomicrographs of the treated map samples: A&A_1 SEM photomicrographs (200X & 500X) of untreated sample; **B.** SEM photomicrograph (500 X) of sample treated with 2% CMC plus 0.1% TiO_2 nanoparticles after aging; **C.** SEM photomicrograph (200 X) of sample treated with 2% CMC plus 0.1% TiO_2 nanoparticles before aging; **D.** SEM photomicrograph (500 X) of sample treated with 2% CMC plus 0.1% ZnO nanoparticles after aging; **E.** SEM photomicrograph (200 X) of sample treated with 2% CMC plus 0.1% ZnO nanoparticles before aging; **F.** SEM photomicrograph (500 X) of sample treated with 2% CMC plus 0.3% TiO_2 nanoparticles after aging; **G.** SEM photomicrograph (200 X) of sample treated with 2% CMC plus 0.3% TiO_2 nanoparticles before aging; **H.** SEM photomicrograph (500 X) of sample treated with 2% CMC plus 0.3% ZnO nanoparticles after aging; **J.** SEM photomicrograph (200 X) of sample treated with 2% CMC plus 0.3% ZnO nanoparticles before aging

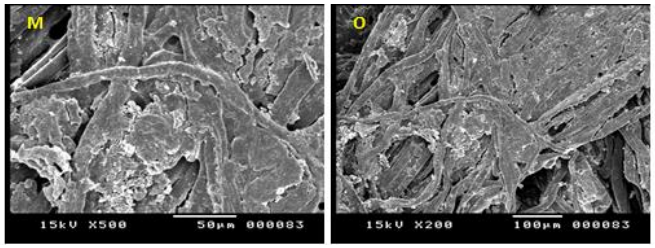
Untreated sample



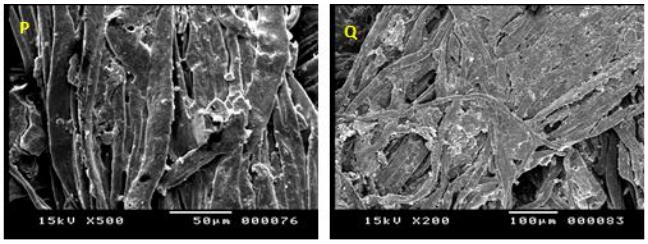
2% Klucel E 0.1% TiO2



with 2% Klucel E 0.1%



2 % Klucel E 0.3% TiO2



2 % Klucel E 0.3% ZnO

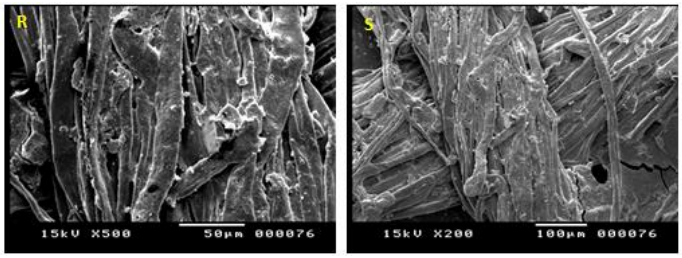


Figure 7: SEM photomicrographs of the treated map samples: K&K_1. SEM photomicrographs (200X & 500X) of untreated sample; **L.** SEM photomicrograph (500 X) of sample treated with 2% Klucel E plus 0.1% TiO_2 nanoparticles after aging; **N.** SEM photomicrograph (200 X) of sample treated with 2% Klucel E plus 0.1% TiO_2 nanoparticles before aging; **M.** SEM photomicrograph (500 X) of sample treated with 2 % Klucel E plus 0.1% ZnO nanoparticles after aging; **O.** SEM photomicrograph (200 X) of sample treated with 2 % Klucel E plus 0.1% ZnO nanoparticles before aging; **P.** SEM photomicrograph (500 X) of sample treated with 2 % Klucel E plus 0.3% TiO_2 nanoparticles after aging; **Q.** SEM photomicrograph (200 X) of sample treated with 2 % Klucel E plus 0.3% TiO_2 nanoparticles before aging; **R.** SEM photomicrograph (500 X) of sample treated with 2 % Klucel E plus 0.3% ZnO nanoparticles after aging; **S.** SEM photomicrograph (200 X) of sample treated with 2 % Klucel E plus 0.3% ZnO nanoparticles before aging

4. Conclusion

The current study showed the importance of studying the interactions between consolidation products and cellulosic supports. In particular, we tested the effectiveness of two products (CMC and Klucel-E emulsion loaded with Nano titanium dioxide and nano zinc oxide) on the historical paper maps, in order to find the best product to preserve the maps from further weathering and degradation. The selected products were tested under thermal aging. The results obtained by SEM, colorimetric test and FTIR showed the differences in efficiency of the two products especially after mixing with nanoparticles. According to the results obtained, cellulosic maps can be safely treated with 2% CMC + 0.3% TiO_2 nanocomposites where, no significant changes are found in all major FTIR signals and also they have acceptable total color difference even after accelerating ageing . It is found that even if the acceptable chromatic variation is considered to be $\Delta E < 10$, some painted samples don't fit within these limits no matter which treatment was applied, and that is due to their composing minerals. This appears to be the case of treated samples with 2% CMC+ 0.1% ZnO, which registered total color change values higher than 10 (≈11) irrelevant of the chemical and physical properties of the nanocomposites applied. In addition, the SEM images show that upon applying with different nanocomposites, the surface of cotton fiber change differently to be more compact and durability. From these results, we can suggest that CMC + TiO_2 nanocomposites can be an ideal consolidant and can be used for treating paper maps. Therefore, before using cellulosic consolidant we have to determine first which chemical composition is involved in the maps, and then select the polymer that will give good stability and durability.

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