INTERNATIONAL JOURNAL OF CONSERVATION SCIENCE

ISSN: 2067-533X Volume 8, Issue 3, July-September 2017: 441-452 www.ijcs.uaic.ro

A COMPARATIVE STUDY OF CONSOLIDATION MATERIALS FOR PAPER CONSERVATION

Asmaa M. RUSHDY[*1], Wafika N. WAHBA[2], Mohamed S. ABD-AZIZ[3], Magda EL SAMAHY[4], Samir KAMEL[5]

[1] Islamic Art Museum, Cairo, Egypt
[2] Conservation Department, Faculty of Archaeology, Cairo University, Giza, Egypt
[3] Microbial Chemistry Department, National Research Centre, El Behooth St., Dokki - Giza- Egypt
[4] Packing and Packaging Materials Department, National Research Centre, El Behooth St., Dokki - Giza- Egypt
[5] Cellulose and Paper Department, National Research Centre, El Behooth St., Dokki - Giza- Egypt

Abstract

Historical paper is an essential part in cultural and economic progress of humanity.So, this study is to improve the physical-mechanical properties and stability of the brightness of historical paper by evaluating some consolidation materials, carboxymethyl cellulose, chitosan, BEVA 371, and soya bean flour, and to show the changes in paper properties, resulting from thermal accelerated ageing. Analytical techniques used for the evaluation process were pH measurements, tensile strength, burst strength,color change, and scanning electron microscopy (SEM). Also AgNP is deposited by the in situ reduction of silver nitrate on the treated paper sheets in the presence of citrate molecules as stabilizing agent. Antimicrobial activities of the paper sheets were also investigated against Gram positive bacterium Staphylococcus aureus, Gram negative bacterium Pseudomonas aeruginosa, yeast Candida albicans, and fungal Aspergillus niger which are model microorganisms for testing bactericidal properties. The result pointed out that chitosan and carboxymethyl cellulose lead to a significant improvement of the paper mechanical properties and AgNP containing papers gave an improvement as antimicrobial for all the consolidation materials.

Keywords: *Paper conservation; Consolidation; Chitosan; Carboxymethyl cellulose; BEVA 371; Soya beans flour; Thermal ageing; Silver Nano-particles; Antimicrobial.*

Introduction

A lot of paper in museums and libraries suffer from unsuitable environmental conditions that can lead to brittleness [1] because the paper is an organic material and it is under the action of many degradation factors like: physical, chemical, biological or social. These factors cause straining, decolorizing, darkening, cracking, melding or lead to insect, bacterial and fungal attacks [2]. So, the conservation and restoration of paper documents refer to the series of operations taken to extend their lifetime by protecting them against deterioration factors, or by repairing the degradation they underwent [3].

Consolidation is considered to be an important stage in restoration process of a document or a book [4]. This research represents an attempt to evaluate available materials for paper consolidation. The treatment should impart strength without changing the paper's appearance, and the materials should age in accordance with the standards for conservation materials:

[*] Corresponding author: samirki@yahoo.com

without the development of color, brittleness, static change, insolubility, or breaking down into undesirable products [5].

So there are many authors, who have used different consolidation materials by different methods of enforcement [6-11]. *D. Erhardt and C.S. Tumosa* [12] compared between the effect of consolidation materials on the manuscript paper made from cotton linter by manual processes and the printing paper made from grasses by mechanical processes.

Paper fiber is held together by hydrogen bonds which affect the distance between the separate cross-linked fibers. To improve the strength of the paper sheets, a number of resins and polymeric materials have been used such as urea, phenol- and melamine-formaldehyde resins in addition to polyacrylamide, polymethyl methacrylate, vinyl acetate and vinyl chloride copolymer [13]. On the other hand, some polymers were used for treatment of paper sheets to decrease its influence to the photo yellowing and these polymers usefully used to treat the old paper documents. Theses polymers remain the interfiber bonding area chemically linked in the presence of water [14].These polymers can be used as additives during paper sheets formation or as solution to dip the paper sheet in it. For good strength, the additives must be: (a) soluble in water, (b) substantive to cellulose so that its retention is efficient, (c) compatible with cellulose, (d) film forming to offer adhesive resistance, (e) contain a functional group capable of ionic or covalent bonding with cellulose fiber [15].

The main purpose of this study was to assess the effect of consolidation materials, carboxymethyl cellulose, chitosan, soya beans flour and BEVA 371. Also, the effect of depositing of silver nano-particles on the properties of paper sheets will be studied.

Materials and Methods

Cotton linter, delivered by Abo Zaable Chemicals Company (Abo Zaable, Egypt) and PARIS Book paper (dating back to 1887 A.D.) were used in this work. Chitosan, carboxymethyl cellulose, soya beans flour, and BEVA 371 were used.

Table 1. Scientific data for the materials of consolidation

Scientific data	Specification	Chemical name	Solubility	Concentration
CMC	CASR no: 9004-32-4	Carboxymethyle Cellulose Sodium salt (High viscosity)	Distilled water	1 and 3 %
CHIT	85% degree of acetylation	Commercial grade Chitosan	Distilled water and acetic acid	1 and 3 %
SOYA		Soya beans flour	Distilled water by heating at 100±2°C	1 and 3 %
BEVA	GUSTAV BERGER’S Oiginal formula 371, hot – sealing adhesive, 40% solution	60% toluene/heptane, 40% mixture of ethylene vinyle acetate copolymer	Toluene	1 and 3 %

Paper manufacture from cotton linter pulp

It has been done in the Egyptian National Library and Archives (Dar al Kutub) Corniche El Nile, Ramlet Boulac, Sabttiya, according to the following method: Pulp was beaten to 40 SR in a Jokro mill beater according to the Swedish Standard Method (SCA). Sheets of basis weight $80g/m^2$ were formed using leaf cast instrument to produce sheet dimension of 62 × 42cm, then dried using dryer under pressure, paper sheets were dipped in 1% of chitosan, carboxymethyl cellulose, BEVA 371, and soya beans flour solutions. After dipping, the paper sheets were pressed between two filter paper sheets to remove the excess polymer, and then dried on drum at 105°C for 2h. In another trial coating of paper sheet was done by brush on one face by 3% chitosan, carboxymethyl cellulose, BEVA 371, and soya beans flour solutions.

