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EVALUATION OF CELLULOSE ACETATE AND CHITOSAN USED FOR THE TREATMENT OF HISTORICAL PAPERS

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ABSTRACT

A lot of papers in museums and libraries suffer from unsuitable environmental conditions that can lead to brittleness and fragility. This study aims to evaluate the efficiency of cellulose acetate and chitosan at different concentrations for the preservation of historical papers. The untreated and treated samples were submitted to different accelerated ageing cycles. Analytical techniques used for the evaluation process were tensile strength and elongation measurement, UV-spectrophotometer, XRD, and SEM. The results revealed that heat-moist-light ageing cycle affected the properties studies more than other ageing cycles. The lower concentrations gave an improvement better than the higher concentrations of cellulose acetate and chitosan.

KEYWORDS: Historical paper, ageing, polymers, tensile strength, elongation, UV-spectrophotometer, XRD, SEM

INTRODUCTION

Manuscripts and other historical documents provide an important record of cultural heritage (Stuart, 2007). Many paper documents are found in their places in advanced state of degradation. These degradation processes of cellulose and/or lignin polymers are related to factors like temperature, moisture, pollutants, light and microorganisms (Proniewicz et al. 2002). Depending upon their natural ageing, the degradation of these documents is mainly due to both acid hydrolysis and oxidation mechanisms (Zou et al. 1994; Chamberlain and Priest 1998). The oxidative degradation of cellulose is primarily induced by the presence of oxygen, but the presence of water plays an essential role in the hydrolytic degradation of cellulose (Porck 2000). Accelerated ageing is considered one of the most important tools to prepare degraded paper similar to naturally aged paper, in order to be used in the experimental studies to evaluate conservation materials and techniques. There are many authors who have used different accelerated ageing techniques with different conditions for different purposes (Sclawy 1981; Mendenhall et al. 1981; Pearlstein et al. 1982; McNatt and Link 1989; Schaeffer et al. 1992; Hanus et al. 1995 and 1996; Letnar and Vodopivec 1997; Łojewska et al. 2004; Shahani 2004; Havermans, 2004; Missori et al 2004; El-Easely and Meeklenburg 2004; Joshi and Bhanot 2005; Kočar et al. 2005; Lattuati-Derieux et al. 2006; Yildiz and Gümüḳay 2007).

Protection of documents is a basic concept of archives conservation. Protection can be achieved in a variety of ways. One important archival protective technique is consolidation of weakened papers. Polymers have been in museums for as long as there have been museums. With the advent of synthetic polymers in the late 19th century, the number and types of polymers found in a museum increased, along with the number and types of associated problems (Baker 2001).

Chitosan is now widely available, is relatively inexpensive, has low toxicity, and shows great potential for varied chemical derivatizations and multiple physical forms. Thus, is an interesting compound to study in different applications (Ponce-Jimenez et al, 2002, Ponce-Jimenez et al., 2002). Cellulose acetate has been used in the preservation of museum collections from the early 1900's to the present day (Ballany et al., 2001). Cellulose acetate has been used for many purposes. It has good chemical stability. It was used as a consolidant, adhesive and as a coating (Horder, 1990, Botti et al., 1996).

This study aims to:

1. Establishing some materials that can be used in the conservation treatment of paper-based cultural heritage.
2. Studying the concentrations and conditions of polymers application in order to choose the best one to apply to the paper-based culture heritage.

MATERIALS AND METHODS

Historical papers

Two types of historical printed papers were used; Austrian Book paper (dating back to 1903 A.D.) and "Rivista di Diritto Commerciale paper" (dating back to 1934 A.D.). They were taken from Berio Library in Genoa, Italy.

Consolidants used

Two consolidants with different concentrations are used (Table 1).

Table 1: Scientific data for cellulose acetate and chitosan

Scientific data	Cellulose acetate	Chitosan
Specification	Substitution rate 40 acetyl groups	DDA 85%
Solubility	Acetone (wt/vol)	Distilled water (wt/vol)
Concentration (%)	1, 2, 3 , 4	0.5, 1, 1.5, 2
Chemical name	Cellulose acetate	Chitosan
Producer	Fluka Chemika	Sigma-Aldrich Co. Ltd.,(Germany)
Application method	Impregnation	Impregnation

I. ACCELERATED AGEING METHODS

Thermal ageing method

The test of temperature 100 °C for 10 days was performed in the laboratory inside the reaction oven using the dry air atmosphere. Moisture was evacuated from the oven using vacuum. The oven used in the thermal ageing is Heraeus D.63450 Hanau, Type: VT 6130M, vacuum type: (vacucenter1 Heraeus Instruments vacutherm, made in Germany).

Heat-moist ageing

This method is based on the exposure of the samples used to a constant temperature (70 °C) and a constant relative humidity (50%) for 10 days.

Heat-moist-light ageing

A temperature of 50 °C and a relative humidity cycling (12 hours) between 50% and 70% were used. Artificial light 300 – 600 nm (source of UV. Light); Xenon light 5000 W was applied for 10 days. The accelerated ageing chamber used was XENOTEST ISO ST, Atlas Material Testing Technology, Germany.

II. INVESTIGATION METHODS

Measurement of mechanical properties (tensile strength and elongation)

Tensile strength and elongation of the untreated and treated samples before and after different methods of ageing were measured by AG-5K NIS Ms (Shimadzu, Kyoto, Japan). These tests were done according to TAPPI Standard (TAPPI T494 om-88) as described by Junior (1999). The size of the samples 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 sample size was due to the fact that the size of the sample holder was 135mm long. The crosshead speed was reduced from 25 to 14 mm/min in order to keep the rate of strength as specified in the TAPPI Standard.

