مجلة كلية الآداب بقنا (دورية أكاديمية علمية محكمة)

Evaluation of Grafting Polymerization Technique Used for the Treatment of Paper

Dr. Gomaa Abdel-Maksoud
Conservation Department, Faculty of Archaeology, Cairo University

Evaluation of Grafting Polymerization Technique Used for the Treatment of Paper

Gomaa Abdel-Maksoud
Conservation Department, Faculty of Archaeology, Cairo University, Giza, Egypt
E-mail: gomaaa@cu.edu.eg

Abstract
Synthetic polymeric materials are used for the treatment of degraded artifacts, in order to improve their mechanical resistance. This paper aims to evaluate whatman paper treated with ethyl acrylate/methyl methacrylate (EA/MMA) monomers in the ratio 75/25 by grafting technique. Different accelerated ageing techniques have been used to follow the changes in some properties. The analytical techniques used are measurement of mechanical properties, investigation of the surface morphology by SEM, change of colour measurement by spectrophotometer, Determination of crystallinity of cellulose by X-ray diffraction and pH measurement. The results revealed that the crystallinity of the treated and aged treated whatman paper is lower than the crystallinity of untreated and aged untreated samples. This may means that the grafting process led to the shrinkage of the cellulose I fibers. It was clear from the investigation of the surface morphology that the grafting technique gave good results even after application of the accelerated ageing techniques.

1. Introduction
A lot of paper artifacts are menaced by paper disintegration through progressive degradation of cellulose chains due to acidic hydrolysis or oxidative processes.[1] There are some treatments are used for the consolidation and protection of papers. These treatments are traditional conservation methods which were not sufficient to improve the mechanical resistance of the degraded artifacts. A few treatments were done by using of synthetic polymeric materials. Among the methods used to

improve the properties of paper, synthesis of grafted cipolymers seems a suitable method to reduce the ageing phenomena of cellulose-based materials.[2] Accelerated ageing is very important in conservation studies in order to evaluate the materials and techniques used. Some authors have used accelerated ageing with different conditions [Schaeffer et al[3], Shahani et al[4], Norris[5], and Lattuati-Derieux et al[6].]. Protection of archival materials 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.[7] This study aims to evaluate whatman papers treated with ethylacrylate (EA) and poly (methyl methacrylate (PMMA) copolymer 75/25 wt %, before and after ageing with different techniques.

2. Materials and methods

2.1. Treated whatman paper samples

Whatman paper grafted with ethyl acrylate/methyl methacrylate 75/25 (polymerization conditions: time = 40 minutes, monomer/cellulose ratio = 4%, grafting = 79%).

2.2. Accelerated ageing methods

2.2.1. Thermal ageing method

The temperature test at 100 °C (the partial pressure was around 365) for 2 weeks was performed in situ in the reaction oven using the dry air atmosphere. Moisture was evacuated from the oven using air vacuum to freeze out the residual water vapour. The oven used in the thermal ageing is Heraeus D.63450 Hanau, Type: VT 6130M, vacuum type: vacucenter1 (Heraeus Instruments vacutherm, made in Germany.

2.2.2. Heat-moist ageing

This method is based on exposure of the samples used to constant temperature 70 °C ± 3 °C and constant relative humidity 50%. The period of ageing was 10 days.2. 2.2.3. 2.2.3. Heat-moist-light ageing

The temperature at 50 °C and relative humidity cycling between 50% and 70%. The cycling of relative humidity was each 12 hours. Artificial light 300 – 600 nm (source of UV. Light);

Xenon light 5000 W. The ageing period was 10 days. Accelerated ageing chamber used in this method is: Operating Instruction, XENOTEST ISO ST, Atlas Material Testing Technology, Germany.

2.3. Evaluation techniques

2.3.1. Measurement of mechanical properties (tensile strength and elongation)

Tensile strength and elongation of the new sample, aged untreated, treated and aged treated samples before and after different methods of ageing were measured by Testing Machine type AG-5K NIS Ms (Shimadzu, Kyoto, Japan). These tests were done according to TAPPI Standard (TAPPI T494 om-88).[8] It should be noticed that the size of the samples tested was smaller than the testing conditions described in TAPPI T494. The width of the sample was 15mm and the length was 130 mm. the reduction in the size of the sample was due that the size of the sample holder was 135mm length. The crosshead speed was reduced from 25 to 14mm/min in order to keep the rate of strength as specified in the TAPPI Standard.

Index method for the evaluation of mechanical properties

The index method is proposed by Abdel-Maksoud[9] in this study for the evaluation of the conservation treatment (consolidants). This method is based on the comparison of the changes of tensile strength and elongation of paper before and after the treatment. In order to compare the changes, the appropriate laboratory investigations have been carried out. Based on the obtained results, the index of the effectiveness of conservation treatment and determination of ageing rate by different ageing cycles was calculated.

The indexes of the parameters used (tensile strength and

$$\text{Indexes of Ts and E} = \frac{X_1 - X_2}{X_3 - X_4}$$

elongation) were as follows:
Where:
Ts = tensile strength, E = elongation, X_1 = tensile strength or elongation of blank sample (untreated or new sample), X_2 = tensile strength or elongation of aged sample, X_3 = tensile strength or elongation of treated sample with consolidant before the accelerated ageing cycle, X_4 = tensile strength or elongation of aged treated sample.

2.3.2. Investigation of the surface morphology by a scanning electron microscope
A scanning electron microscope FEI (Netherlands) Model Quanta 200 was used to observe the surface morphology. Blank sample (untreated), aged untreated sample, treated sample and aged untreated sample were examined.

2.3.3. Measurement of colour change by spectrophotometery
Colour changes caused by the effect of accelerated ageing cycles were measured using CIE*Lab system, commonly used to compare the colours of two samples. [Abdel-Maksoud and Marcinkowska[10], and Abdel-Maksoud and Marcinkowska[11]]. 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 means green; the b-scale measures yellow-blue, +b meaning more yellow, -b more blue. Differences in colour between two specimens are determined by the use of the Greek letter Delta (ΔL, Δa, Δb); the total colour difference (ΔE) is found according to the following equation[12]:
The measurement was made using Macbeth color eye 7000 (U.S.A.) UV-Spectrophotometer.