Loading of silver nanoparticles into paper sheets

The AgNP were loaded into the treated paper sheet by using the following method; the treated paper sheet was put in $AgNO_3$ solution (15mg $AgNO_3$ in 40mL distilled water) for 12h, to reduce Ag^+ ions into AgNP. The material, so produced, was allowed to dry. In this way, AgNP loaded paper sheet was prepared.

Thermal ageing

Untreated and treated sample were hung in an drying oven (Heraeus type 5042) Kottermanalhanigsen w - Germany set at $100^{\pm}5$ºC for period 6 days = 144h [16, 17], selected to be equivalent to 50 years of natural ageing [18, 19].

pH measurements

The pH of papers is considered the most important factor determining its stability towards natural and accelerated ageing. Cold extraction measurements conformed to Tappi method (T509 SU-68) was used [20, 21].

Tensile strength

The untreated and treated paper samples were conditioned for 24h in a standard atmosphere (at 23°C and 50% relative humidity), prior to testing for tensile strength [22]. Tensile testing was carried out on 15mm wide strips between jaws set 100mm apart, using a universal testing machine, model 4201 from Instron Corporation equipped with a tension cell of 500N at a stretching speed of $5mm\cdot min^{-1}$ [23].

$$Length\ (m) = (Tensile\ strength \times 6,\ 67 \times 10{,}000)/Grammage\ (g) \qquad (1)$$

Grammage, i.e. weight of $1m^2$, from it the retained amount (g/m^2) of materials or its derivatives on paper sheets were calculated.

Burst strength.

Burst strength was measured according to (TAPPI T403 om-02). The standard size of samples is 10 × 10cm [24].

Measurements of Color change.

Color changes caused by the effect of accelerated ageing cycles were measured using CIE L*a*b* system commonly used to compare the colors of two samples. The L* - scale measures lightness, and varies from 0 (black) to 100 (perfect white). The a* - scale measures red-green; +a* means more red, -a* measures green; the b* - scale measures yellow-blue; +b* meaning more yellow, -b* more blue [25-33]. The total color difference (ΔE*) is calculated according to the following equation:

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

In order to determine the chromatic evolution, the deviation was calculated for every coordinate (L*, a* and b*) in rapport with its initial value, on each sample and on the same place. Finally, the total change of colors was calculated in each point, using the above equation [25, 26, 28].

The measurement was made using Ultra Scan PRO Hunter Lab D65, 10 A.

SEM/EDAX analysis

Samples for SEM/EDAX were taken using FEI INSPECTS Company, Philips, Holland environmental scanning without coating. Elemental micro-probe and elemental distribution mapping techniques were used for analyzing the elemental constitution of solid samples.

Assay of Antibacterial Activity

Agar plate method has been established to evaluate the antimicrobial activities of prepared paper samples containing different additives [34-36]. four different test microbes; *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Candida albicans* and *Aspergillus niger* were selected to evaluate the antimicrobial activities as representatives of Gram positive bacteria, Gram negative bacteria, yeast and fungal groups. The bacterial and yeast test microbes were grown on a nutrient agar medium. On the other hand, the fungal test microbe was cultivated on Czapek-Dox medium. The culture of each test microbe was diluted by distilled water (sterilized) to 10^7 to 10^8 colony forming units (CFU)/ml then 1mL of each was used to inoculate 1L-Erlenmeyer flask containing 250mL of solidified agar media [35]. These media were put onto previously sterilized Petri dishes (10cm diameter having 25mL of solidified media). Filter paper discs (5mm Ø, Whatman No. 1 filter paper) loaded with 0.2mg of each extract. The discs were dried at room temperature under sterilized conditions. The paper discs were placed on agar plates seeded with test microbes and incubated for 24h at the appropriate temperature of each test organism. Antimicrobial activities were recorded as the diameter of the clear zones (including the film itself) that appeared around the films [36].

Results and discussion

pH measurements

Table 2 shows data on surface pH of untreated and treated samples on cotton linter and book paper, all samples showed a small general decrease in pH measurements, while chitosan has higher decrease especially on cotton linter, the decreasing of pH of samples treated with chitosan is due to the acidity media of chitosan solution (chitosan/acetic acid). Table 3 shows the results of conciliations materials samples after the addition of nano-silver material as antimicrobial agent. All the samples showed high change in pH except CMC. *D.M. Evetts et al.* [5] studied the pH measurements of some consolidation materials and found all untreated and treated samples have decreased after ageing.

