EFFECT OF METHYL METHACRYLATE/HYDROXYETHYL METHACRYLATE COPOLYMER ON OPTICAL AND MECHANICAL PROPERTIES AND LONG-TERM DURABILITY OF PAPER UNDER ACCELERATED AGEING

Rushdya Rabee Ali HASSAN[1*], Wael Sabry MOHAMED[2]

[1] Conservation Department, Faculty of Archaeology, Cairo University, Egypt
[2] Polymer Department National Research Centre, Dokki, Giza, Egypt

Abstract

The main goal of this study was to study and evaluate the effect of MMA/HEMA copolymer on the mechanical properties and chemical composition of wood pulp and cotton linter cellulose fibers samples under accelerated ageing .The change of the physical and chemical properties of the untreated and treated paper after ageing was assessed by different methods. The results revealed that copolymer improves the mechanical properties of the paper sheets with reduction in the E, but after heat ageing the value increased, which is a point to consider. From the micrographs, it is clear that the treated fibers are more bundled to each other than the untreated fibers where this fiber bundles increased by increasing the copolymer concentration.

Keywords: Wood pulp; Ageing; Scanning Electron Microscope; Mechanical properties; Copolymer

Introduction

A major part of our cultural heritage has been recorded in various forms on paper for centuries; paper has been used by man science very early time for making notations, writing, drawing, and painting. As a result, a large number of documents, manuscripts and books have been produced in each era in all parts of the world initially; paper is mostly made from cellulose and non-cellulose (hemicelluloses and lignin) with small amounts of organic and inorganic additives .These materials are held together with hydrogen bonds[1, 2]. The cellulose chemical formula is $C_6H_{10}O_5$ [3]. The glucose base units are linked together by -1,4 glycosidic bonds formed between the carbon atoms C-1 and C-4 of adjacent glucose units. Terminal hydroxyl groups are present at both ends of the cellulose chain molecule. The C-1 hydroxyl group has a reducing activity, while the C-4 hydroxyl group at the other end of the chain is non-reducing. Three reactive hydroxyl groups are also present in each of the anhydroglucose (AGU) base unit at C-2, C-3 and C-6 positions [4]. The paper may be strong and white, but in the course of time, on account of physical, chemical and biological factors, their properties undergo change, and they deteriorate and get damaged [5]. The documents that become brittle or fragile due to different causes are to be reinforced physically so that they're strengthened for study, storage or display. In such a case, minor repairs will not suffice, before reinforcing all steps of cleaning, removal of stains, deacidification, etc. are completed. Badly deteriorated paper, however, may

---

* Corresponding author: rushdyarabii@yahoo.com

be too friable to clean and therefore impossible to clean without causing extensive damage. In such cases, it may be best to focus on stabilizing the paper [6]. The improvement of the mechanical properties between these constituents in paper can be achieved by increasing the crossing between the cellulose fibers .A number of polymer materials have been applied, which increase the inter fiber bonding between the cellulose chains in the formed paper sheets. These include PVB (Butvar®B-98) [7], carboxymethyl cellulose (CMC) [8], poly(ethylacrylate) (PEMA) [9], cellulose acetate [10], phenol formaldehyde resin solution [11], cationic starch, cationic polyacrylamides and polyvinyl alcohol (PVA) [12]. Each of these polymers must enable the inter fiber bonding areas to remain chemically linked in the presence of water. Accelerated tests are designed to find materials which can be safe for long term use and would not cause degradation of treated artefacts [13]. Water Dispersed Nano Polymers had been used in treatment and maintenance of textile. Abdel-Kareem (in 2010) studied the maintenance of old wool textile through reinforcing using monomer of MMA and HEMA [14].

In the present work, a preliminary study was carried out to select an adequate polymer, specifically methyl meth acrylate (MMA)/hydroxy ethyl meth acrylate (HEMA) copolymer for archaeological paper preservation. MMA/HEMA was selected due to its excellent abrasion resistance, crack resistance, and generally better ageing characteristics. Paper samples was prepared and artificially aged in a way to simulate archaeological paper; for it is wealth wasting to carry out unguaranteed results tests on archaeological paper. The criteria used to evaluate MMA/HEMA copolymer as preservative material for paper was the mechanical properties (tensile strength and elongation at break percent), degree of colour change, SEM scans, and pH.

Experimental

Samples preparation
In this study wood pulp and purified cotton linter cellulose (32g/m²) were used to prepare paper sheets according to Swedish Standard Method (SCA), pulps were beaten to 40 SR (smooth rough) in a Jokro mill beater. Besides a paper sheet delivered from Rakta (paper mill – Alexandria).

Chemicals
The monomers. Methyl methacrylate (MMA) — Across Company, New Jersey, USA — and butyl acrylate (BA) — Sigma Company, Germany — were washed of inhibitor via filtration through an alumina column and silica gel column, respectively. Washed monomers were stored in a dark container, refrigerated and used within one month of purification.

Emulsifier system
Sodium dodecyl sulfate (SDS) — Across Company, New Jersey, USA — and materials potassium persulfate (PPS) — BDH Laboratory Supplies Poole, BH15 1TD, England — was used as water soluble initiator. Double distilled water was used in all experiments. Hydroquinone was supplied by AdwicProlabo Company, France. Dodeca-phosphotungstic acid A.R. was purchased from Nen Tech Ltd., Brixworth Northamptonshire, UK.

Preparation of poly(MMA/HEMA) by Emulsion Polymerization
In 250mL round flask, the emulsion copolymerization of methyl methacrylate (MMA) and HEMA in a different weight ratio (MMA:HEMA) to produce poly(MMA-co-HEMA) by a batch process in an emulsion containing 10% monomer mixture content with sodium dodecyl sulphate (SDS) as emulsifier were stirred for 30 minutes at room temperature, and then the mixture was heated to 70°C. Then the initiator (PPS) is added to the mixture and stirring was continued for 5h. The polymerization was carried out by dissolving all contents of the emulsifier, the initiator and the monomer mixture in the defined amount of aqueous phase. Paper sheets were dipped in the different concentration of polymer solution for 30 seconds. After dipping, the paper sheets were pressed between two filter paper sheets to remove the excess polymer, after the treatment is over the paper samples are allowed to dry.