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

2.3.3. X-Ray diffraction analysis (XRD) for the crystallinity of paper
The crystallinity of selected of untreated and treated samples before and after their treatment with different ageing cycles was

carried out on Lab X.R.D. 6000, X-ray diffractometer (Shimadzu, Japan).

2.3.4. Determination of pH of paper

The determination of pH of paper samples studied was made by "micro determination of pH", since the samples are cut out with a sharpened surgical needle of inner diameter 0.8mm. the average weight of such samples was approximately 10 µg. Deionized water was added tell 15 ml and the pH was determined once the reading stabilished (after Max. 10 mi.) using pH meter (pH315i Inhaltsverzeich, Wiscenschaftlich-technische Werkstallen GmbH & Co. KG) provided with a combination electrode and calibrated between 4 and 7 at 21-22 °C and 65% R.H.

3. Results and discussion

3.1. Mechanical properties (Tensile strength and elongation)

The data obtained (Fig. 1, and appendix 1) showed that there is a reduction in tensile strength and elongation.

Tensile strength

Tensile strength gave positive results; since the treated and aged treated with all ageing cycles gave an improvement in tensile strength more than untreated and aged untreated samples. The results of index method were 2.35 for heat ageing cycle, 1.17 for heat-moist ageing cycle and 1.16 for heat-moist-light ageing cycle. The reduction increased with decreasing the number of index.

Elongation

It should be said that the reduction between untreated and aged untreated, and the treated and aged treated was little as a comparison with tensile strength. The variation in index method with heat-moist and heat-moist-light ageing cycles was higher than tensile strength. from mechanical properties, It should be said that the treatment of whatman paper by grafting process gave a resistance against ageing cycles more than those samples without treatment.

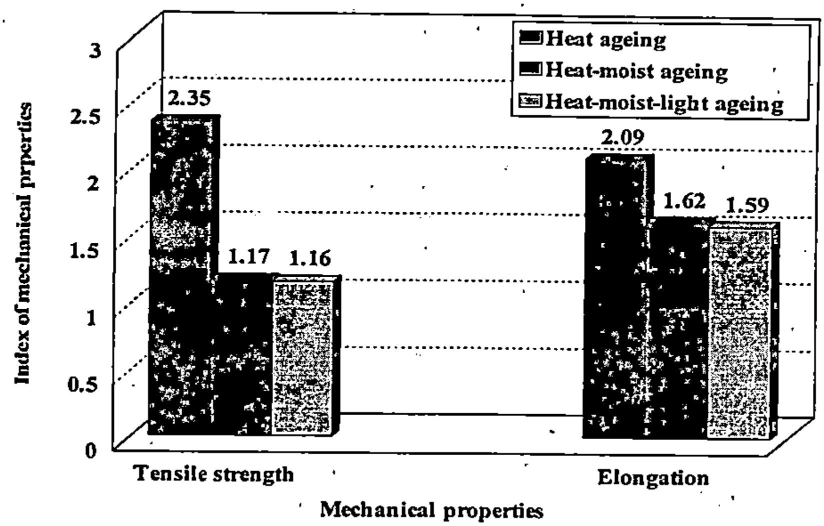

Fig. 1: Tensile strength (N/mm^2) and elongation (%) of grafted whatman paper with all accelerated ageing cycles

3.2. Investigation of the surface morphology by SEM of grafted whatman paper

It was clear from the investigation of the surface morphology (Fig. 2) by a scanning electron microscope of untreated sample (control) (Fig. 2, picture 1) that the distribution of the fibers was good. The fibers were compact. The fibers are from cotton material. The distribution of the heat-moist aged untreated sample (Fig.2, picture 2) was randomly, the fibers were rolled and some destruction was found in some area. It was clear from the treated sample (Fig. 2, picture 3) that the fibers became strong more than the untreated sample, and the polymer distribution on the surface was good, but it is still of the surface. This may indicates that the fibers saturated with polymer and the remaining of the polymer on the surface may due to increasing of time treatment. The fibers of heat-moist aged treated sample (Fig. 2, picture 4) were also strong and the fibers distribution was also good.

It was clear that heat-moist-light ageing (Fig. 3, picture 2) led to destructive of the fiber structure more than the heat-moist ageing cycle. The distribution of the fibers was randomly and the increasing the distance between fiber structures was also noticed. It was noticed from the heat-moist-light aged treated sample (Fig. 3, picture 4) that the fiber was also strong. Some bubbles were also found on the surface of the fibers.

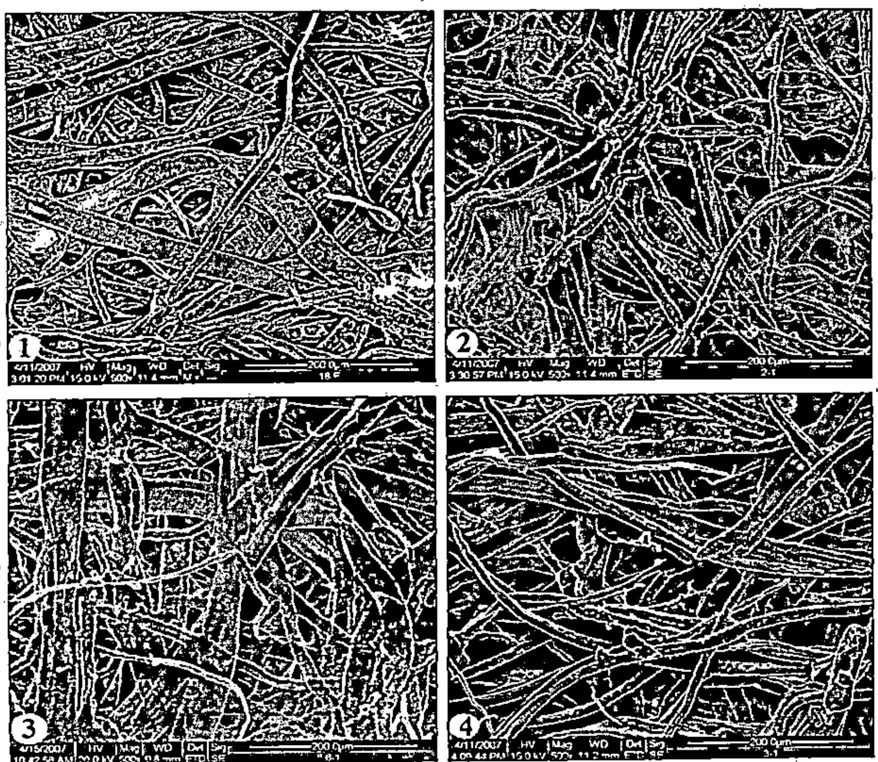

Fig. 2: SEM micrograph of grafted whatman paper before and after heat-moist ageing process: (1) Untreated sample, (2) Heat-moist aged untreated sample, (3) Treated sample, (4) Heat-moist aged treated sample