Table 2. pH values of cotton linter paper and book paper before and after ageing

	Cotton linter paper		Book paper	
Materials	**Before aging**	**After ageing**	**Before aging**	**After ageing**
BLANK	6.60	6.48	6.75	6.51
		First Concentration		
CMC	6.61	6.57	6.64	6.50
CHIT	5.80	5.22	6.30	6.05
SOYA	6.44	5.74	6.67	6.35
BEVA	6.39	5.66	6.55	6.49
		Second Concentration		
CMC	6.47	6.46	6.67	6.38
CHIT	5.18	5.03	6.05	5.69
SOYA	6.43	6.04	6.69	6.39
BEVA	6.49	5.61	6.46	6.32

Table 3. pH values of cotton linter paper and book paper consolidated with nano-silver before and after ageing

	Cotton linter paper		Book paper	
Materials	**Before aging**	**After ageing**	**Before ageing**	**After ageing**
BLANK	6.11	5.71	6.00	5.53
		First Concentration		
CMC	6.54	6.25	6.20	5.36
CHIT	4.65	4.52	4.47	4.42
SOYA	5.40	5.01	5.94	4.88
BEVA	6.13	5.05	6.09	4.97
		Second Concentration		
CMC	6.56	6.43	6.36	5.40
CHIT	4.45	4.25	4.64	4.17
SOYA	5.47	4.79	5.84	4.78
BEVA	5.52	4.94	5.82	5.13

Breaking length

Generally, the treated samples by chitosan or CMC gave best results in breaking length on cotton linter and book paper compared with the treated samples by soybean or BEVA 371, but after the thermal ageing processes all untreated and treated samples have decreased (Figs. 1 and 2).

After the addition of nano-silver as antimicrobial, it was observed that the paper samples have increased in breaking length, the treated by chitosan gave the highest breaking length, and in all untreated and treated samples have decreased after the thermal ageing (Figs. 3 and 4).

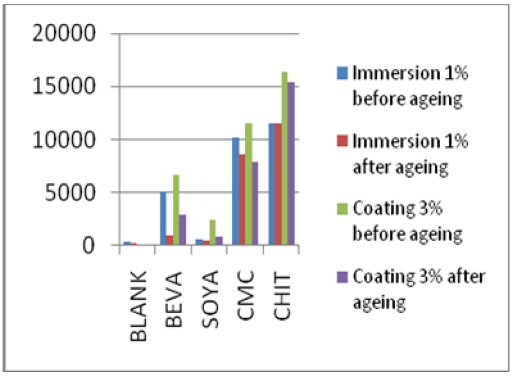

Fig. 1. Breaking length of consolidation materials on cotton linter paper before and after ageing.

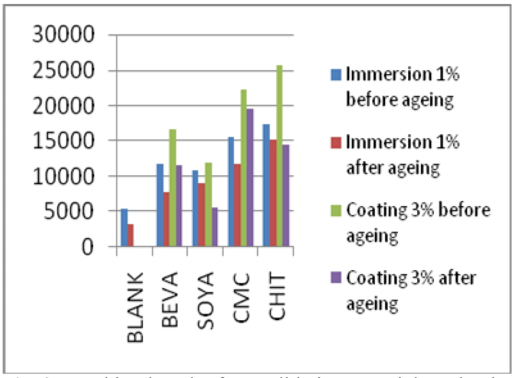

Fig. 2. Breaking length of consolidation materials on book paper before and after ageing.

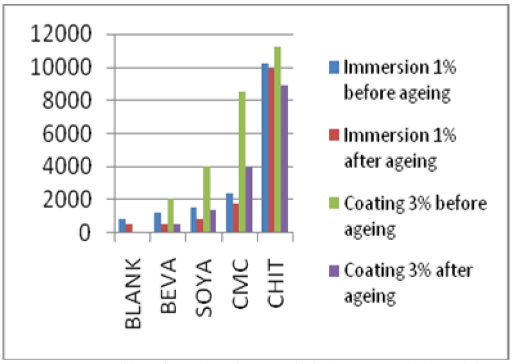

Fig. 3. Breaking length of consolidation materials with nano silver on cotton linter paper before and after ageing.

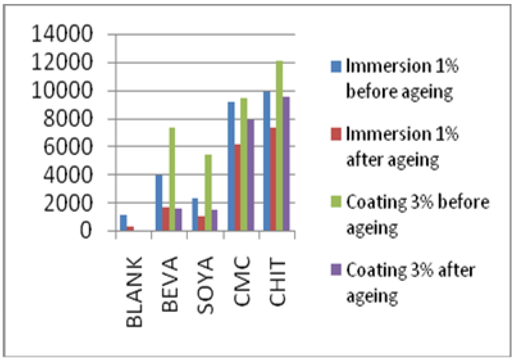

Fig. 4. Breaking length of consolidation materials with nano silver on book paper before and after ageing.

Burst strength

The chitosan or CMC treated samples have increased in the burst on cotton linter but those treated with soya bean or BEVA 371 didn't have consolidation compared with the untreated samples. The samples that treated by chitosan and CMC gave the best results in the burst (Figs. 5 and 6). After the addition of nano-silver materials antimicrobial, the paper samples have increased in burst, and also chitosan and CMC gave the best results, compared with soya bean and BEVA371 (Figs. 7 and 8).

Generally, the breaking length and burst increase by increasing the concentration of consolidation materials. This is attributed to the increase of the interfiber bonding and compatibility between the materials and fiber of paper sheets [37]. *E. Ardelean et al.* [2, 3] studied the effects of mechanical properties of consolidation materials on old documents paper and found that CMC gave good results for old paper consolidation.

Measurement of Color change

Tables 4 and 5 if observed, there are changes in value of color between the untreated and treated samples, it was clear from the data that L*-value of the sample before ageing was near white color, but after ageing the sample become less lighter. This means that the ageing technique led to samples darkening.

a*-value of the samples of cotton linter before ageing was near green color, but after ageing the samples become near red color. In the samples of book paper before ageing was near red color, but after ageing the samples become more red color.

b*-value of the samples before ageing was near yellow, but after ageing the samples become more yellow, and the samples increased in yellow color with increasing the concentration of the consolidation materials [26-30].

ΔE* value (total color difference) there was high change between the samples before and after ageing especially in the materials of chitosan and soya bean. *G. Abdel-Maksoud and Z. Al-Saad* [1] studied the values of color change on book paper sheets that untreated and treated by chitosan and found high change on the samples that treated by chitosan before and after ageing.