Accelerated ageing

The accelerated ageing experiments were performed on experimental cotton and wood papers. The ageing method was selected for the purpose of imitating an average deterioration observed for historical papers, at artificial or accelerated ageing methods, a material 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 – moist - light ageing

The treated and untreated (control) paper samples were artificially thermally aged at 80°C and relative humidity between 60–65% [15] by using saturated salt solution of sodium nitrate [16] and artificial light 300–600nm (source of UV lamp, Xenon light, 5000Watt). The ageing period was 30 days.

Heat – moist - ageing

Heating in oven at temperature 90±3°C and constant relative humidity 65% in accelerated ageing chamber. The ageing period was 30 days. The presence of water has a pronounced effect on paper ageing owing to its role in hydrolysis. Paper in equilibrium with the atmosphere contains between 3…8 weight % water [17], which is why some accelerated ageing experiments attempt to preserve humidified conditions at higher temperatures [18, 19].

Mechanical properties

All paper samples were conditioned according to ISO 187 [20] before measurements at a temperature of 23°C and a RH of 50% over 24 hours. The experiments, which were focused on the mechanical properties of paper, were performed in compliance with ISO standards [21, 22], using a Zwick-Z010 tensile testing machine, at 25°C and cross-head speed of 50mm·min^{-1} at room temperature. The mean values of tensile strength and stretch were calculated from 5 measurements with a precision in the ±10% range. The sample was cut in the machine direction with 15cm length and 1.5cm width as per the requirement of the test standard [23].

Colour Measurement

Colour difference parameter ($E*_{ab}$) was measured by using Optimatch 3100 spectrophotometer. For each sample the average of three measurements were recorded. In order to have a relative evaluation of the induced damage degree on colour changes, the overall colour differences ($E*_{ab}$) between reference and aged samples were calculated using the CIE 1976 (*L*a*b**) equation [24].

FTIR

FTIR was used for monitoring the chemical characterization and modification which occurred in the paper after treatment with MMA/HEMA. Thus, the samples were analyzed before and after treatment with a FTIR spectrometer (Model 6100 Jasco, Japan). Each spectra was obtained in the transmission mode with TGS detector and by using KBr method and represents (2mm/s) co-added scans at the spectral region ranging from 4000 to 400cm^{-1} with resolution of 4cm^{-1}.

pH measurement

Measurement of the pH was in accordance with Tappi 509 om-02 (cold extraction, 1g of sample per 70 mL of water [25, 26], the paper samples were cut into very small pieces. The pH was measured approximately 6h after the suspension had been prepared to allow the ions to migrate into the solution The pH values of the aqueous paper extracts were measured by using ML1010PH, Misura Line, Romania.

Scanning electron microscopy (SEM)

Specimens for this study were cut from the samples. Specimen size was 10 mm diameter and it was circular in shape. These samples subjected to sputter coating (Edwards's model

S140A) of gold ions to have a conducting medium. Sputter coated samples were scanned with JEOL Model JSM-T20 SEM.

Results and discussion

Effect of BA monomer ratio in the prepared poly (MMA/BA) Latex

The effect of BA ratio on the properties of the prepared poly (MMA/BA) was investigation in terms of the particle size investigation and molecular weight determination of the prepared emulsion latex.

Particle Size investigation. The effect of HEMA ratio on the particle morphology was studied using Transmission Electronic Microscopy (TEM). Typical micrographs taken are shown in Figure 1, which indicate that the polymeric particles are quite spherical and almost uniform in size, and there are no aggregates.
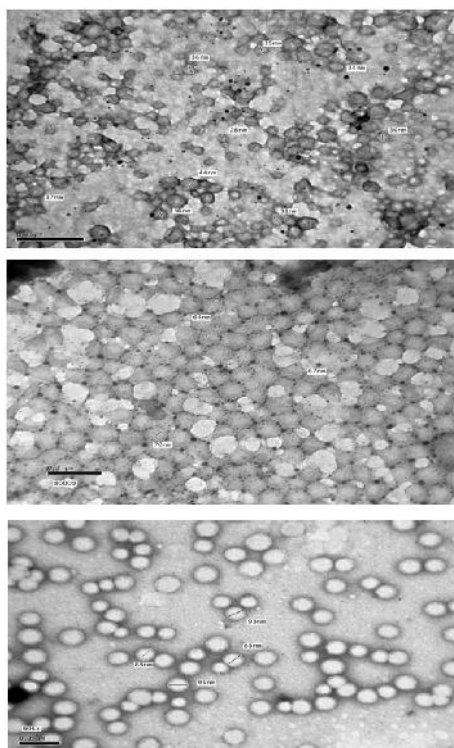

Fig. 1. The effect of HEMA ratio on the particle morphology under Transmission Electronic Microscopy (TEM) Top: MMA/BA is 60:40; middle: MMA/BA is 50:50; bottom: MMA/BA is 40:60.

From the Figure 1, it is obvious that, the particle size increases with increasing the BA monomer ratio where the average particle size was 28:44nm in case of MMA/BA ratio is 60:40 monomer ratio where the particle size increased to 70–76nm when BA monomer percentage increased to 50% and reached to 95nm when the ratio of MMA/BA was 40:60 monomer ratio. These results could be related to the monomer partitioning in different phases where MMA monomer is less soluble in water than BA monomer, partitions mainly in the micelle, where BA partitions between the aqueous phase and the micelle–water interface and the water soluble initiator generates free radicals in the aqueous phase. So, MMA grow inside the micelle, while BA grow at the interface leading to grower in the particle size with increasing in BA ratio**.**

Molecular weight determination

The data listed in Table 1 show the molecular weights of the polymers produced via emulsion polymerization using SDS as surfactant and PPS as initiator were determined by gel permeation chromatography (GPC), dimethyl form amide (DMF) was used as the eluent with flow rate 1mL·min⁻¹. It is clear that the highest molecular weights was observed for the monomer ratio MMA/BA 60:40 and the molecular weight of the prepared latex was decreased as the BA monomer ratio increased which also indicated that the solid content decreased as BA monomer ratio increase.