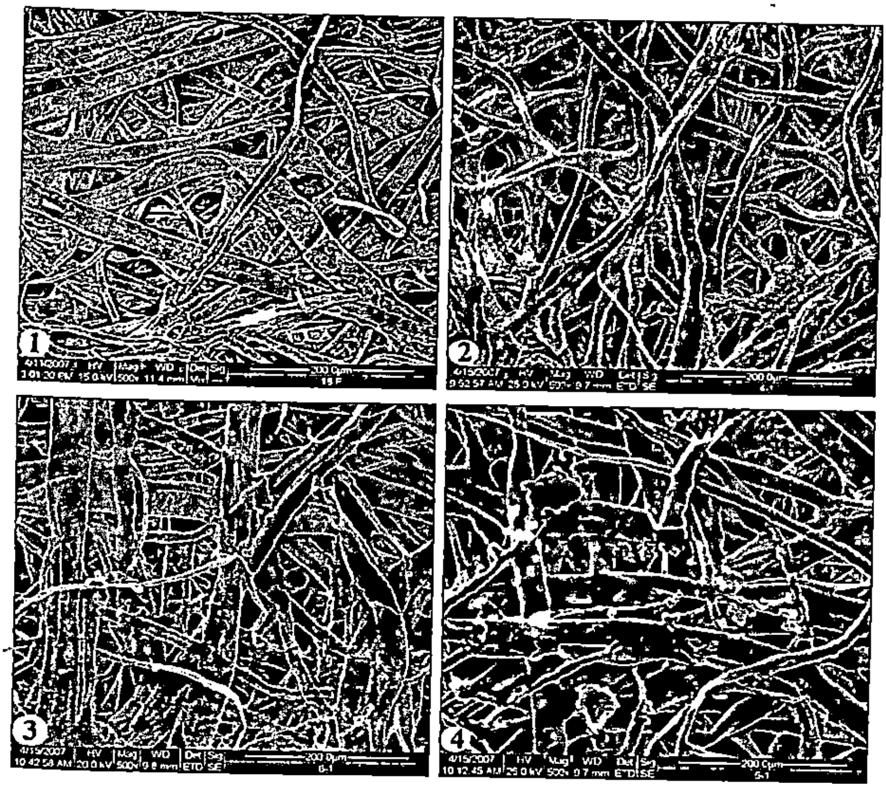

Fig. 3: SEM micrograph of grafted whatman paper before and after heat-moist ageing process: (1) Untreated sample, (2) Heat-moist aged untreated sample, (3) Treated sample, (4) Heat-moist aged treated sample

3.3. Change of color

Change of color of any conservation material is considered one of the most important factors that governing the selection of this material. Successful material should not change the material being treated. In experimental study, this property is very necessary to be tested to show the advantage and disadvantage of the materials used. The conservation material should give as less change as possible especially in experimental study, since the changes in color can be noticed step by step. In this study all arameters of change of color were measured with all ageing cycles.

Lightness (CIE*L)

The results obtained (Fig. 4) showed that there is a reduction in the lightness for all samples studied with all ageing cycles. The percentage loss in lightness of aged untreated, treated and aged treated samples respectively with heat ageing cycle was 6.03%, 1.87% and 8.11%, with heat-moist ageing cycle was 6.44%m 1.87% and 8.94%, and with heat-moist-light ageing cycle was 5.72, 1.87% and 7.59%. It was noticed that the higher effect was obtained from heat-moist ageing cycle, followed by heat ageing and the lower effect was obtained from heat-moist-light ageing cycle.

Red-green color (CIE*a)

It was noticed from the data (Fig. 5) that the untreated and aged untreated samples were in red color. The red color of heat aged untreated sample was near or close to the untreated sample, but the red color of heat-moist and heat-moist-light samples decreased more than untreated samples.

For treated and aged treated samples with all ageing cycles give more less in red color and tend to be green color. The highest loss in red color was obtained from heat-moist-light ageing cycle, and the lowest was obtained from heat ageing cycle.

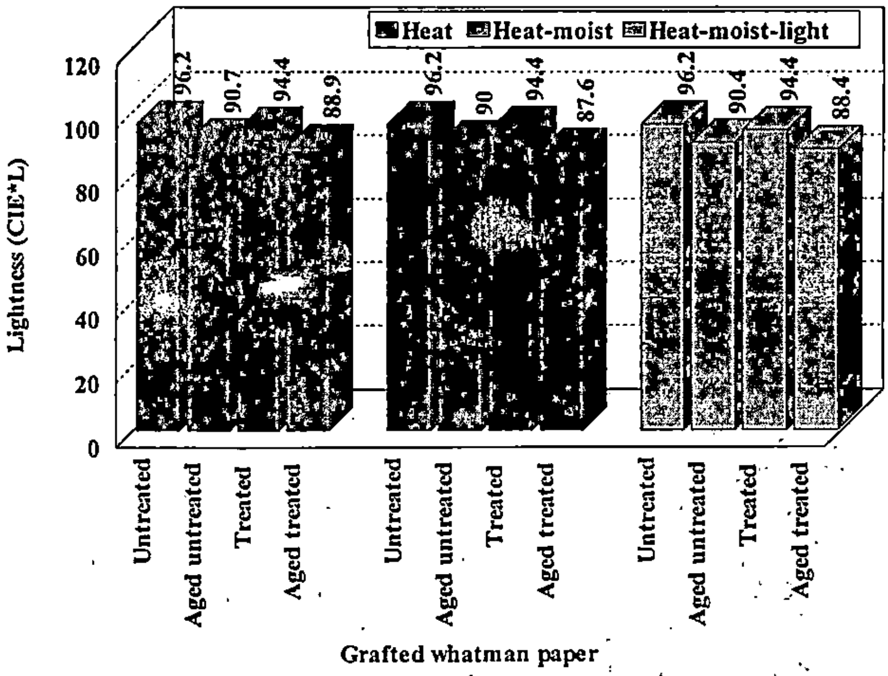

Fig.4: Lightness (CIE*L) of grafted whatman paper with all accelerated ageing cycles

Yellow – blue color (CIE*b)

The yellow color (Fig. 6) was obtained from all samples studied except the aged untreated sample with all ageing cycles. It should be said that the untreated sample gave very slight yellow color. The highest yellow color was obtained from treated and aged treated samples. The highest change in the yellow color was obtained from heat-moist ageing cycle, followed by heat-moist-light ageing cycle, and the lowest change in the same parameter was obtained from heat ageing cycle.