Measurement of color change by UV-spectrophotometery

Color changes caused by the effect of accelerated ageing cycles were measured using CIE L*a*b* system (Abdel-Maksoud and Marcinkowska 1999; Abdel-Maksoud and Marcinkowska 2000). 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. The total color difference (ΔE*) is calculated according to the following equation (Billmeyer 1981):

The measurement was made using Macbeth color eye 7000 (U.S.A.) UV-Spectrophotometer.

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

X-Ray diffraction (XRD) for the determination of the paper crystallinity

The selected untreated and treated samples before and after their treatment

with different ageing cycles was carried out on lab XRD 6000 (Shimadzu, Japan). The results of heat-moist-light ageing only were included as an example of ageing cycles used. Three peaks for the cellulose crystalline peaks (101, 10$\bar{1}$, and 002 peaks) were selected in the fitting of each diffractogram. The position (2θ degrees), the full width at half maximum (FWHM) (2θ degrees), and intensity were obtained from each fitted peak. The intensity was evaluated by two methods; the first method was in accordance with Uhlin (1990); and the second was in accordance with Dimick (1976).

Investigation of the surface morphology by SEM

A scanning electron microscope FEI (Netherlands) Model Quanta 200 was used to observe the surface morphology.

RESULTS AND DISCUSSION

Measurement of mechanical properties (tensile strength and elongation)

Austrian Book Paper samples: It was clear from data (Table 1) that ageing cycles used affected the untreated sample. The percentage of loss in tensile strength and elongation of aged untreated samples compared to untreated sample with heat-moist-light, heat-moist and heat ageing cycles respectively were 38%, 32%, and 21% for tensile strength, 52%, 44% and 29% for elongation. The treatment of Austrian Book paper samples with cellulose acetate and chitosan gave an improvement in tensile strength and elongation.

The data (Table 1) showed that the tensile strength and elongation of the samples treated with cellulose acetate increased with increasing the concentration of polymer. With aged treated samples, the percentage loss with all ageing cycles decreased with increasing the concentration of polymer (from the first to the third concentration). The loss percentage at the fourth concentration was higher than the other concentrations used except with heat-moist-light ageing cycle at the first concentration, and it was equal with the percentage of loss at the first concentration with heat-moist ageing cycle.

It was noticed from the data obtained (Table 2) that the tensile strength of the Austrian Book paper treated with chitosan increased with increasing the concentration of polymer. The loss in tensile strength of aged treated sample decreased with the first and the second concentrations, and increased with the third and the fourth concentrations. This may be due to that the viscosity of the polymer at the third and fourth concentrations increased, and the penetration of the polymer through the fibers structure became low. For elongation (Table 2), the first, second and the third concentrations gave an improvement. The loss of elongation decreased with increasing the concentration of polymer. The fourth concentration gave bad result and the loss of elongation increased more than the other concentrations used.

Rivista de Diritto Commerciale paper samples: It was clear from data (Table 3) that ageing cycles used affected the untreated sample. The loss percentage in tensile strength and elongation of aged untreated samples compared to untreated sample with heat-moist-light, heat-moist and heat moist ageing cycles respectively were 59%, 47%, and 29% for tensile strength, 57%, 44% and 30% for elongation.

Table 1: Tensile strength (N) and elongation (%) of untreated, aged untreated, treated and aged treated Austrian Book paper samples with cellulose acetate

Samples	Heat-moist-light ageing cycle		Heat-Moist ageing cycle		Heat ageing cycle	
	Tensile	Elongation	Tensile	Elongation	Tensile	Elongation
Untreated	34	1.33	34	1.33	34	1.33
Aged Untreated sample	21	0.642	23	0.75	27	0.94
	First concentration (1%)					
Treated sample	36	1.42	36	1.42	36	1.42
Aged treated sample	27	0.93	28	0.95	29	1.05
	Second Concentration (2%)					
Treated sample	37	1.55	37	1.55	37	1.55
Aged treated sample	29	1.05	30	1.10	31	1.20
	Third concentration (3%)					
Treated sample	40	1.60	40	1.60	40	1.60
Aged treated sample	32	1.10	33	1.15	34	1.25
	Fourth concentration (4%)					
Treated sample	43	1.58	43	1.58	43	1.58
Aged treated sample	31	1.04	31	1.07	32	1.10

Generally, the reduction in tensile strength and elongation of aged samples treated with cellulose acetate and chitosan was high with heat-moist-light, followed by heat-moist and heat ageing cycles. It was noticed for "Rivista di Diritto Commerciale" paper treated with cellulose acetate (Table 3) that the first and the second concentrations were enough. The third and the fourth concentrations were considered high and gave high loss in tensile strength with all ageing cycle. Loss of elongation was higher at the fourth concentration more than the other concentrations used.

For the samples treated with chitosan (Table 4), it was noticed for tensile strength that at the third concentration, the heat ageing affected the treated sample and the percentage of loss was higher than the second concentration with the same ageing method.

Table 2: Tensile strength (N) and elongation (%) of untreated, aged untreated, treated and aged treated Austrian Book paper samples with chitosan

Samples	Heat-moist-light ageing cycle		Heat-Moist ageing cycle		Heat ageing cycle	
	Tensile	Elongation	Tensile	Elongation	Tensile	Elongation
	First concentration (0.5%)					
Treated sample	35	1.39	35	1.39	35	1.39
Aged treated sample	25	0.85	26	0.88	27	1.0
	Second Concentration (1%)					
Treated sample	37	1.44	37	1.44	37	1.44
Aged treated sample	27	0.95	29	1.01	30	1.09
	Third concentration (1.5%)					
Treated sample	39	1.47	39	1.47	39	1.47
Aged treated sample	28	1.0	29	1.05	31	1.13
	Fourth concentration (2%)					
Treated sample	41	1.45	41	1.45	41	1.45
Aged treated sample	28	0.94	30	0.97	31	1.0