Table 1. The effect of BA ratio on molecular weights of the polymer

MMA/BA ratio	$M_{wv}(*10^5)$ (g/mol)
60 : 40	10.23
50 : 50	9.56
40 : 60	7.98

Mechanical Properties

Changes in the mechanical properties reflect not only the changes in chemical structure of the polymer system but also its morphology. Figures 2 and 3 show the dramatic increase in both tensile strength and elongation properties of the treated samples. But in reality for treated cotton samples with 3% we can observe a reduction in the elongation and an increase in the stiffness which is not positive are another point to consider. After ageing the values began to decrease. The change in the mechanical properties can be correlated with the change in chemical groups with the ageing procedures.
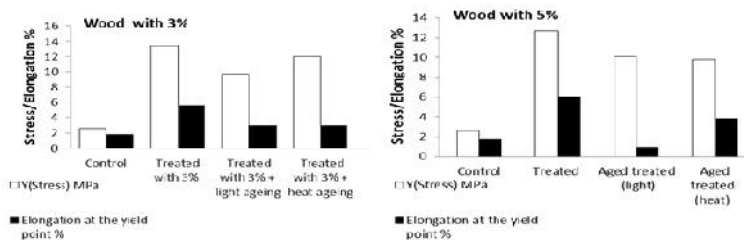

Fig. 2. The tensile strength (TS) and elongation at break (E%) of wood pulp paper treated with 3% and 5% of MMA/HEMA in water
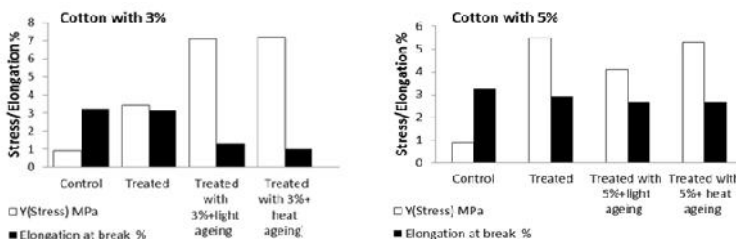

Fig. 3. The tensile strength (TS) and elongation at break (E%) of cotton paper treated with 3% and 5% of MMA/HEMA in water

Cross linking in thermally-degraded celluloses can take two forms: hydrogen bonding between adjacent chains, or the formation of covalent bridges which join chains together creating a network in this way leads to increased stiffness and brittleness because although

mechanical strength can be increased in a polymer by cross linking up to a point, cellulose is already highly cross linked by intermolecular hydrogen bonds and any additional links are detrimental [27]. This result indicates that the MMA/HEMA copolymer improved mechanical properties of paper in comparison with the untreated paper under accelerated ageing. It is generally known that the effects of accelerated ageing processes on paper are interpreted in terms of cellulose chain scission producing weaker fibers, and covalent cross linking by the additional hydrogen bonds leading to increased brittleness [28]. It is well known that the effect of exposure to moisture and heat or a combination of these parameters may damage paper stiffness and strength [29, 30].

The results confirmed that the addition of copolymer into paper composites leads to impressive enhancements in the electrical and mechanical properties of the treated paper. Furthermore, a number of researchers have reported that MMA improved the strength and durability [31, 32].

The results show that the loss (%) in tensile strength of both aged treated and untreated paper by heat are more than the loss (%) in tensile strength of these samples aged by light especially for wood pulp paper.

Colour Changes

The overall colour differences (E^*_{ab}) was calculated in accordance with the following equation [24, 33-38]:

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

where L^* represent the lightness/darkness coordinate and varying from 0 (black) to 100 (white), a^* is the red/green coordinate (+a^* indicating red and -a^* green), and b^* means the yellow/blue coordinate (+b^* indicating yellow and -b^* blue).

The results in Tables 2 and 3 confirmed that there is a notable change in the colour change difference between treated and untreated samples after ageing. It is clear that aged untreated sample turned from bluish to yellowish after accelerated ageing. The absorption in the blue spectra causes the yellowing. Light fastness normally decreases with increasing atmospheric humidity, the extent of the effect depending on the dye-substrate system, which is very pronounced with cellulosic fibers [39, 40]. Heat and moisture are two of the most important environmental influences on the stability of papers. Moreover, exposure to light can cause fading and can shorten the use-life of paper. The degree of fading varies with the type of illumination and is greater with higher intensity light [41]. There is a general agreement that the coloration occurs due to the remaining lignin constituents in the pulp, although neither the precise nature of the chromophores responsible for this nor the exact mechanism for their formation has been conclusively established [42]. Results are shown in Tables 2 and 3 confirmed that MMA/HEMA copolymer improved the durability of paper against the deterioration by light.

FTIR

Figures 4 and 5 show the IR spectra of the native paper, treated paper and aged treated paper. It is evident that both spectra have similar peaks such as a wide band at 3451cm^{-1} which is corresponding to the hydroxyl group. The presence of short peaks around 3303cm^{-1} and 2900cm^{-1} are due to the asymmetrical stretching bands of O-H and C-H, respectively. The presence of new characteristic band at 1730cm^{-1} is related to C=O groups of acrylate ester, in the spectrum of treated paper samples confirm the presence of the nano-sized copolymer in the structure of the paper. After ageing no major changes in the paper samples are observed for aged treated samples, a slight increase in the relative intensity of the 1643 and 3400cm^{-1} peaks are observed.