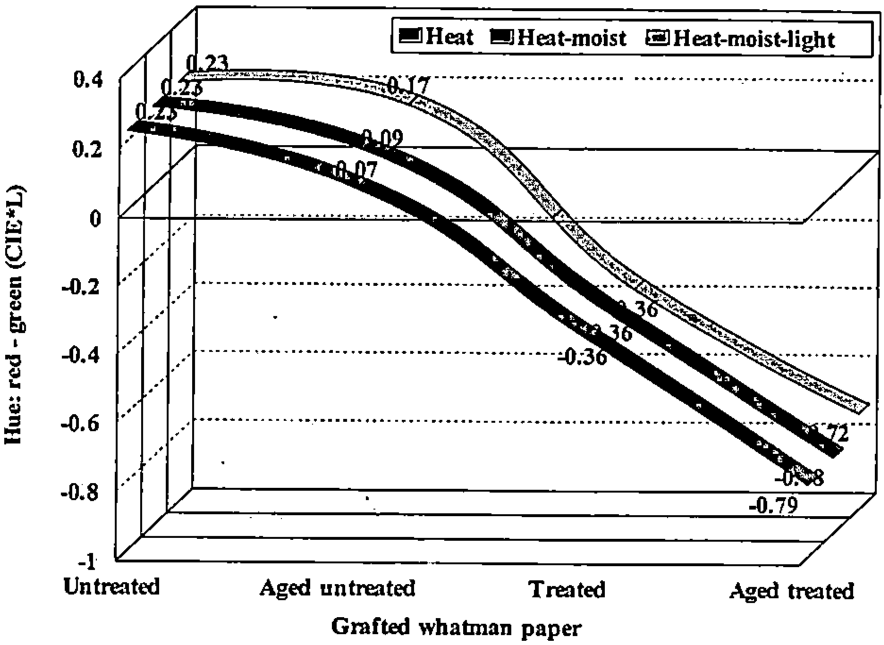

Fig.5: Red – green color (CIE*a) of grafted whatman paper with all accelerated ageing cycles

Total color index (CIE*E)

The reduction in the total color (Fig. 7) of the aged untreated, treated and aged treated samples respectively was as follow: with heat ageing cycle 6.03%, 1.83% and 8.09%, with heat-moist ageing cycle was 6.44%, 1.83% and 8.72%, and with heat-moist-light ageing cycle was 5.72%, 1.83%, and 7.58%. the highest change in the total color was obtained from heat-moist ageing cycle, and the lowest change was obtained from heat-moist-light ageing cycle.

Total olor differences

It was clear from the total color differences (ΔE) (Table 1) that the highest change was obtained from heat-moist ageing cycle, followed by heat-moist-light ageing cycle and the lowest change was obtained from heat ageing cycle. It should be noticed that the aged treated samples gave more change than aged untreated samples with all ageing cycles.

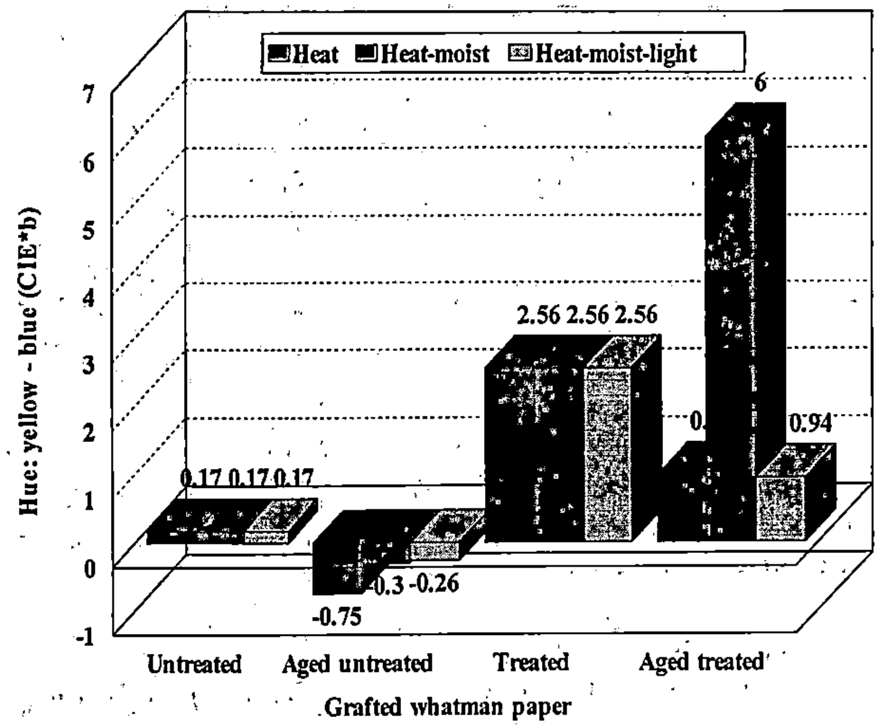

Fig.6: Yellow – blue color (CIE*b) of grafted whatman paper with all accelerated ageing cycles

3.4. X-ray diffraction of grafted whatman paper with all ageing cycles

Evaluation of cellulose I crystallinity

Trip[13] said that the crystallinity of cellulose has been aptly described as an "elusive" variable. Indeed the whole concept of crystallinity as applied to solid polymers in rather nebulous.[14]