Table 3: Tensile strength (N) and elongation (%) of untreated, aged untreated, treated and aged treated "Rivista de Diritto Commerciale" paper samples with cellulose acetate

Samples	Heat-moist-light ageing cycle		Heat-Moist ageing cycle		Heat ageing cycle	
	Tensile	Elongation	Tensile	Elongation	Tensile	Elongation
Untreated	17	1.4	17	1.4	17	1.4
Aged Untreated sample	7	0.6	9	0.6	12	0.98
	First concentration (1%)					
Treated sample	19	1.48	19	1.48	19	1.48
Aged treated sample	10	0.95	13	0.98	14	1.05
	Second Concentration (2%)					
Treated sample	20	1.53	20	1.53	20	1.53
Aged treated sample	13	0.99	14	1.03	15	1.10
	Third concentration (3%)					
Treated sample	22	1.57	22	1.57	22	1.57
Aged treated sample	15	1.04	15	1.08	16	1.14
	Fourth concentration (4%)					
Treated sample	23	1.54	23	1.54	23	1.54
Aged treated sample	14	0.98	15	1.01	16	1.07

Table 4: Tensile strength (N) and elongation (%) of untreated, aged untreated, treated and aged treated "Rivista de Diritto Commerciale" paper samples with chitosan

Samples	Heat-moist-light ageing cycle		Heat-Moist ageing cycle		Heat ageing cycle	
	Tensile	Elongation	Tensile	Elongation	Tensile	Elongation
	First concentration (0.5%)					
Treated sample	19	1.45	19	1.45	19	1.45
Aged treated sample	10	0.92	11	0.94	14	1.02
	Second Concentration (1%)					
Treated sample	20	1.49	20	1.49	20	1.49
Aged treated sample	13	0.95	14	0.98	15	1.07
	Third concentration (1.5%)					
Treated sample	21	1.52	21	1.52	21	1.52
Aged treated sample	14	0.99	15	1.03	15	1.11
	Fourth concentration (2%)					
Treated sample	22	1.50	22	1.50	22	1.50
Aged treated sample	14	0.94	15	0.97	15	0.98

For elongation, it was also noticed that the loss of elongation was high with the fourth concentration both with cellulose acetate and with chitosan.

Change of color

Austrian Book paper samples: It was clear from the data that there was a big variation between the untreated, aged untreated, treated and aged treated with ageing techniques used. The color values can be explained as follows:

L-value: It was clear from the data (Table 5) that L-value of the untreated sample was near white color. After heat-moist-light ageing the sample became more lighter. This means that the ageing technique led to bleach the sample. After heat-moist and heat ageing cycles, the sample became darker compared to the untreated sample. The data showed that

the L-value of the heat-moist ageing was darker than the L-value obtained from the heat ageing cycle. L – value of the Austrian Book paper treated with cellulose acetate was lower than L-value of the untreated sample with all the concentrations used. With heat-moist-light ageing cycle, L-value of aged treated samples increased with increasing the concentration of the polymer. With heat-moist and heat ageing cycles, L-value decreased with increasing the concentration of the polymer. L-value of the aged treated Austrian Book paper increased with heat-moist-light ageing at all concentrations more than the treated samples with cellulose acetate.

For L-value of the Austrian Book paper treated with chitosan (Table 6), it became clear that L-value of the treated samples decreased with increasing the concentration of chitosan. L-value of the heat-moist-light aged sample was less than the untreated sample and more than the treated samples at all the concentrations used. With heat-moist and heat ageing cycles, L-value decreased with increasing the concentration of chitosan. The high decreasing in the L-value of the treated sample was with heat ageing cycle (4%) compared to the untreated sample.

a-value: a-value of the untreated sample was less red in color. The aged untreated samples with heat-moist ageing and heat ageing was red, but with heat-moist-light ageing cycle was less red. a-value of the treated samples with cellulose acetate and chitosan (Tables 5, 6) increased in red color with increasing the concentration of the polymers. It can be said that a-value of the aged treated samples became less red in color. The highest decreasing in the red color was obtained from heat ageing, followed by heat-moist ageing, except with the first concentration of chitosan with heat-moist ageing cycle. The lower reduction in the red color was obtained from heat-moist-light ageing cycle.

b-value: b-value of the untreated sample was 13.73. After ageing, this value decreased with heat-moist-light ageing cycle. With heat-moist and heat ageing cycles, this value increased more than the untreated sample. The increasing of b-value with heat-moist ageing cycle was higher than the value obtained from heat ageing cycle. b-value of the treated samples with cellulose acetate and chitosan (Tables 5, 6) increased more than the untreated sample. b-value increased with increasing the concentration of polymers used. For the aged treated samples, b-value decreased with increasing the concentration of polymers. The lower reduction in b-value of the aged treated samples was obtained from heat-moist-light ageing, followed by heat-moist and heat ageing cycles.

ΔE (total color difference): there was a big variation between the untreated and aged treated samples. For the aged untreated samples, the highest change in ΔE was obtained from heat-moist ageing cycle, followed by the heat-moist-light ageing and heat ageing. For the samples treated with cellulose acetate, the total color differences decreased. The E-value of the aged treated samples increased in regard to the treated samples.

Rivista de Diritto Commerciale paper samples: L-value: it was clear from the data (Table 7) that the L-value of the aged untreated sample decreased compared to the untreated sample. The highest decreasing in L-value was obtained from heat-moist ageing, followed by heat-moist-light and heat ageing cycles.