Table 2. The effect of accelerated ageing on change of colours of cotton
paper treated with 3% and 5% MMA/HEMA copolymer in water

Copolymer	Samples	Heat-moist ageing				Heat-light ageing			
		L	a	b	**E**	L	a	b	**E**
MMA/HEMA 3%	untreated	0	0	0	*0*	0	0	0	*0*
	treated	0.65	-0.22	0.99	*1.20*	0.65	-0.22	0.99	*1.20*
	untreated aged	-1.40	0.40	6.05	*6.22*	0.19	-0.30	3.61	*3.62*
	treated aged	-1.59	0.50	6.74	*6.94*	0.18	-0.20	3.51	*3.52*
MMA/HEMA 5%	untreated	0	0	0	*0*	0	0	0	*0*
	treated	-0.37	-0.13	0.15	*0.42*	-0.37	-0.13	0.15	*0.42*
	untreated aged	-0.60	0.18	4.00	*4.04*	0.54	-0.22	4.89	*4.92*
	treated aged	-0.56	0.17	4.20	*4.24*	0.53	-0.22	4.83	*4.86*

Table 3. The effect of accelerated ageing on change of colour of wood pulp paper treated
with 3% and 5% MMA/HEMA copolymer in water.

| Copolymer	Samples	Heat-moist ageing				Heat-light ageing			
		L	a	b	**E**	L	a	b	**E**
MMA/HEMA 3%	untreated	0	0	0	*0*	0	0	0	*0*
	treated	-0.69	0.14	1.95	*2.07*	-0.69	0.14	1.95	*2.07*
	untreated aged	-1.20	-0.07	5.48	*5.61*	-2.29	-0.45	4.96	*5.48*
	treated aged	-1.17	-0.06	5.45	*5.57*	-2.28	-0.37	4.96	*5.47*
MMA/HEMA 5%	untreated	0	0	0	*0*	0	0	0	*0*
	treated	0.72	0.04	1.82	*1.95*	0.72	0.04	1.82	*1.95*
	untreated aged	-1.49	0.36	5.56	*5.76*	-1.10	-0.69	5.69	*5.83*
	treated aged	-1.48	0.35	5.55	*5.75*	-1.08	-0.59	5.59	*5.72*
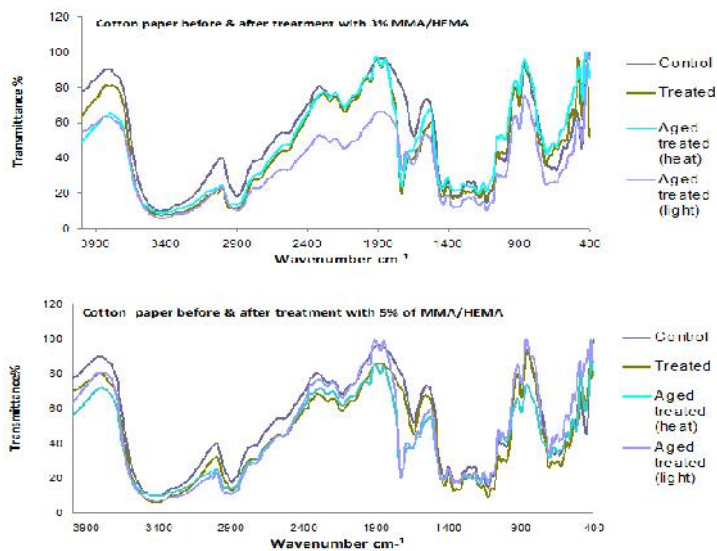
Fig. 4. FTIR Spectra of cotton paper before and after treatment with 3 and 5% of MMA/HEMA in water

We can also observe the existence of the strong peaks at 1114 and 2900cm⁻¹, and are attributed to the C-O and C–H stretching modes, respectively. Many researchers reported that C–O group of ester formation or new C–OH groups appeared in aged paper resulting from opening of the pyranose ring, where the oxidation process of cellulose to occur where heat oxidized hydroxyl group cellulose molecule to the carbonyl and carboxyl group [43-45]. More carbonyl groups were formed as a result of further oxidation of C–OH groups cellulose molecules and there has been the removal of the association CH stretching. More carbonyl groups were formed as a result of further oxidation of C–OH groups cellulose molecules and there has been the removal of the association CH stretching,
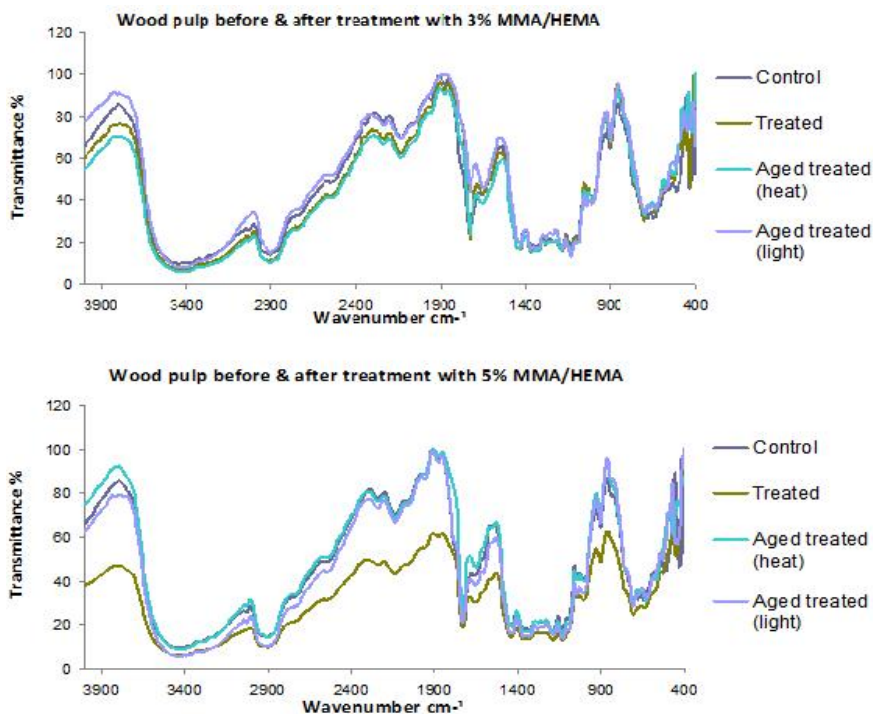