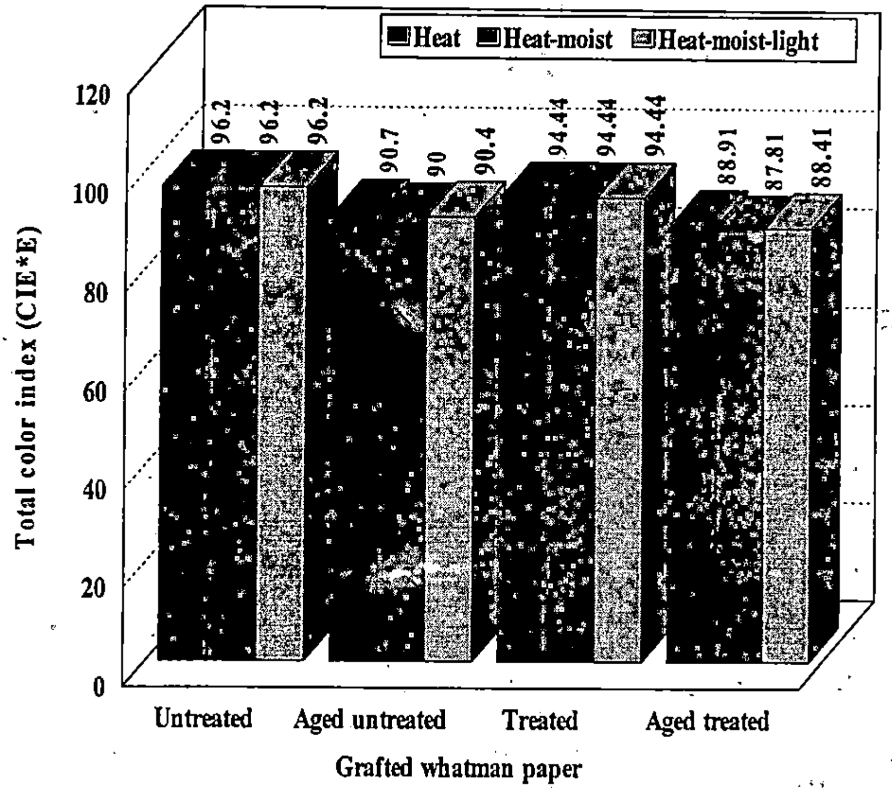

Fig.7: Total color index (CIE*E) of grafted whatman paper with all accelerated ageing cycles

Three peaks were selected in the fitting of each diffractogram, three peaks for the cellulose crystalline peaks (101, 10$\bar{1}$, and 002 peaks). In this study, the position (2θ degrees), the full width at half maximum (FWHM) (2θ degrees), and intensity were obtained from each fitted peak.

Table 1: Color differences of grafted whatman paper with all accelerated ageing cycles

Samples	Heat ageing			
	ΔL	Δa	Δb	ΔE
Untreated sample	0.0	0.0	0.0	0.0
Aged untreated sample	5.5	0.16	0.58	5.53
Treated sample	1.8	0.13	-2.39	2.99
Aged treated sample	7.3	0.56	-0.81	7.37
Samples	Heat-moist ageing			
	ΔL	Δa	Δb	ΔE
Untreated sample	0.0	0.0	0.0	0.0
Aged untreated sample	6.2	0.14	0.13	6.20
Treated sample	1.8	0.13	-2.39	2.99
Aged treated sample	8.6	0.55	-5.83	10.40
Samples	Heat-moist-light ageing			
	ΔL	Δa	Δb	ΔE
Untreated sample	0.0	0.0	0.0	0.0
Aged untreated sample	5.8	0.06	0.09	5.80
Treated sample	1.8	0.13	-2.39	2.99
Aged treated sample	7.8	0.49	-0.77	7.85

Peak positions (2θ degrees)

The positions of the peaks in an x-ray diffractogram reflect the dimensions of the crystalline of cellulose unit cell. It was noticed from the data obtained (Figs. 8-9) that the peaks were shifted to lower value with heat ageing cycle. The positions of the (101) peaks were shifted to higher value with heat-moist and heat-moist-light ageing cycles. The position of the (10Ī) peaks were shifted to lower value with heat-moist and heat-moist-light ageing cycles as a comparison with untreated sample (control). The position of the same peaks (10Ī) with heat ageing cycle was equal with control sample. It was noticed for the treated samples before and after ageing cycles that the dimensions of the crystalline cellulose increased in the entire sample studied except the aged treated sample with heat-moist ageing cycle. The peak positions (101) of heat aged treated sample increased more than the sample treated before ageing. The position of the (10Ī) peaks shifted to higher values in the treated sample. The heat aged treated sample shifted to higher value as a comparison with treated sample before ageing. The heat-moist and heat-moist-light aged samples shifted to lower value as a comparison with treated sample. The position of the (002) peaks increased as a comparison with untreated and aged untreated samples. The positions of untreated and treated samples were equal. Heat aged treated sample was shifted to higher value, but heat-moist and heat-moist-light aged treated samples were shifted to lower value.

Peak width (2θ degrees)

The width at half maximum is a measurement of the degree of crystallinity in a material. The definition of the peak width is the width at half height parameters in degrees 2θ were calculated by taking the difference between the peak position and the half height intersection of multiplying by two. These parameters should represent the width of the peak at half its height if no other peaks interfered.

Gjonnes and et al[15] resolved the (002) reflection of cellulose I into a caushy distribution profile. From this analysis they were able to get a measure of crystallinity. According to