Table 5: The effect of ageing cycles on the change of color of the untreated, aged untreated, treated and aged treated Austrian Book paper samples with cellulose acetate

Samples	Heat-moist-light ageing				Heat-moist ageing				Heat ageing			
	Color values				Color values				Color values			
	L	a	b	ΔE	L	a	b	ΔE	L	a	b	ΔE
Untreated	88.13	1.00	13.73	0.0	88.13	1.00	13.73	0.0	88.13	1.00	13.73	0.0
Aged untreated	88.65	-0.29	5.71	8.07	81.13	1.56	19.70	9.22	82.20	1.12	17.20	6.87
	First concentration											
Treated	88.0	1.20	13.50	0.33	88.0	1.20	13.50	0.33	88.0	1.20	13.50	0.33
Aged treated	89.35	-0.33	10.15	3.84	87.13	-0.50	11.15	.81	87.05	-0.60	12.19	1.92
	Second concentration											
Treated	87.95	1.35	14.20	0.61	87.95	1.35	14.20	0.61	87.95	1.35	14.20	0.61
Aged treated	89.50	-0.40	9.50	4.49	86.80	-0.70	10.40	3.60	86.75	-0.78	11.37	2.74
	Third concentration											
Treated	87.90	1.60	14.70	1.16	87.90	1.60	14.70	1.16	87.90	1.60	14.70	1.16
Aged treated	89.73	-0.75	8.53	5.45	86.40	-1.30	9.89	4.22	86.20	-1.50	.30	3.97
	Fourth concentration											
Treated	87.80	1.80	15.30	1.79	87.80	1.80	15.30	1.79	87.80	1.80	15.30	1.79
Aged treated	89.92	-1.10	7.30	6.68	86.10	-1.70	9.50	4.74	85.90	-1.85	9.90	4.5

Table 6: The effect of ageing cycles on the change of color of the untreated, aged untreated, treated and aged treated Austrian Book paper samples with chitosan

Samples	Heat-moist-light ageing				Heat-moist ageing				Heat ageing			
	Color values				Color values				Color values			
	L	a	b	ΔE	L	a	b	ΔE	L	a	b	ΔE
	First concentration											
Treated	87.12	1.28	14.75	1.46	87.12	1.28	14.75	1.46	87.12	1.28	14.75	1.46
Aged treated	87.70	-0.56	13.20	0.81	86.22	0.67	13.55	1.95	86.0	-1.05	13.85	2.13
	Second concentration											
Treated	86.80	1.40	15.20	2.02	86.80	1.40	15.20	2.02	86.80	1.40	15.20	2.02
Aged treated	87.50	-0.82	11.50	2.32	85.90	-0.93	12.30	2.65	85.50	-1.22	13.0	2.74
	Third concentration											
Treated	86.14	1.62	16.10	3.16	86.14	1.62	16.10	3.16	86.14	1.62	16.10	3.16
Aged treated	86.85	-0.95	10.14	3.81	85.16	-1.12	11.95	3.46	84.70	-1.37	12.50	3.66
	Fourth concentration											
Treated	85.90	1.87	16.66	3.78	85.90	1.87	16.66	3.78	85.90	1.87	16.66	3.78
Aged treated	86.15	-1.15	10.12	4.12	84.80	-1.25	11.06	4.28	84.17	-1.52	11.92	4.38

For the treated samples with cellulose acetate and chitosan (Table 7, 8), the L-value decreased more than with the un-treated sample. This reduction in L-value increased with increasing the concentration of polymers used. The reduction in L-value

with chitosan was higher than with cellulose acetate. For the aged treated samples, the reduction in L-value was higher than the treated and aged untreated samples with most of the concentrations used.

a-value: a-value of the untreated sample was less red in color. After ageing, the untreated sample was less red with heat-moist-light ageing, and became red in color with heat-moist and heat ageing cycles. a-value of the treated samples with cellulose acetate and chitosan was red in color with the first concentration and less red in color with the other concentrations used. a-value of the aged treated samples was red in color with all the concentrations used.

b-value: b-value of the heat-moist-light aged samples decreased more than the untreated samples, but the heat-moist aged sample and heat aged sample increased more than the untreated sample.

b-value for the treated and the aged treated samples with all ageing techniques were higher than the untreated and aged untreated samples. This means that the polymers used lead to change the b-value to be more yellow.

ΔE (the total color difference): the total color difference ΔE of the aged samples varied. ΔE with heat-moist-light ageing was 3.42, with heat-moist ageing was 6.75 and with heat ageing was 6.42. For the treated and aged treated samples, the changes in the total color were higher than the aged untreated samples. It was noticed that the change in the total color increased with increasing the concentration of the polymers used.

Table 7: The effect of ageing cycles on the change of color of the untreated, aged untreated, treated and aged treated "Rivista di Diritto Commeriale" paper samples with cellulose acetate

Samples	Heat-moist-light ageing				Heat-moist ageing				Heat ageing			
	Color values				Color values				Color values			
	L	a	b	ΔE	L	a	b	ΔE	L	a	b	ΔE
Untreated	87.20	-1.61	9.03	0.0	87.20	-1.61	9.03	0.0	87.20	-1.61	9.03	0.0
Aged untreated	84.80	-0.32	7.55	3.42	82.70	1.20	13.20	6.75	83.50	1.30	13.40	6.42
	First concentration											
Treated	83.70	0.98	14.15	6.72	83.70	0.98	14.15	6.72	83.70	0.98	14.15	6.72
Aged treated	82.50	2.23	17.60	10.5	82.75	2.05	16.20	9.20	82.05	2.37	17.83	10.95
	Second concentration											
Treated	83.20	-0.52	14.80	7.34	83.20	-0.52	14.80	7.34	83.20	-0.52	14.80	7.34
Aged treated	82.05	2.53	18.50	11.55	82.47	2.10	17.30	10.22	81.93	2.78	18.85	11.98
	Third concentration											
Treated	82.60	-0.62	15.67	8.38	82.60	-0.62	15.67	8.38	82.60	-0.62	15.67	8.38
Aged treated	81.25	2.27	19.20	12.41	81.73	1.97	18.10	11.18	80.92	2.45	19.46	12.83
	Fourth concentration											
Treated	82.07	-0.71	16.10	9.04	82.07	-0.71	16.10	9.04	82.07	-0.71	16.10	9.04
Aged treated	80.50	2.45	19.93	13.42	81.20	2.06	18.56	11.84	80.08	2.83	20.20	13.97