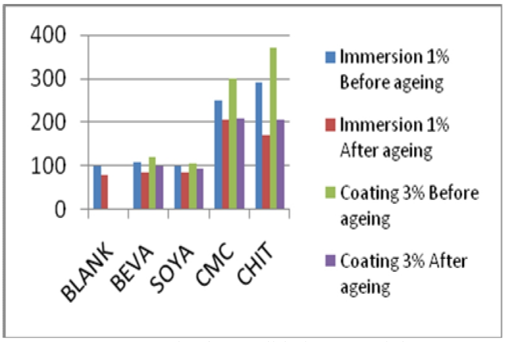

Fig. 5. Burst strength of consolidation materials on cotton linter paper before and after ageing.

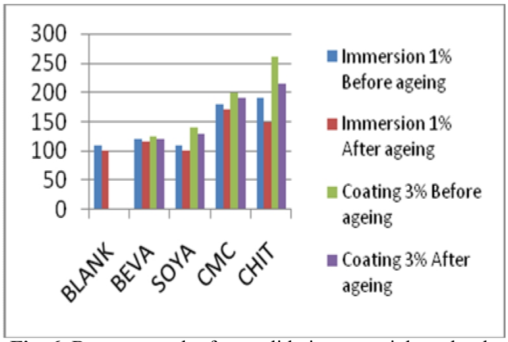

Fig. 6. Burst strength of consolidation materials on book paper before and after ageing.

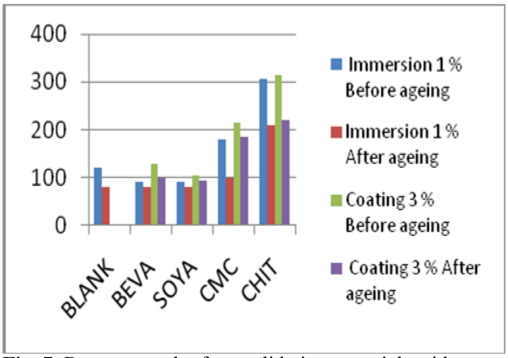

Fig. 7. Burst strength of consolidation materials with nano silver on cotton linter paper before and after ageing.

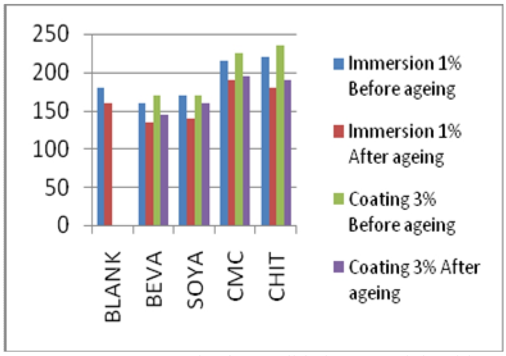

Fig. 8. Burst strength of consolidation materials with nano silver on book paper before and after ageing.

Table 4. The effect of color changes on cotton linter paper consolidation before and after ageing.

	color values before aging				**color values after aging**			
	L*	**a***	**b***	**ΔE***	**L***	**a***	**b***	**ΔE***
Blank	92.58	-0.06	3.95	0.0	90.09	0.48	8.63	0.0
				First concentration				
CMC	92.14	-0.6	4.09	0.46	87.65	1.56	12.86	5.01
CHIT	89.96	-0.90	9.16	5.89	80.22	4.61	27.21	21.88
SOYA	91.57	0.18	7.41	3.61	87.68	0.94	15.54	7.33
BEVA	91.66	0.10	4.61	1.13	89.00	0.18	10.56	2.24
				Second concentration				
CMC	90.68	-0.10	4.98	2.16	86.42	1.78	14.06	6.69
CHIT	90.82	-1.28	12.36	8.67	76.43	7.09	32.25	28.08
SOYA	92.51	-0.30	7.99	4.04	86.56	1.16	19.58	11.53
BEVA	91.65	0.01	5.46	1.55	89.20	0.16	11.10	2.65

Tables 6 and 7 showed the color change after the addition of nano silver as antimicrobial for all the consolidation materials, L*-value of the samples with addition of nano silver decreased compared with the samples that consolidated only, but can be observed the increasing in a* and b*-value for the samples after the addition of nano silver. For the data of ΔE* there was high change especially in the samples that treated by CMC or Chitosan on cotton linter paper.

Table 5. The effect of color changes on book paper consolidation before and after ageing.

	color values before aging				color values after aging			
	L*	a*	b*	ΔE*	L*	a*	b*	ΔE*
Blank	89.60	1.38	10.14	0.0	86.59	2.12	13.99	0.0
First concentration								
CMC	86.68	2.48	15.21	5.95	83.63	3.00	17.16	4.48
CHIT	87.51	2.02	14.59	4.71	82.65	3.87	21.81	8.93
SOYA	89.95	1.16	10.97	0.92	82.09	4.22	19.13	7.15
BEVA	88.46	1.52	11.92	2.11	86.22	2.27	16.20	2.32
Second concentration								
CMC	85.98	1.56	13.03	4.63	81.09	3.85	20.11	8.41
CHIT	85.62	1.64	20.00	10.63	64.98	13.37	38.52	34.82
SOYA	90.17	0.78	10.82	1.07	86.06	2.35	18.17	4.22
BEVA	87.94	1.70	11.72	2.31	84.50	2.80	15.90	2.91

Generally, when we compared between the untreated samples before and after the addition of nano silver, we observed decreasing in L*-value and increasing in a* and b*-value. It was observed a high change in value of color change of cotton linter paper compared with book paper.