Fig.5. FTIR Spectra of wood pulp before and after treatment with 3 and 5% of MMA/HEMA in water

It is apparent from these results that the MMA/HEMA copolymer solution reduced oxidation process of cellulose under thermal and light ageing which could be to the percent of HEMA in the nano-polymeric copolymer, previous ageing studies of papers in the laboratory, in air, showed an increase in absorbance in the FTIR spectrum in the region of 1600–1700cm⁻¹. However, the changes were masked by sample to sample variation, due to the presence of an O-H stretch from free water in the paper near 1700cm⁻¹.

pH values

The degradation of cellulose is known to depend on the pH of the macromolecular environment. The main mechanism leading to depolymerisation of cellulose with low initial pH values is acid-catalysed hydrolysis [46].

From data reported in Figure 6 it is evident that the MMA/HEMA copolymer 5% decreases the pH value of treated samples by nearly 0.1% for cotton sample, but in the same time, no dramatic changes was observed after treatment by the MMA/HEMA 3%. So, we can conclude that MMA/HEMA 3% can be applied on paper artefacts to conserve and prevent their degradation due to the high acidity levels. After ageing, decreasing of pH values of treated

samples with MMA/HEMA 3% was nearly 0.3% only upon heat ageing; however the results confirm that there are no noticeable differences between the pH values in the paper samples treated with 3% before and after light ageing. So, we can conclude that MMA/HEMA 3% reduced photo-degradation of treated paper. It is generally known that fluorescent and halogen exposure produced similar depolymerisation rates, and north window exposure was only somewhat more damaging. Also, cellulose depolymerisation leaves carboxyl groups on the final chain, which would tend to accelerate further paper decay by promoting acid hydrolysis. The creation of acidic end groups in lignin-free papers is suggested by the drop in surface pH [47].
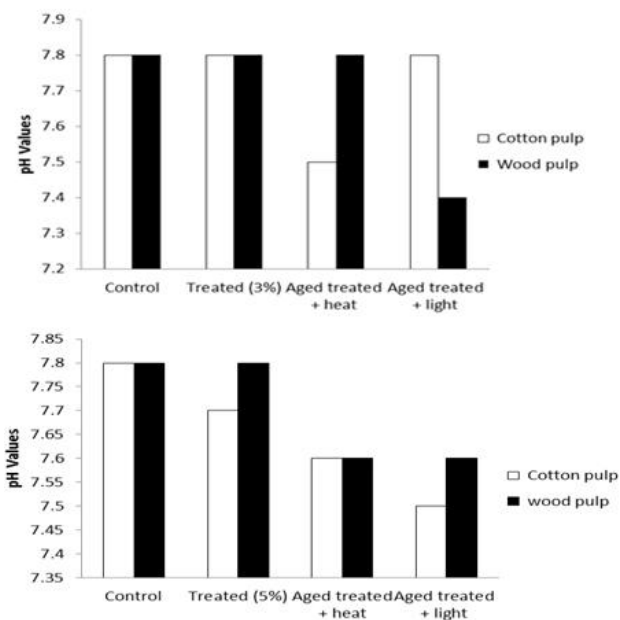

Fig.6. pH values of paper samples.

Scanning electron microscopy (SEM)

Figures 7 and 8 show the scanning electron microscope of untreated cotton sample (B), sample treated with 3% and 5% polymer concentration (G1 and G2), sample treated with 3% polymer concentration after lighting aging (GL1), sample treated with 3% polymer concentration after thermal aging (GT1), sample treated with 5% polymer concentration after lighting aging (GL2) and sample treated with 5% polymer concentration after thermal aging (GT2) at 250X magnification.

From the micrographs it is clear that the untreated fibers are completely separated from each other, whereas in case of polymer treated sample, full fibers can be noticed which may be due to the formation of the fibre bundles between cotton and polymer matrix where this fibre bundles increased by increasing the polymer concentration. Also, some aggregates of the polymer can be noticed on cotton fibres in GL and GT sample which is a good evidence for the success of the polymer treatment process (R1). For the micrograph related to the cotton treated with the polymer after aging thermally and lighting, it can be observed, that the cotton surface showed smooth fibres, soft grain and the fibres interfered with each other (R2 and R3).
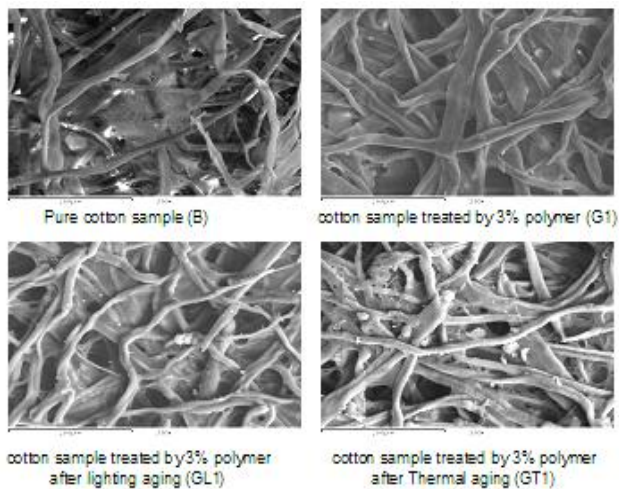
Pure cotton sample (B)

cotton sample treated by 3% polymer (G1)

cotton sample treated by 3% polymer
after lighting aging (GL1)

cotton sample treated by 3% polymer
after Thermal aging (GT1)