Table 8: The effect of ageing cycles on the change of color of the untreated, aged untreated, treated and aged treated "Rivista di Diritto Commeriale" paper samples with chitosan

Samples	Heat-moist-light ageing				Heat-moist ageing				Heat ageing			
	Color values				Color values				Color values			
	L	A	b	ΔE	L	a	b	ΔE	L	a	b	ΔE
	First concentration											
Treated	83.30	1.10	14.32	7.11	83.30	1.10	14.32	7.11	83.30	1.10	14.32	7.11
Aged treated	82.33	2.31	16.88	10.04	82.80	2.31	15.30	8.60	82.10	2.50	16.30	9.79
	Second concentration											
Treated	82.97	-0.75	14.55	7.34	82.97	-0.75	14.55	7.34	82.97	-0.75	14.55	7.34
Aged treated	81.95	2.72	18.71	11.83	82.41	2.42	17.07	10.19	81.70	2.80	17.20	10.79
	Third concentration											
Treated	82.23	-0.71	15.80	8.71	82.23	-0.71	15.80	8.71	82.23	-0.71	15.80	8.71
Aged treated	81.17	2.38	19.20	12.48	81.21	2.10	18.18	11.55	80.78	3.10	18.40	12.30
	Fourth concentration											
Treated	81.98	-0.83	15.95	9.0	81.98	-0.83	15.95	9.0	81.98	-0.83	15.95	9.0
Aged treated	80.41	2.62	19.99	13.57	80.70	2.17	18.53	12.12	79.40	4.5	19.20	14.20

X-RAY DIFFRACTION (XRD) FOR THE DETERMINATION OF THE PAPER CRYSTALLINITY AND THE AUSTRIAN BOOK PAPER

Peak position (2θ degrees)

It was clear from the data obtained (Fig. 1) increased more that the heat aged untreated sample than the untreated sample.

This may indicate that the heat ageing increased the dimension of the crystalline area. After the treatment with cellulose acetate and chitosan, the peak position (101) decreased more than the untreated sample. This may indicate that the treatment with polymers caused the shrinkage of the fibers and crystalline area. The peak position (101) of the aged treated sample slightly increased more than the treated samples. The position of the $10\bar{1}$ peak of the heat aged samples was shifted to lower position than the untreated sample (this decreasing was 0.24%). The position of the $10\bar{1}$ peak of the treated sample with chitosan was lesser than the untreated sample (0.71%), but the treated sample with cellulose acetate slightly increased more than the untreated sample. The position of the ($10\bar{1}$) peak of the aged treated samples with cellulose acetate and chitosan were lesser than the untreated sample.

The peak position (002) of the heat aged untreated sample was lesser than the untreated sample. The treated samples increased (0.44%) and the aged treated samples increased with chitosan and decreased with cellulose acetate.

Peak width (2θ degrees)

The width of the peaks (101, $10\bar{1}$ and 002) of the heat aged untreated samples was higher than that of the untreated sample. The increasing of the peak width affected the intensity of the same peak. In this study, the intensity of the untreated sample was higher than the intensity of the aged untreated sample.

The peak width of the treated and aged treated was lesser than that of the untreated sample. It should also be said that the width of the peaks of the aged samples treated with cellulose acetate or chitosan was equal to or more than the width of the treated sample.