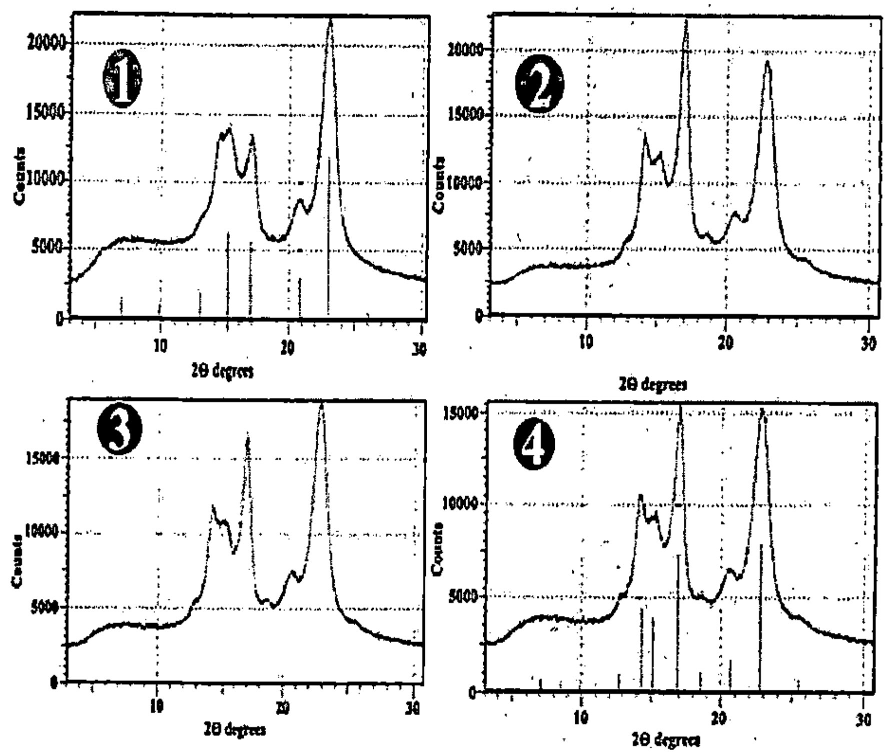

Fig. 1: X-ray difractograms of whatman paper: (1) Untreated sample (2) Heat aged untreated sample (3) Heat-moist aged untreated sample (4) Heat-moist-light aged untreated sample

their analysis, cellulose I *".... very likely consists of aggregates of distorted crystallites and that only small quantities of highly disordered material are present".*

It was clear from the data obtained (Figs. 8-9) that the width of the (101) peak of untreated and heat aged untreated samples were equal, but this width decreased with heat-moist and heat-moist-light aged samples. The width of the ($10\bar{1}$) peak of heat aged untreated sample was decreased, but heat-moist and heat-moist-light aged samples increased as a

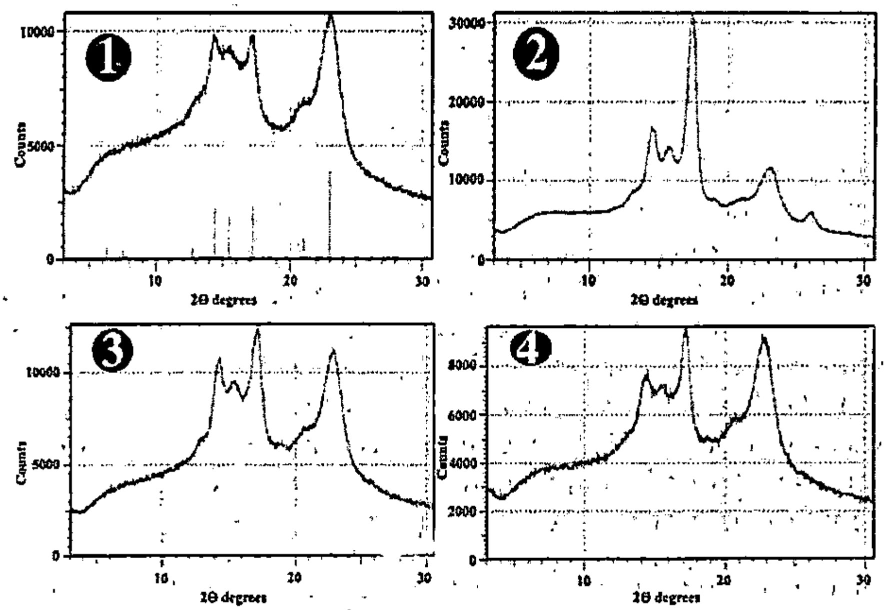

Fig. 2: X-ray difractograms of whatman paper: (1) Treated sample (2) Heat aged treated sample (3) Heat-moist aged treated sample (4) Heat-moist-light aged treated sample

comparison with untreated sample. The width of the (002) peak of heat aged sample increased, but the width of heat-moist and heat-moist-light aged samples were equal with untreated sample (control). The data obtained proved that the width of treated and aged treated samples increased more than the width of untreated and aged untreated samples. For grafted sample, the width of the (10Ī) and (002) peaks increased as a comparison with untreated sample. The width of aged treated whatman paper was wider than the aged untreated sample.

Intensity (2θ degrees)

There are two methods for the evaluation of the intensity of untreated, aged untreated, treated and aged treated whatman paper samples. The evaluation of these methods was as follow:

First method

This method was in accordance with Uhlin.[16] In this method, the intensities of the (10Ī) and (002) peaks were normalized against the (101) peak intensity. It was clear that the intensity of the (101) and peaks in the control sample are very closed (approximately equal), but intensity of the (002) peak was more than the (101) peak. The results (Figs. 8-9, and Table 2,3) revealed that accelerated heat ageing cycles led to increase of the (10Ī and 002) peaks more than the (101) peak. The highest increasing was obtained from the (10Ī) peak with heat ageing cycle. For the treated sample, the (10Ī and 101) peaks was approximately equal. The (002) peak slightly increased more than (101) peak. It should be said that the aged treated samples was lower in intensity more than aged untreated samples except the aged treated sample with heat ageing cycle, since it was approximately twice of the (101) peak.

Table 2: Intensity of untreated and aged untreated samples according to first method

Cellulose I	Control	Heat ageing	Heat-moist ageing	Heat-moist-light ageing
101	13750	13500	11500	10500
10Ī	0.98	1.69	1.43	1.48
002	1.36	1.44	1.65	1.45

Table 3: Intensity of treated and aged treated samples according to first method

Cellulose I	Control	Heat ageing	Heat-moist ageing	Heat-moist-light ageing
101	9500	16000	10750	7800
10Ī	1.03	1.94	1.14	1.22
002	1.16	0.75	1.05	1.18

Second method

Dimick[17] proposed a widely adopted crystallinity index for cellulose I which is quite easy to apply. The index is simply a linear intensity ratio of the (002) plane reflection and the minimum between the (002) and the (10$\bar{1}$) plane which is at about 19^{O} 2θ for Cu Kα radiation. The crystallinity index is calculated according to equation:

$CrI = [(I_{002} - I_{am})/(I_{002})] \times 100$

Where:

CrI = crystallinity index

I_{002} = intensity at approximately 22.6^{o} 2θ

I_{am} = intensity at approximately 19^{o} 2θ

This crystallinity index, which is based on the two-phase model of cellulose, has no absolute theoretical significance, but it is as good as any other approach for the relative ranking of cellulose I crystallinities. Therefore, this method was used in ranking the crystallinities of the cellulose examined.