Fig.7. SEM micrographs of cotton cellulose fibers: untreated (B), treated (G1);
aged treated with light (GL1) and thermal aged treated (GT1)

cotton sample treated by 5% polymer (G2)

cotton sample treated by 5% polymer
after lighting aging (GL2)

cotton sample treated by 5% polymer
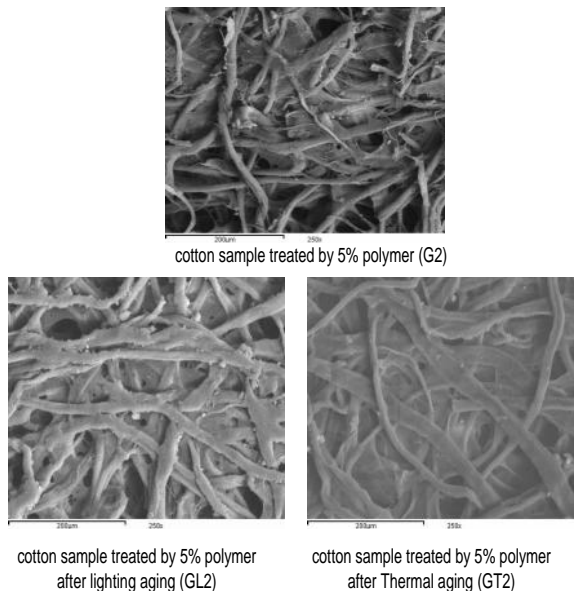after Thermal aging (GT2)

Fig.8. SEM micrographs of cotton cellulose fibers: treated with 5% (G2);
aged treated with light (GL2) and thermal aged treated (GT2)

Figures 9 and 10 show the scanning electron microscope of untreated wood sample (W), sample treated with 3% and 5% polymer concentration (S1 and S2), sample treated with 3% polymer concentration after lighting aging (SL1), sample treated with 3% polymer concentration after thermal aging (ST1), sample treated with 5% polymer concentration after lighting aging (SL2), and sample treated with 5% polymer concentration after thermal aging (ST2) at 250X magnification. From the micrographs it is clear, that the treated fibres are more bundle to each other than the untreated fibres where this fibre bundles increased by increasing the polymer concentration. After the treated wood sample was thermally and lighting aged , it

was noticed that the fibres were not significantly changed, nor were changes observed in the fibre bundles or in the polymer film that coats the wood fibres.
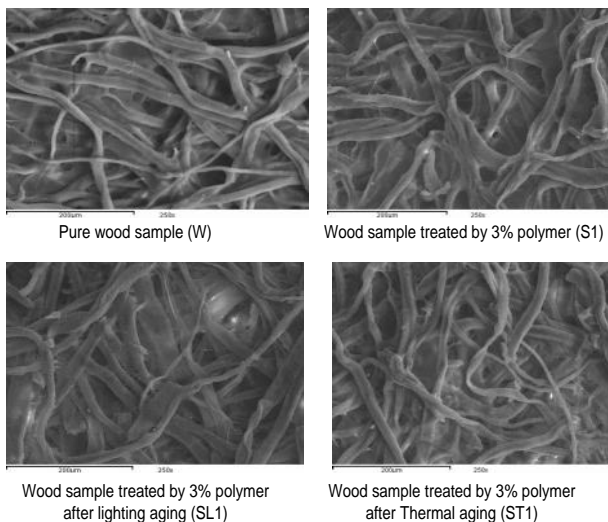

Pure wood sample (W)

Wood sample treated by 3% polymer (S1)

Wood sample treated by 3% polymer
after lighting aging (SL1)

Wood sample treated by 3% polymer
after Thermal aging (ST1)

Fig.9. SEM micrographs of wood pulp cellulose fibers: untreated (W),
treated (S1); aged treated with light (SL1) and
thermal aged treated (ST1)

Wood sample treated by 5% polymer (S2)

Wood sample treated by 5% polymer
after lighting aging (SL2)

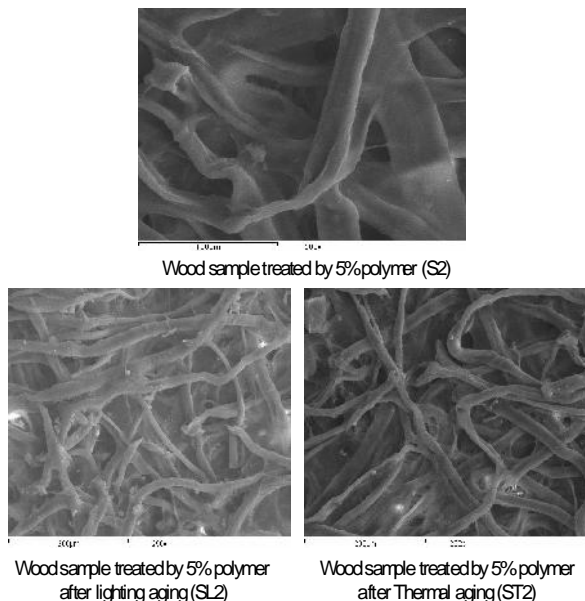Wood sample treated by 5% polymer
after Thermal aging (ST2)

Fig.10. SEM micrographs of cotton cellulose fibers: treated with 5% (S2);
aged treated with light (SL2) and thermal aged treated (ST2)

Conclusions

The use of MMA/HEMA copolymer in the treatment of cotton and wood paper fibers has been investigated using different experimental techniques, including mechanical properties

assessment, pH measurements, FTIR spectroscopy, measurement of colour change, and SEM after heat and light accelerated ageing methods.