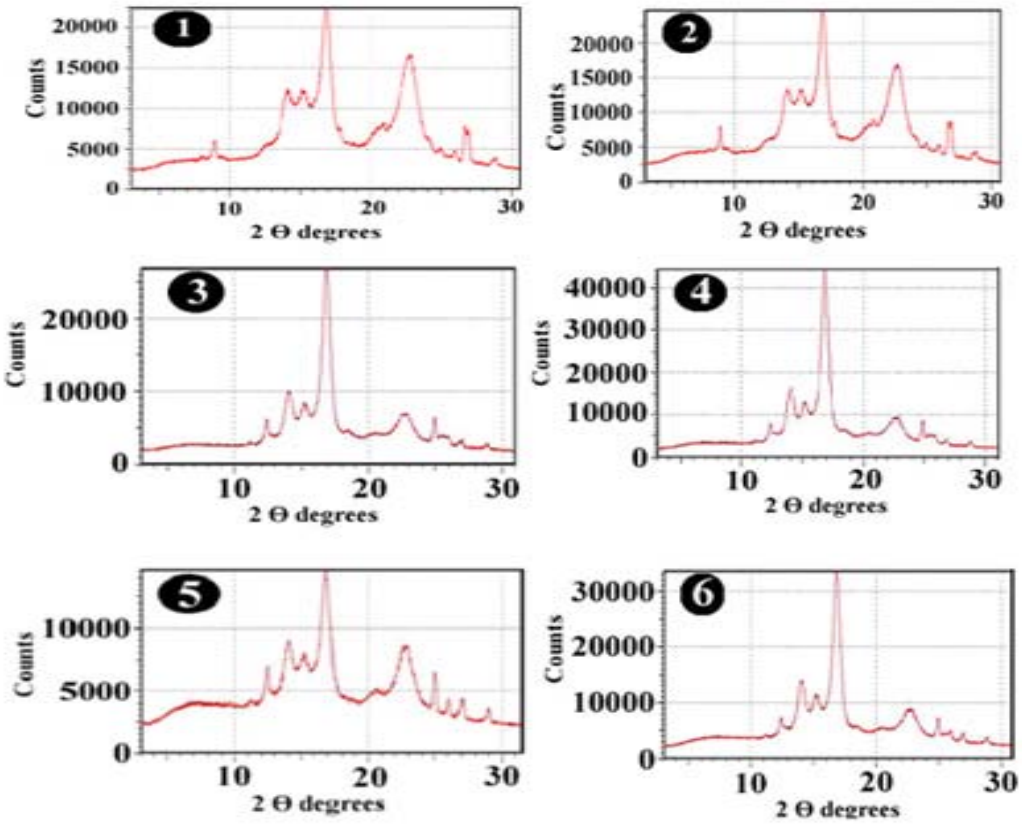

Fig. 1: X-ray diffractogram of Austrian Book paper treated with cellulose acetate and chitosan at the second concentration before and after accelerated heat ageing cycle: (1) Untreated sample, (2) Heat aged untreated sample, (3) Treated sample with cellulose acetate, (4) Aged treated sample with cellulose acetate, (5) Treated sample with chitosan, (6) Aged treated sample with chitosan

Peak intensity (2θ degrees)

First method

It was clear from the data obtained (Table 9) that the intensity of the (10$\bar{1}$) and (002) peaks of the untreated and aged untreated samples was higher than the intensity of the 101 peak. The intensity of the 10$\bar{1}$ peak with the treated and aged treated samples with cellulose acetate and chitosan was also higher than the intensity of the 101 peak. The intensity of the 002 peak of the treated and aged treated samples with cellulose acetate were lower than the intensity of 101 peak. The intensity of 002 peak of the treated sample with chitosan was higher, and the aged treated was lower than the intensity of the 101 peak.

Second method

It was clear from the data (Table 9) that the crystallinity of the aged untreated sample decreased compared to the untreated sample. The treated and aged treated samples with cellulose acetate increased the crystallinity of cellulose fibers. The treated sample with chi-

tosan increased the crystallinity but the aged treated sample decreased the crystallinity of the cellulose fiber. Generally, it can be said that the results obtained by x-ray diffraction from cellulose acetate were better than the results obtained from chitosan.

Table 9: Intensity and crystallinity index of the Austrian Book paper treated with cellulose acetate and chitosan before and after accelerated heat ageing cycle at the second concentration

Samples	*Intensity of cellulose 1*			*Crystallinity index*
	101	**10Ξ**	**002**	
UNTREATED SAMPLE	12500	1.8	1.32	67
Aged untreated sample	13000	1.88	1.27	64
Treated sample with cellulose acetate	10000	2.7	0.7	79
Aged treated sample with cellulose acetate	16000	2.81	0.59	79
Treated sample with chitosan	9000	1.66	1.5	69
Aged treated sample with chitosan	15000	2.27	0.57	41

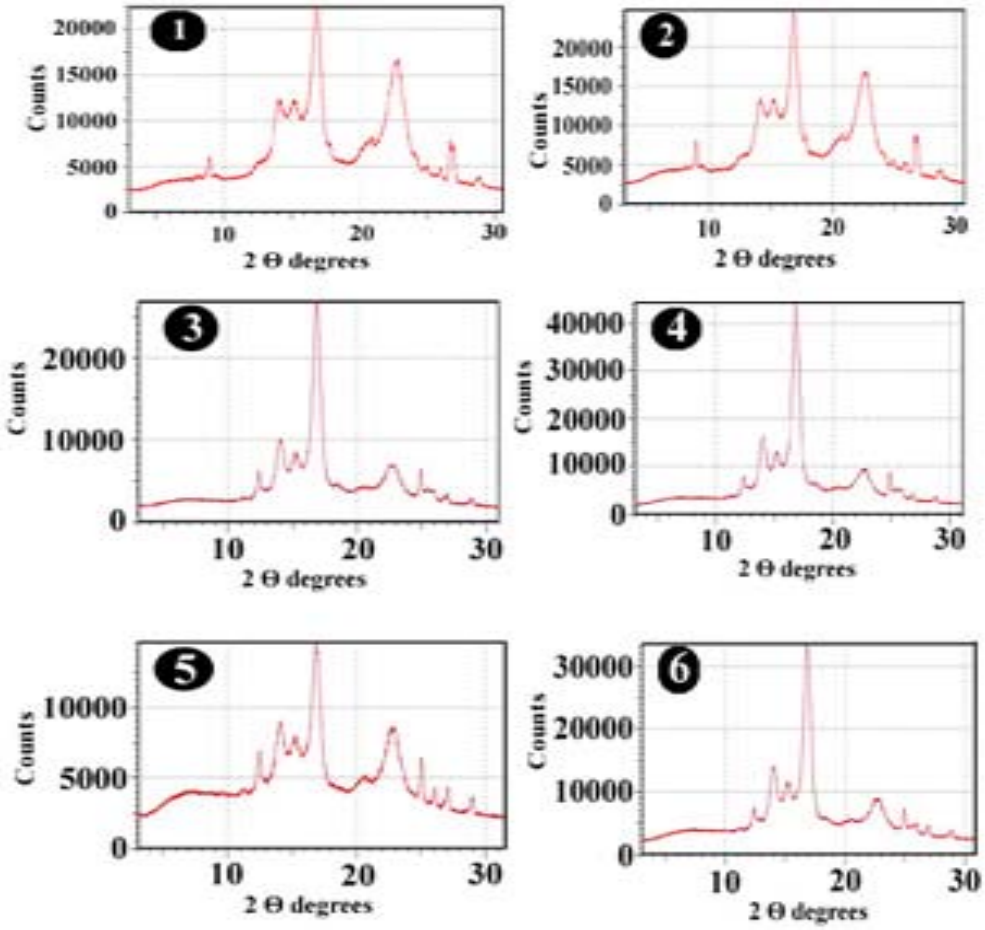

Fig. 2: X-ray diffractogram of Rivista de Diritto Commerciale paper treated with cellulose acetate and chitosan at the second concentration before and after accelerated heat ageing cycle: (1) Untreated sample, (2) Heat aged untreated sample, (3) Treated sample with cellulose acetate, (4) Aged treated sample with cellulose acetate, (5) Treated sample with chitosan, (6) Aged treated sample with chitosan