The data obtained (Figs. 8, 9 and Table 4) showed that the highest crystallinity was obtained from untreated sample (control). With ageing the crystallinity decreased especially with heat-moist-light ageing cycle. It should be noticed that the crystallinity of treated paper was largely decreased as a comparison with untreated sample. The crystallinity of aged treated paper decreased to lower percentage. The low crystallinity was obtained from heat aged treated paper. The heat-moist-light aged treated paper gave better crystallinity more than heat and heat-moist ageing cycles.

Table 4: Crystallinity index of untreated, aged, treated and aged treated samples with all accelerated ageing cycles

Untreated and untreated samples	Crystallinity Index (%)	Treated and aged treated samples	Crystallinity Index (%)
Untreated sample	74.44	Treated sample	45.45
Heat aged sample	71.79	Heat aged treated sample	41.66
Heat-moist aged sample	73.68	Heat-moist aged treated sample	48.88
Heat-moist-light aged sample	67.21	Heat-moist-light aged treated sample	55.65

3.5. pH value of paper

pH of paper, like that of other materials, is expressed in terms of the concentration of hydrogen ions, which can be read off from a pH meter with a scale from 1 to 14.

It was clear from the data obtained (Fig. 10, and appendix 2) that the pH value of aged, treated and aged treated samples with all ageing cycles reduced as a comparison with untreated sample (control). The data proved that pH value of whatman paper was in the acidity level. By the application of index method proposed by Abdel-Maksoud[18], it was clear that the treated sample and aged treated samples were better than the untreated and aged untreated samples. This improvement of pH value of treated and aged treated was 4, 2.5 and 1.86 times with heat, heat-moist and heat-moist-light ageing cycles respectively.

The acidity of whatman paper either untreated or grafted may due to the following reasons:

- Overall weakness of the paper caused by inherent acidity of whatman paper. This causes the brittleness of the paper;
- A new discovery made in the research laboratories of the library of congress[19] (2006) shows that, as it ages, cellulose itself generates several acids, such as formic acid, lactic and oxalic acid, measurable quantities of these acids were observed to form within weeks of the manufacture of paper white stored under ambient conditions. It was also reported that these acids continue to accumulate within paper as they attach themselves to paper through strong intermolecular bonds, this explains why acid-free (pH neutral) papers also become increasingly acidic as they age. Acids are formed even in alkaline paper, although in this case they are probably neutralized by the alkaline reserve before they can do any damage to the cellulose molecule.
- Like cotton paper (such as whatman paper), acids formed within the papers or those absorbed from the environment (in this study, accelerated ageing act as strong environment) are neutralized before they have a chance to degrade cellulose chains. The primary source of acid in modern paper is the alum-rosin sizing agent introduced in the manufacturing

process. Size is added so that writing and printing inks do not feather – in the presence of moisture, the alum in the sizing agent generates sulfuric acid[20].

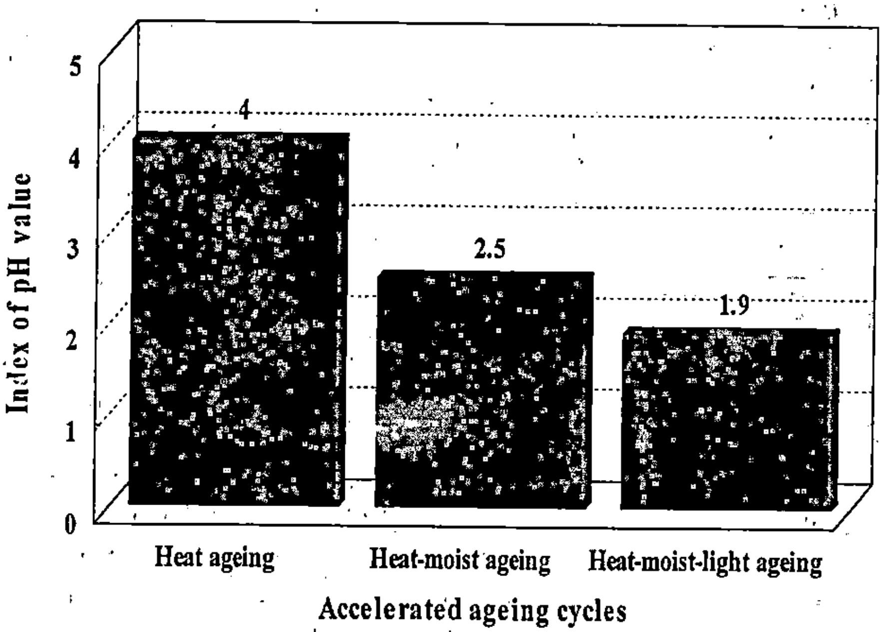

Fig. 10: Index of pH value of grafted whatman paper

4. Conclusion

1. The reduction in tensile strength was higher with untreated and aged untreated samples more than treated and aged treated samples. The big variation between untreated, aged untreated, and treated and aged treated, was obtained from heat-moist-light, heat-moist and heat ageing cycles respectively;
2. In elongation, the variation in the index method between ageing cycles for untreated, aged untreated, treated and aged treated was higher that tensile strength except with the heat ageing cycle;
3. For change of colour, little change was obtained from the treated samples. The change in colour increased with aged

untreated and aged treated samples. This means that the method of the treatment had a resistant against ageing cycles used.