Table 6. The effect of color changes on Cotton linter paper with nanosilver consolidation before and after ageing.

	color values before aging				color values after aging			
	L*	a*	b*	ΔE*	L*	a*	b*	ΔE*
Blank	75.42	7.94	17.58	0.0	72.68	9.96	21.64	0.0
First concentration								
CMC	76.24	7.11	20.56	3.20	67.51	11.19	32.13	15.17
CHIT	84.32	1.80	10.25	13.06	70.13	9.92	13.90	12.31
SOYA	73.88	8.51	22.44	5.14	71.04	8.74	23.43	6.69
BEVA	77.55	6.98	16.58	2.54	78.65	6.68	16.29	5.52
Second concentration								
CMC	70.90	8.11	17.03	4.56	64.57	13.60	28.14	15.93
CHIT	87.99	-0.25	14.30	15.35	65.99	10.78	27.24	13.18
SOYA	73.27	8.81	25.74	8.49	66.19	10.51	24.91	12.03
BEVA	81.90	5.13	13.11	5.23	69.90	10.87	25.95	9.65

Table 7. The effect of color changes on book with nanosilver consolidation before and after ageing.

	color values before aging				color values after aging			
	L*	a*	b*	ΔE*	L*	a*	b*	ΔE*
Blank	77.97	5.68	17.76	0.0	76.20	7.69	19.71	0.0
First concentration								
CMC	81.75	4.38	16.22	4.28	73.80	7.75	25.01	5.82
CHIT	83.92	2.86	14.23	7.47	72.92	7.57	23.87	5.31
SOYA	77.50	6.58	20.91	3.31	80.48	3.85	15.11	7.36
BEVA	80.18	4.71	20.09	3.39	73.21	10.24	20.75	4.87
Second concentration								
CMC	83.71	3.84	15.95	6.29	80.69	4.16	16.67	6.47
CHIT	83.11	3.04	13.09	7.43	70.23	8.76	23.65	7.24
SOYA	87.21	6.67	20.98	3.41	65.81	8.79	22.25	10.76
BEVA	78.82	5.61	20.95	4.95	78.13	7.59	15.14	5.33

Investigation and Analysis by using Scanning Electron Microscopy (SEM)

The Scanning Electron Microscopy of CMC loaded by nano silver on cotton linter paper was shown in Figure 9. The fibers of cotton linter paper were very clear, smooth and strong, by CMC consolidation the distances between fiber structures were close. In Figure 10, the material of CMC showed individual crosslinking that resulted in emerging branching networks with the fibers of the Book paper. Figure 11 shows the fibers of cotton linter treated with chitosan were covered with the polymer used. And also in Figure 12 the penetration of chitosan between the fiber structures of book paper was very good. According to EDAX analysis, the highest load of nanosilver was by using chitosan on book paper sheets.

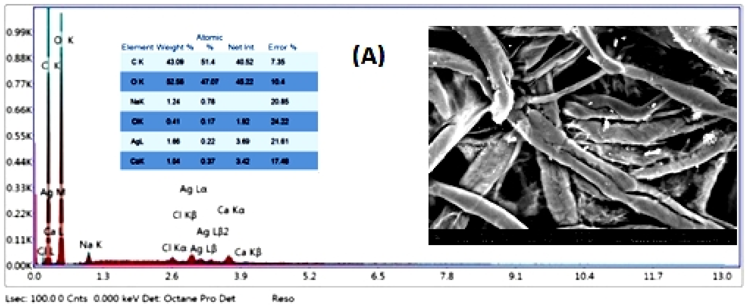

Fig. 9. EADX analysis of cotton linter papers that coating by CMC 3% loading with nano silver

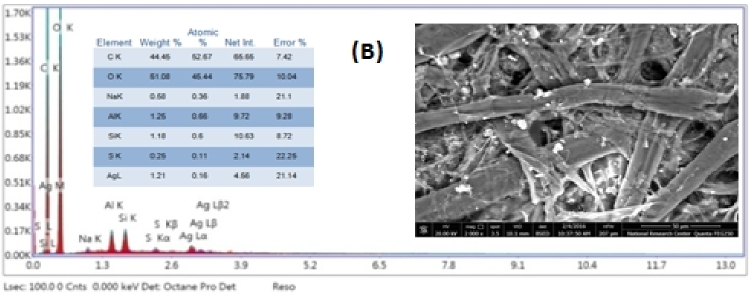

Fig. 10. EADX analysis of book papers that coating by CMC 3% loading with nano silver

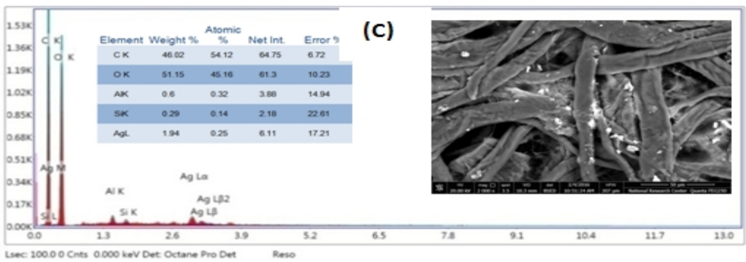

Fig. 11. EDAX analysis of cotton linter papers that coating by CHIT 3% loading with nano silver

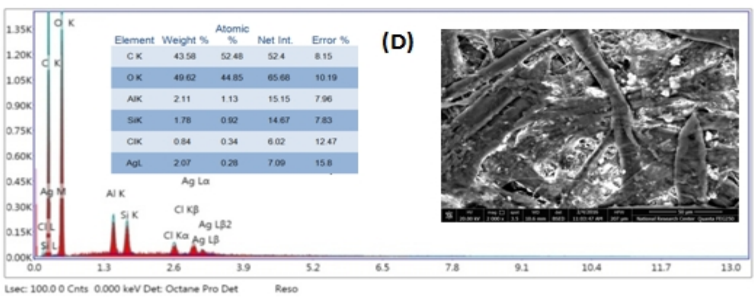

Fig. 12. EDAX analysis of book papers that coating by CHIT 3% loading with nano silver