X-RAY DIFFRACTION OF THE RIVISTA DE DIRITTO COMMERCIALE PAPER

Peak position (2θ degrees)

It was clear from the data (Fig. 2) that the position of the peaks 101, 10$\bar{1}$, 002 of the aged untreated sample was higher than the position of the same peaks of the untreated sample. It means that the heat ageing caused expanding of the dimension of the crystalline area. For the samples treated with cellulose acetate, the dimensions of the 101, 10$\bar{1}$, and 002 peaks expanded more than those of the untreated samples. For the heat aged treated sample, the dimensions of the peak 101 was contracted and the dimensions of the peaks 10$\bar{1}$ and 002 were expanded. For the treated and aged treated samples with chitosan, the peaks 10$\bar{1}$ and 002 were expanded. The peak 101 was contracted after the treatment and the peak position was equal with the peak position of the untreated sample.

Peak width (2θ degrees)

The width of the peaks 101, 10$\bar{1}$ and 002 of the aged untreated sample were higher than the peak width of untreated sample. The width of the peaks 101, 10$\bar{1}$ and 002 of the treated and aged treated samples with chitosan and cellulose acetate were lower than the untreated and aged untreated samples.

Peak intensity (2θ degrees)

First method

The data obtained (Table 10) showed that the intensity of the 101 peak of the aged untreated, treated and aged untreated samples was lower than the intensity of the untreated sample except with the treated sample with cellulose acetate. For the intensity of the peak (10$\bar{1}$) of the aged untreated and treated sample with cellulose acetate was lower than the intensity of the untreated sample. The intensities of the aged treated sample with cellulose acetate, treated and aged treated samples with chitosan were higher than the intensity of the untreated sample. For the intensity of the peak 002, the aged untreated sample was higher and the treated and the aged treated samples with cellulose acetate and chitosan were lower than the intensity of the untreated sample.

Second method

It was clear from the data (Table 10) that the crystallinity of the treated and aged treated sample with cellulose acetate and chitosan were lower than the untreated sample except with the treated sample with cellulose acetate.

Table 10: Intensity and and crystallinity index of the Rivista de Diritto Commerciale paper treated with cellulose acetate and chitosan before and after accelerated heat ageing cycle at the second concentration

Samples	*Intensity of cellulose 1*			*Crystallinity index*
	101	**10Ξ**	**002**	
UNTREATED SAMPLE	18000	2.17	0.83	53
Aged untreated sample	13000	1.77	1.23	56
Treated sample with cellulose acetate	27500	0.84	0.29	56
Aged treated sample with cellulose acetate	12000	2.5	0.66	50
Treated sample with chitosan	16000	2.63	0.34	9
Aged treated sample with chitosan	8500	2.35	0.53	33

Investigation of the surface morphology by SEM

It was clear from the data (Fig. 3A) that the fibers of the untreated sample were very clear and strong. The fibers were from Agricultural fibers. The distances between fiber structures were very close. The distribution of the fibers was changes with the changes of the ageing technique. With heat aged sample (Fig.3B), there was very this cracks, the distribution of the fibers was randomly. With heat aged sample (Fig.3C) some destruction was noticed and the fibers seem to be very week. The low reduction of the fiber structure was noticed from heat aged sample (Fig.3D).

After the treatment of the Austrian Book paper with cellulose acetate (Fig. 4A), the fibers became more strong and smooth. The penetration of the polymer used was very good. With heat-moist-light ageing (Fig. 4B), some destruction was noticed. The bibbers became little thin compared to the untreated sample. With heat-moist ageing (Fig. 4C), the destruction was more than with heat-moist-light ageing. Very small amount of the fillers was noticed. With heat ageing (Fig. 4D), the fibers were stronger compared to the other ageing techniques used. The treatment of the Austrian Book paper sample with chitosan, the distance between the fiber structures was not noticed (Fig. 5A).

The penetration of the polymer was not good compared with cellulose acetate. With heat-moist-light (Fig. 5B)), high destruction was noticed. The destruction with heat-moist ageing (Fig. 5C) was less compared with heat-moist-light ageing cycle. The lower destruction was obtained from heat ageing cycle (Fig. 5D).

For the untreated Rivista de Diritto Commerciale paper (Fig. 6A), the fibers was from wood fibers. the fibers were flat and coarse. With heat-moist-light ageing (Fig. 6B), many destruction such as cracks, and not complete fillers were also noticed. The filler seems to be from calcite. With heat-moist ageing (Fig. 6C), the signs of the wood fibers were also noticed. Much destruction was observed. The effect of heat ageing cycle was lesser than the other ageing methods used.

For the treated sample with cellulose acetate (Fig. 7A), the fibers were strong and smooth and the penetration of the polymer between the fiber structure was goo. It can be said that little destruction was noticed with all ageing cycles (Figs. 7B, 7C and 7D). The fibers treated with chitosan (Fig. 8A) were covered with the polymer used. The fibers were strong. Very big destruction was obtained with all ageing cycles (Figs. 8B, 6C and 8D) especially with heat-moist-light ageing. The lower destruction was obtained from heat aged sample (Fig. 8D).