The conclusions that can be reached from this research can be summarized as follows:

- treatment of paper sheet with co-polymeric solution of MMA/HEMA improves the mechanical properties of the paper fibres;
- the positive effect of MMA/HEMA copolymer on degradation of paper depends both on the concentration and on the composition of the paper;
- MMA/HEMA copolymer need further research to evaluate their use in consolidation archaeological paper. Moreover, the copolymer results are so diverse that it is difficult to determine positively for $E*_{ab}$ of archaeological paper are another point to consider, especially after aging;
- MMA/HEMA copolymer treatment could be a promising method for consolidating archaeological paper, compared to the traditional method;
- although the data obtained from both the SEM and infrared techniques were completely compatible, it is useful to note that sometimes there are changes in the chemical composition of archaeological paper observed using infrared spectroscopy, whereas they didn't appear in the structure;

MMA/HEMA copolymer has been shown to be effective in preserving archaeological paper from thermal and light degradation, and this copolymer could be used separately for paper reinforcement. It must be clear that the knowledge of the type (i.e. cotton, wood pulp, etc.) and the chemical composition of the paper used for the preparation of the archaeological paper, in addition to its properties, leads to good results during treatment, as it contributes to the selection of the best method to be applied, also reducing the amount of polymer used in the reinforcement process, the length of time the paper is exposed to the polymer, and increases the chances of good reinforcement.

Acknowledgements

References

[1] S. Kamel, M. El-Sakhawy, A.M.A. Nada, *Mechanical properties of the paper sheets treated with different polymers*, **Thermochimica Acta, 421**, 2004, pp. 81-85.
[2] K.J. Ward, **Chemical Modification of Paper Making**, Marcel Dekker, New York, 1973, p. 23.
[3] D. Klemm, B. Philipp, T. Heinze, U. Heinze, W. Wagenknecht, **Comprehensive Cellulose Chemistry**, Vol. 1, Wiley-VCH, Weinheim, 1998, pp. 12-13.
[4] M.N. Le Moigne, *Mecanismes de gonflement et de dissolution des fibres de cellulose swelling and dissolution mechanisms of cellulose fibres,* **PhD Thesis**, l'Ecole Nationale Supérieure des Mines de Paris, 2008.
[5] A. Grawal, P.O. Barkeshli, **Conservation of Books, Manuscripts and Paper Documents**, Indian Council of Conservation Institutes, Lucknow, 1997, p. 111.
[6] C.W. Smith, **Archaeological Conservation Using Polymers: Practical Applications for Organic Artifact Stabilization**, 1st edition, Chapter 4, Texas A&M University, Anthropology Series, 2003, pp. 122-123.
[7] C.V. Horie, **Materials for Conservation Organic Consolidations, Adhesive and Coating**, Butter Worths, England, 1987, pp.101-102.
[8] C.C. Richman, **Conservation Chinese Works of Arts on Paper**, New York, Nova Publishing, 1988, p. 49.
[9] G. Zampano, M. Bertoldoand, S. Bronco, *Poly(ethyl acrylate) surface-initiated ATRP grafting from wood pulp cellulose fibers*, **Carbohydrate Polymer, 75**, 2009, pp. 22-31.
[10] A.A. Ibrahem, A.M.A. Nada, S. El-Meadawy, M.A. Yousef, *Improvement of paper properties by impregnation in cellulose derivative solution.1. cellulose-acetate solution,* **Acta Polymerica**, **34**(3), 1983, pp. 178-180.

[11] A.M.A. Nada, A.A. Ibrahem, M.A. Yousef, **Indian Pulp Paper, 21**(2), 1981, Paper no. 23636.

[12] A.M.A. Nada H. Abo Shosha, A.A. Ibrahem, *Paper sheet treatment with polyvinyl alcohol* **Polymer Plastics Technology and Engineering, 35** , 1996, p. 305.

[13] L.R. Lee, D. Thickett, **Selection of Materials for the Storage or Display of Museum Objects**, BritishMuseum, London, 1996, pp. 54-56.

[14] O. Abdel-Kareem, H. Nasr, *Enhancing the long-term durability of historical wool textiles using water dispersed nano polymers*, **Journal of American Science**, **6**(10), 2010, pp. 1186-1194.

[15] C. Shahani , *Accelerated aging of paper: can it really foretell the permanence of paper*, **Preservation Research and Testing Series, no. 9503,** November 1995, Proceedings from the ASTM/ISR Workshop on the Effects of Aging on Printing and Writing Papers. Philadelphia, PA July 1994.

[16] Standard OIML R 121: *The scale of relative humidity of air certified against saturated salt solutions*, **Organisation Internationale de Métrologie Légale, OIML**, 2007.

[17] D.D. Robertson, *The evaluation of paper permanence and durability*, **Tappi, 59**(12), 1976, pp. 63-69.

[18] X. Zou, N. Gurnagul, T. Uesaka, J. Bouchard, *Accelerated aging of papers of pure cellulose: mechanism of cellulose degradation and paper embrittlement*, **Polymer Degradation and Stability**, **43**(3), 1994, pp. 393-402.

[19] X. Zou, N. Gurnagul, *The role of lignin in the mechanical permanence of paper: part II. Effect of acid groups***. Journal of Wood Chemistry and Technology**, **15**(2), 1995, pp. 247-262.

[20] Standard ISO 187:1990, *Paper, board and pulps – standard atmosphere for conditioning and testing and procedure for monitoring the atmosphere and conditioning of samples*, **International Organization for Standardization**, Geneva, Switzerland, 1990.

[21] Standard ISO 1924-2:1994, *Paper and board – determination of tensile properties – Part 2: Constant rate of elongation method*, **International Organization for Standardization,** Geneva, Switzerland, 1994.

[22] Standard ISO 1924-3:2005, *Paper and board – determination of tensile properties – Part 3: Constant rate of elongation method (100 mm/min)*, **International Organization for Standardization**, Geneva, Switzerland, 2005.

[23] *Tensile breaking properties of paper and paper board, No. T-494, om-88*, **Tappi Test Standards**, Tappi Technology Park, Atlanta GA, USA, 1988.

[24] K. McLaren, *An introduction to instrumental shade passing and sorting and a review of recent developments,* **Journal of the Society of Dryers and Colorists, 92**(9), 1976, pp. 317-326.