Assay of Antibacterial Activity

Results represented in Tables 7 and 8 and Figure 13 showed the samples that treated with silver nanoparticles exhibited anti-microbial activity. Silver nanoparticles are able to contact with the microbial cell wall and go through it and make disturbances in the cell wall construction especially in the cell membrane thus its permeability lost and cell death [38]. Also, the free radicals that could be formed from silver nanoparticles were considered as a reason of this cell death [39, 40]. Also, silver ions freed from silver nanoparticles were proposed as a way of the antimicrobial activity [41]. Another postulate has been put considering that DNA contains sulfur and phosphorous as main constituents of its structure and as a result of this, silver nanoparticles (soft acids) may react with them (soft bases) destroying its assembly and thus cause microbial death by changing the DNA replication of microorganisms [42]. Moreover, silver nanoparticles may change the phosphorylation outline of microbial peptides leading to signal transduction stop and thus leading to growth inhibition [43].

Table 7. The antimicrobial activity of silver nanoparticles treated samples on cotton linter

	Staphylococcusaureus	***Pseudomonas. aeruginosa***	***Candida albicans***	***Aspergillusniger***
Nano Silver on cotton linter	7	7	7	8
		First Concentration		
CMC	8	7	8	9
CHIT	7	7	8	8
SOYA	7	7	8	7
BEVA	7	7	8	7
		Second Concentration		
CMC	8	8	8	8
CHIT	7	7	8	10
SOYA	7	7	8	10
BEVA	7	7	8	7

Table 8. The antimicrobial activity of silver nanoparticles treated samples on book paper

	Staphylococcus aureus	***Pseudomonas. aeruginosa***	***Candida albicans***	***Aspergillusniger***
Nano Silver on Book paper	7	7	8	8
		First Concentration		
CMC	7	7	8	10
CHIT	7	7	8	8
SOYA	7	7	7	8
BEVA	7	7	7	8
		Second Concentration		
CMC	7	7	7	8
CHIT	7	7	7	7
SOYA	7	7	7	7
BEVA	7	7	7	8

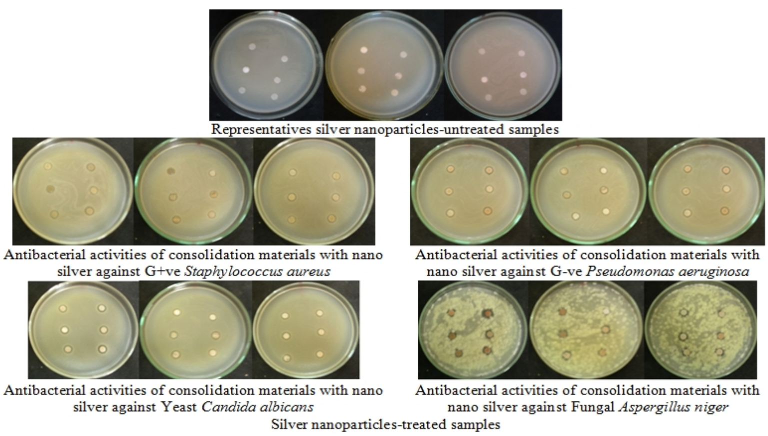

Fig. 13. The antimicrobial activity of silver nanoparticles untreated samples and treated samples

Figure 14 illustrates the different mechanisms of the effect of silver nanoparticles as antimicrobial agent as postulated by *S. Prabhu, E.K. Poulose* [44].

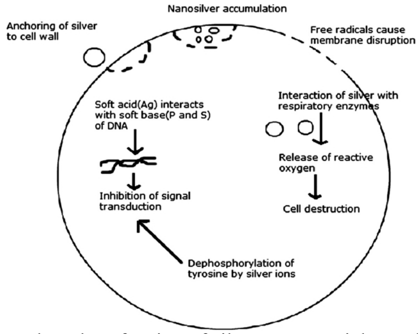

Fig. 14. The suggested modes of action of silver nano particles on bacterial cells [36]

Conclusion

In this study, historical paper can be consolidated by natural materials like carboxymethyle cellulose, chitosan, soya bean flour, and BEVA 371. The materials of Chitosan and CMC improved the mechanical properties of paper sheet than BEVA or soya bean, and green chemical or methyl methacrylate/hydroxyethyl methacrylate copolymer treatments [45, 46]. But chitosan has high color changes and low in pH measurements.

AgNPs acts as antimicrobial agent and improve the mechanical properties of paper sheet, but has changed in color especially with CMC and chitosan.

References

[1] G. Abdel-Maksoud, Z. Al-Saad, *Evaluation of cellulose acetate and chitosan used for the treatment of historical papers,* **Mediterranean Archaeology and Archaeometry, 9**(1), 2009, pp. 69 - 87.

[2] E. Ardelean, D. Asandei, M. Tanase, E. Bobu, *Study on some resizing and consolidation methods of old paper support,* **European Journal of Science Theology, 3**(3), 2007, pp. 53 - 61.

[3] E. Ardelean, E. Bobu, G. Niculescu, C. Groza, *Effects of different consolidation additives on ageing behavior of archived document paper,* **Cellulose Chemistry and Technology, 45**(1-2), 2011, pp. 97-103.

[4] E. Ardelean, R.N. Parpalea, D. Asandei, E. Bobu, *Carboxymethyl chitosan as consolidation ageing for old documents on papersupport,* **European Journal of Science Theology, 5**(4), 2009, pp. 67-75.