4. Most of positions of the (101, 10Ī and 002) peaks of aged untreated and aged treated samples were shifted to lower values as a comparison with untreated and treated samples. This means that ageing cycles reduced the dimensions of the crystalline cellulose. The peak width of treated and aged treated whatman paper increased more than untreated and aged untreated samples. This indicates that the whatman paper treated decreased the degree of crystallinity of cellulose.
5. From the first method for the evaluation the intensity, it can be said that the intensity of heat aged untreated and heat aged treated samples, was high as a comparison with aged untreated, aged treated samples with heat-moist and heat-moist-light ageing cycles. The lower intensity was also obtained from the (002) peak with heat aged treated sample. The grafting process led to decrease the intensity of the (10Ī and 002) peaks with most of the sample studied as a comparison with untreated and aged treated with different ageing cycles. from the second method for the evaluation of the intensity, it can be said that the crystallinity of cellulose I not reached to complete crystallinity (100%). The crystallinity of treated and aged treated whatman paper is lower than the crystallinity of untreated and aged untreated samples. This may means that the grafting process led to the shrinkage of the cellulose I fibers;
6. The heat-moist-light ageing cycle was the most effective ageing cycle that reduced pH value of aged untreated and treated sample, followed by heat-moist ageing and the lowest reduction in pH of aged untreated and treated sample was obtained from heat ageing cycle.

References

1. Łojėwska, J., Miskowiec, P., Łojewska, T., Proniewicz, L.M., Cellulose oxidative and hydrolysis degradation in situ FTIR approach, Journal of Polymer Degradation and Stability, Vol. 88, 2005, pp. 512-520.
2. Cappitelli, F., Sorlini, C., Pedemonte, E., Princi, E., Vicini, S., Effectiveness of graft synthetic polymers in preventing biodeterioration of cellulose-based materials, Journal of Mcromol. Symp. Vol. 238, 2006, pp. 84-91.
3. Schaeffer, T.T., Baker, M.T., Blyth-hill, V., Reyden, D.V.D., Effects of aqueous light bleaching on the subsequent aging of paper, Journal of the American Institute for Conservation, Vol. 31, 1992, pp. 289-311.
4. Shahani, C.J., Hengemihle, F.H., Weberg, N., The effect of fluctuations in relative humidity on library and archival materials and their aging within contained microenvironments. In: Proceedings of the Pan-African Conference on Preservation and Conservation of Library and Archival Materials, Nairobi, Kenya, 21-25 June, 1993, pp. 61-70.
5. Norris, T.O., Overview of paper deterioration, In: Proceedings of the workshop on the effects of aging on printing and writing papers, ASTM Institute for Standards Research, Philadelphia, 1994, pp. 14-21.
6. Lattuate-Derieux, A., Bonnassies-Termes, S., Lavėdrine, B., Characterisation of compounds emitted during natural and artificial ageing of a book. Use of headspace – solid – phase micro extraction/ gas chromatography/ mass spectroscopy, Cultural Heritage, 7, 2006, pp. 123-133.
7. Baker, M.T., Historic textiles, papers, and polymers in museums, Chapter 10 "polymers in museums", Edited by Jeanette M. Cardamore and Marry T. Baker, American Chemical Society, Washington, Oxford University press, 2001, pp. 128-135.
8. Junior, J.L.P., 1999, The development of Micro-analytical methodologies for the characterization of the condition of

paper, 9th International Congress of IADA, Copenhagen, August 15-21, 1999, p. 107-114.

9. Abdel-Maksoud, G., Evaluation of wax or oil, fungicide formulations for preservation of vegetable-tanned leather artifacts, Journal of the Society of Leather Technologists and Chemists (JSLTC), No.2, Vol.90, 2006, pp.58-67.
10. Abdel-Maksoud, G., Marcinkowska, E., 1999, Evaluation of vegetable tanned leather after artificial ageing compared with archaeological samples, ICOM Committee for Conservation, 12th triennial meeting Lyon, 29 August-3 September 1999. P. 913.
11. Abdel-Maksoud, G., Marcinkowska, E., 2000, Changes in some properties of aged and historical parchment, Restaurator 2000; 21: 138.
12. Billmeyer, F.W., Saltzman, M., Principles of Colour Technology, New York, Wiley, 1981.
13. Trip, V.W., Measurement of crystallinity. In: Cellulose and cellulose derivatives, Vol. 5, Part 4, New York, Wiley-Interscience, 1971, pp. 305-324.
14. Kakudo, M., And Kasai, N., X-ray diffraction by polymers, Tokyo, Kodansha Ltd., 1972, p. 139.
15. Gjonnes, J., Morman, N., and Vierroll, H., Acta Chem. Scand. 12, 1958, pp. 489-494.
16. Uhlin, K.I., The influence of hemicellulose on the structure of bacterial cellulose, Doctor's dissertation, the Institute of Paper Science and Technology, Atlanta, Georgia, 1990, p.53.
17. Dimick, B.E., The importance of the structure of alkali metal hydroxide solutions in decrystallizing of cellulose I, Doctor's dissertation, the Institute of Paper Science and Technology, Atlanta, Georgia, 1976, p.48.
18. Abdel-Maksoud, G., Op.cit, 2006, pp. 58-67.
19. The Library of Congress., The deterioration and preservation of paper: some essential facts, October 18, 2006.

20. Gresp, C., and Vinas, V., The preservation and restoration of paper records and book: A ramp study with guidelines, UNESCO, 1985, pp. 11-16.

Appendix 1: Tensile strength and elongation of grafted whatman paper with accelerated ageing cycles

Samples	Heat ageing cycle	
	Tensile strength	Elongation
Untreated sample	22.74	2.65
Aged untreated sample	19.15	2.19
Treated sample	26.38	2.37
Aged treated sample	24.85	2.15
Samples	**Heat-moist ageing cycle**	
	Tensile strength	**Elongation**
Untreated sample	22.74	2.65
Aged untreated sample	17.80	1.97
Treated sample	26.38	2.37
Aged treated sample	22.15	1.95
Samples	**Heat-moist-light ageing cycle**	
	Tensile strength	**Elongation**
Untreated sample	22.74	2.65
Aged untreated sample	17.45	1.65
Treated sample	26.38	2.37
Aged treated sample	21.83	1.74

Appendix 2: Index method for the Determination of pH value of grafted whatman paper with all ageing cycles

Samples	pH value		
	Heat ageing cycle	Heat-moist ageing cycle	Heat-moist-light ageing cycle
New sample	6.58	6.58	6.58
Aged sample	6.50	6.48	6.45
Treated sample	6.54	6.54	6.54
Aged treated sample	6.52	6.50	6.47