[25] D. Ko ar , M. Strli , J. Kolar, B. Pihlar, *Determination of pH of Paper*, **Proceedings of the International Conference Durability of Paper and Writing**, November 16–22, 2004, Ljubljana, Slovenia, editors: Jana Kolar, Matija Strlic, John B.G.A. Havermans, Published by National and University Library, Ljubljana, Slovenia, 2004, pp. 26-27.

[26] Standard ISO 6588-1: 2005, *Paper, board and pulps — Determination of pH of aqueous extracts - Part 1: Cold extraction,* **International Organization for Standardization**, Geneva, Switzerland, 2005.

[27] J.L. Gordon, R. Steele, *Some theoretical considerations of cellulose cross-linking,* **Textile Research Journal**, **31**(2), 1960, pp. 160-171.

[28] B. Havlinova, S. Katuscak, M. Petrovicova, A. Makova, V. Brezova, *A study of mechanical properties of papers exposed to various methods of accelerated ageing. Part I. The effect of heat and humidity on original wood-pulp papers*, **Journal of Cultural Heritage, 10**(2), 2009, pp. 222-231.

[29] M.S. Islam, K.L. Pickering, N.J. Foreman, *Influence of accelerated ageing on the physico-mechanical properties of alkali-treated industrial hemps fibre reinforced poly(lactic acid) (PLA) composites*, **Polymer Degradation and Stability**, **95**(1), 2010, pp. 59-65.

[30] M. Karlovits, D. Gregor-Svetec, *Durability of cellulose and synthetic papers exposed to various methods of accelerated ageing*, **Acta Polytechnica Hungarica**, **9**(6), 2012, pp. 81-100.

[31] J.N.Coleman, U. Khan, Y.K. Gun'ko, *Mechanical reinforcement of polymers using carbon nanotube*s, **Advanced Materials**, **18(6)**, 2006, pp. 689-706.

[32] B. Marrs, R. Andrews, T. Rantell, D. Pienkowski, *Augmentation of acrylic bone cement with multiwall carbon nanotubes*. **Journal of Biomedical Materials Research Part A**, **77A**(2), 2006, pp. 269-276.

[33] V. Pelin, I. Sandu, M. Munteanu, C.T. Iurcovschi1, S. Gurlui, A.V. Sandu, V. Vasilache, M. Branzila, I.G. Sandu, *Colour change evaluation on UV radiation exposure for Paun-Repedea calcareous geomaterial*, **IOP Conference Series: Materials Science and Engineering, 133**, 2016, 012061, doi:10.1088/1757-899X/133/1/012061.

[34] I. Hutanu, I. Sandu, V. Vasilache, L. Nica, I.C.A. Sandu, *Study on the Consolidation of Degraded Pictural Layer with Acrylic Binder,* **Revista de Chimie, 66**(6), 2015, pp. 895-900.

[35] V. Popescu, I.C.A. Sandu, G. Popescu, G. Lisa, A. Popa, *Study of the Effects by Tinctorial Method Obtained at Polyethylene Terephtalate Functionalization with Alcohols,* **Revista de Chimie, 66**(10), 2015, pp. 1607-1613.

[36] 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.

[37] E. Bercu, I. Sandu, C.D. Radu, V. Vasilache, V. Toma, H.A. Aldea, *Influence of Anionic Maleic Polyelectrolytes on the Colour Parameters at Dyeing the Melana Types Fibres with Crystal Violet,* **Materiale Plastice, 49**(4), 2012, pp. 270-274.

[38] V. Pelin, I. Sandu, S. Gurlui, M. Brinzila, V. Vasilache, I.G. Sandu, *Evaluation of the artificial aging rate through UV radiation exposure of indigenous carbonate rocks, treated with water-solvated nano-dispersions, with the interest of consolidation and the formation of a waterproof character*, **Revista de Chimie**, **67**(12), 2016, pp. 2568-2572.

[39] R.L. Feller , **Accelerated Aging: Photochemical and Thermal Aspects**, Research in conservation, The Getty Conservation Institute, Michigan, USA, 1996, pp.183-184.

[40] H.J. Porck, **Rate of Paper Degradation**. **The Predictive Value of Artificial Aging Tests**. European Commission on Preservation and Access, Amsterdam, Holland, 2003, pp.11-23.

[41] * * *, **A Consumer Guide to Traditional and Digital Print Stability**, http://www.imagepermanenceinstitute.org,[Accessed on March 2016].

[42] B. Durbeej, L.A. Eriksson, *Photodegradation of substituted stilbene compounds: What colors aging paper yellow ?*, **The Journal of Physical Chemistry A**, **109**(25), 2005, pp. 5677-5682.

[43] J. Lojewska, A. Lubanska, T. Lojewski, P. Miskowiec, L.M. Proniewicz, *Kinetic approach to degradation of paper. In situ FTIR transmission studies on hydrolysis and oxidation*, **e-Preservation Science.org, 2** , 2005, pp. 1–12. Online available at: http://www.morana-rtd.com/e-preservationscience/2005/Lojewska-04-01-2005.pdf

[44] H. Mohammad , M. Roger, A. Maim, F. Samira, *Thermoplasticization of Bagasse. Preparation and characterization of Etherified bagasse fibers*, **Journal of Applied Polymer Science**, **76**(4), 2000, pp. 561-574.

[45] M. Ali, A.M. Emsley, H. Herman, R.J. Heywood, *Spectroscopic studies of the ageing of cellulosic paper*, **Polymer, 42**(7), 2001, pp. 2893-2900.

[46] J. Malesic, D. Kocar, A.B. Fabjan, *Stabilization of copper- and iron-containing papers in mildly alkaline environment*, **Polymer Degradation and Stability, 97(1)**, 2012, pp.118-123.

[47] C. Hunt, X. Yu, J. Bond, U. Agarwal, R. Atalla, *Aging of printing and writing paper upon exposure to light. Part 2. Mechanical and chemical properties,* **12th edition ISWPC, International Symposium on Wood and Pulping Chemistry,** 2003, Madison, Wisconsin, USA - proceedings volume III, 2003, 231-234.

_____