[5] D.M. Evetts, A. Lockwood, N. Indictor, *Evaluation of some impregnating agents for use in paper conservation,* **Restaurator, 10**(1), 1989, pp. 1-15.

[6] W. H. Phelan, N. S. Baer, N. Indictor, *An Evaluation of Adhesives for Use in paper Conservation,* **Bulletin of the American Group,** American Group International Institute for Conservation of Historic and Artistic Works, **11**(2), 1971, pp. 1-18.

[7] S.M. Rodgers, *AIC Book and paper Group (Consolidation / fixing / facing),* **Bulletin of the American Group,** American Institute for Conservation of Historic and Artistic Works**, 31**(1), 1992, pp.1-20. http://www.conservation-wiki.com/wiki/Consolidation/Fixing/Facing

[8] M. D. P. Ponce-Jimenez, F. A. L. Toral, E. D. Fornue, *Antifungal protection and sizing of paper with chitosan salts and cellulose ethers. Part I: physical effects,* **Journal of American Institute for Conservation, 41**(3), 2002, pp. 243-254.

[9] M.D.P. Ponce-Jimenez, F.A.L. Toral, H. Gutierrez-Pulido, *Antifungal protection and sizing of paper with chitosan salts and cellulose ethers. Part II: Antifungal affects,* **Journal of American Institute for Conservation, 41**(3), 2002, pp .255-268.

[10] C.A. Baker, *Sodium Carboxymethylcellulose (SCMC) Re-evaluated for Paper, Book, Papyrus, and Parchment Conservation ,* **Book & Paper Group Annual**, 2010, pp. 1-18.

https://www.lib.umich.edu/files/collections/papyrus/2010_Baker_LauLamb_SCMC.pdf
[11] H. Abou-Yousef, S. Kamel, *High efficiency antimicrobial cellulose-based nanocomposite hydrogels,* **Journal of Applied Polymer Science, 132**(31)**, 2015,** No paper 42327.
[12] D. Erhardt, C.S. Tumosa, *Chemical Degradation of Cellulose in paper over 500 year ,* **Restaurator-International Journal for the Preservation of Library and Archival Material, 26**(3), 2005, pp. 151-158.
[13] S. Kamel, M. El Sakhawy, A.M.A. Nada, *Mechanical properties of the paper sheets treated with different polymers,* **Thermochimica Acta, 421**(1-2), 2004, pp. 81- 85.
[14] A.M.A Nada, M. El-Sakhawy, S. Kamel, M.A.M. Eid, A.M. Adel, *Mechanical and electrical properties of paper sheets treated with chitosan and its derivatives*, **Carbohydrate Polymers, 63**(1), 2006, pp. 113-121.
[15] A.M.A Nada, S. Kamel, M. El-Sakhawy, *Physicomechanical properties of paper treated with polymers*, **Restaurator-International Journal for the Preservation of Library and Archival Material, 21**(4), 2000, pp. 238-247.
[16] H.J. Porck, **Rate of paper degradation. The predictive value of artificial aging tests,** European Commission on Preservation and Access, Amsterdam, 2000, 16p. https://www.ica.org/sites/default/files/WG_2000_PAAG-rate-of-paper-degradation_EN.pdf
[17] S. Zervos, *Natural and Accelerated ageing of cellulose and paper. A Literature Review***, Cellulose: Structure and Properties, Derivatives and Industrial Uses,** Nova Science Publishers, Inc., 2010, pp. 155-203.
[18] J.C. Williams*, Chemistry of the Deacidification of paper,* **Bulletin of the American Group.** International Institute for Conservation of Historic and Artistic Works**, 12**(1), 1971, pp. 16-32.
[19] H. Bansa, *Accelerated ageing of paper, some ideas on its practical benefit,* **Restaurator-International Journal for the Preservation of Library and Archival Material, 23**(2), 2002, pp. 106-117.
[20] N. Joel, N. Indictor, J.F. Hanlan, N.S. Baer, *The Measurement and Significance of pH in Paper Conservation,* **Bulletin of the American Group,** International Institute for Conservation of Historic and Artistic Works**, 12**(2), 1972, pp. 119-125.
[21] M. Strlic, B. Pihlar, L. Mauko, J. Kolar, S. Hocevar, B. Ogorevc, *A new Electrode for Micro-Determination of paper pH,* **Restaurator-International Journal for the Preservation of Library and Archival Material, 26**(3), 2005, pp. 159-171.
[22] J.L. Pedersoli Junior, *The development of micro-analytical methodologies for the characterization of the condition of paper,* **9th International Congress of IADA, Copenhagen,** August 15-21, 1999, pp. 107-114. http://www.iada-home.org/ta99_107.pdf
[23] M. Mucha, *Rheological properties of chitosan blends with poly (ethylene oxide) and poly (vinyl alcohol) in solution,* **Reactive and Functional Polymers, 38**(1), 1998, pp. 19-25.
[24] D.G. Suryawanshi, *Like paper, Birch Bark and its Mechanical Properties,* **Restaurator-International Journal for the Preservation of Library and Archival Material, 25**(2), 2004, pp.75-80.
[25] J. Schanda, **Colorimetry. Understanding the CIE System**, New Jersey, Wiley-Interscience, John Wiley & Sons, Inc, Hoboken, 2007.
[26] G. Sharma, **Digital Color Imaging Handbook**, CRC Press LLC, New York, 2003.
[27] G. Abdel-Maksoud, E. Marcinkowska, *Changes in some Properties of Aged and Historical Parchment*, **Restaurator-International Journal for the Preservation of Library and Archival Material, 21**(3), 2000, pp. 138-157.
[28] G.V. Atodiresei, I.G. Sandu, E.A. Tulbure, V. Vasilache, R. Butnaru, *Chromatic characterization in CieLab system for natural dyed materials, prior activation in atmospheric plasma type DBD*, **Revista de Chimie**, **64**(2), 2013, pp. 165-169.
[29] S. Pruteanu, V. Vasilache, I.C.A. Sandu, A.-M. Budu, I. Sandu, *Assessment of cleaning effectiveness for new ecological systems on ancient tempera icon by complementary microscopy techniques*, **Microscopy Research and Technique**, **77**(12), 2014, pp. 1060-1070.
[30] V. Vasilache, I.C.A. Sandu, S. Pruteanu, A.T. Caldeira, A.E. Simionescu, I. Sandu, *Testing the cleaning effectiveness of new ecological aqueous dispersions applied on old icons*, **Applied Surface Science**, **367**, 2016, pp. 70-79.

[31] S. Hrdlickova Kuckova, M. Crhova Krizkova, C.L.C. Pereira, R. Hynek, O. Lavrova, T. Busani, L.C. Branco, I.C.A. Sandu, *Assessment of green cleaning effectiveness on polychrome surfaces by MALDI-TOF mass spectrometry and microscopic imaging*, **Microscopy Research and Technique**, **77**(8), 2014, pp. 574-585.
[32] C. Pereira, T. Busani, L.C. Branco, I. Joosten, I.C.A. Sandu, *Nondestructive characterization and enzyme cleaning of painted surfaces: Assessment from the macro to nano level*, **Microscopy and Microanalysis**, **19**(6), 2013, pp. 1632-1644.
[33] S. Pruteanu, I. Sandu, M.C. Timar, M. Munteanu, V. Vasilache, I.C.A. Sandu, *Ecological systems applied for cleaning gilding in old icons*, **Revista de Chimie**, **65**(12), 2015, pp. 1467-1472.
[34] C.H. Collins, P.M. Lyne, J.M. Grange, J.O. Falkinham III (Editors), **Collins and Lyne's Microbiological Methods***,* 8th edition, Arnold, London**,** 2004.
[35] A.M. Youssef, M.S. Abdel-Aziz, S.M. El-Sayed, *Chitosan nanocomposite films based on Ag-NP and Au-NP biosynthesis by Bacillus subtilis as packaging materials*, **International Journal of Biological Macromolecules, 69,** 2014, pp. 185-191.
[36] M.S. Abdel-Aziz, K.S. Abou-El-Sherbini, E.M.A. Hamzawy, M.H.A. Amr, S. El-Dafrawy, *Green synthesis of silver nanoparticles by Macrococcusbovicus and its immobilization onto montmorillonite clay for antimicrobial functionality,* **Applied Biochemistry and Biotectnology, 176**(8), 2015, pp. 2225-2241.
[37] S. Kamel, M. El Sakhawy, A.M.A. Nada, *Mechanical properties of the paper sheets treated with different polymers*, **Thermochimica Acta, 421**(1-2), 2004, pp. 81-85.
[38] I. Sondi, B. Salopek-Sondi, *Silver nanoparticles as antimicrobial agent, a case study on E. coli as a model for Gram-negative bacteria,* **Journal of Colloid Interface Science 275**(1), 2004, pp. 177-182.
[39] M. Danilcauk, A. Lund, J. Saldo, H. Yamada, J. Michalik, *Conduction electron spin resonance of small silver particles,* **Spectrochimaca Acta Part A-Molecular and Biomolecular Spectroscopy, 63**(1), 2006, pp. 189-191.
[40] J.S. Kim, E. Kuk, K.N Yu, J.H. Kim, S.J. Park, H.J. Lee, S.H .Kim, Y.K. Park, Y.H. Park, C.Y. Hwang, Y.K. Kim, Y.S. Lee, D.H. Jeong, M.H. Cho, *Antimicrobial effects of silver nanoparticles,* **Nanomedicine-Nanotechnology Biology and Medicine, 3**(1), 2007, pp. 95-101.
[41] Q.L. Feng, J. Wu, G.Q. Chen, F.Z. Cui, T.N. Kim, J.O. Kim, *A mechanistic study of the antibacterial effect of silver ions on Escherichia coli and Staphylococcus aureus*, **Journal of Biomedical Materials Research, 52**(4), 2008, pp. 662-668.
[42] D.W. Hatchett, H.S. White, *Electrochemistry of sulfur adlayers on low-index faces of silver*, **Journal of Physical Chemistry, 100**(23), 1996, pp. 9854-9859.
[43] S. Shrivastava, T. Bera, A. Roy, G. Singh, P. Ramachandrarao, D. Dash, *Characterization of enhanced antibacterial effects of novel silver nanoparticles,* **Nanotechnology, 18**(2), 2007, 225103.
[44] S. Prabhu, E.K. Poulose, *Silver nanoparticles, mechanism of antimicrobial action, synthesis, medical applications, and toxicity effects,* **International Nano Letters, 2,** 2012, p. 32. https://link.springer.com/content/pdf/10.1186%2F2228-5326-2-32.pdf
[45] R. Caminiti, L. Campanella, S.H. Plattner, E. Scarpellini, *Effects of innovative green chemical treatments on paper. Can they help in preservation?,* **International Journal of Conservation Science, 7**(Special Issue: 1), 2016, pp. 247-258.
[46] R.R.A. Hassan, W.S. Mohamed, *Effect of methyl methacrylate/hydroxyethyl methacrylate copolymer on optical and mechanical properties and long-term durability of paper under accelerated ageing,* **International Journal of Conservation Science, 8**(2), 2017, pp. 237-250.

Received: September 22, 2016
Accepted: August 20, 2017