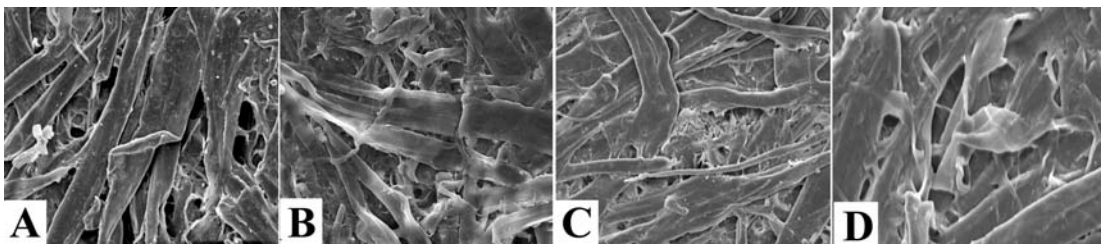

Fig. 3: Scanning electron micrographs of the untreated and aged untreated of the Austrian Book paper: (3A) Untreated sample (Magn. 1000), (3B) Heat-moist-light aged untreated sample (Magn. 1000), (3C) Heat-moist aged untreated sample (Magn. 1000) (3D) Heat aged untreated sample (Magn. 1000).

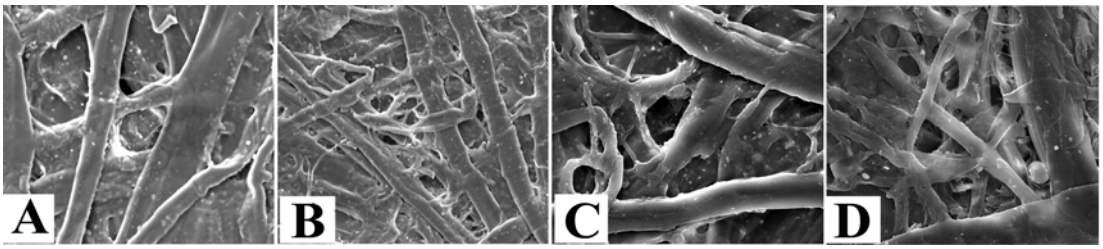

Fig. 4: Scanning electron micrographs of the treated and aged treated of the Austrian Book paper with cellulose acetate at the second concentration: (4A) Treated sample (Magn. 1300), (4B) Heat-moist-light aged treated sample (Magn. 1300), (4C) Heat-moist aged treated sample (Magn. 1300), (4D) Heat aged treated sample (Magn. 1300)

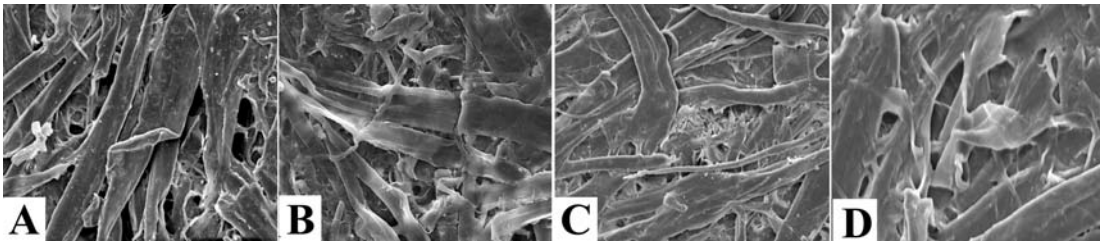

Fig. 5: Scanning electron micrographs of the treated and aged treated of the Austrian Book paper with chitosan at the second concentration: (5A) Treated sample (Magn. 900), (5B) Heat-moist-light aged treated sample (Magn. 1100), (5C) Heat-moist aged treated sample (Magn. 1000), (5D) Heat aged treated sample (Magn. 1000)

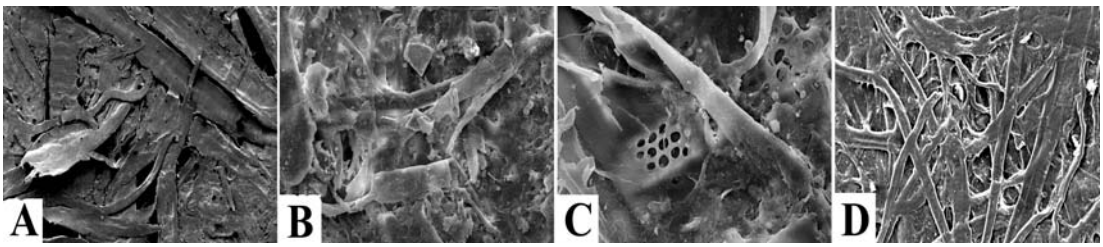

Fig. 6: Scanning electron micrographs of the untreated and aged untreated of the Rivista de Diritto Commerciale paper: (6A) Untreated sample (Magn. 600), (6B) Heat-moist-light aged untreated sample (Magn. 600), (6C) Heat-moist aged untreated sample (Magn. 600) (6D) Heat aged untreated sample (Magn. 600).

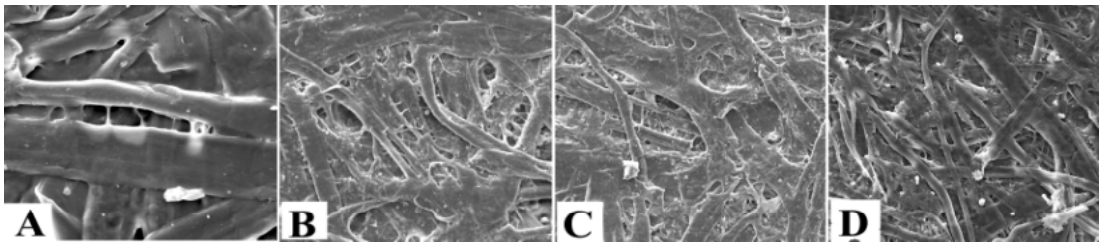

Fig. 7: Scanning electron micrographs of the treated and aged treated of the Rivista de Diritto Commerciale paper with cellulose acetate at the second concentration: (7A) Treated sample (Magn. 1100), (7B) Heat-moist-light aged treated sample (Magn. 1000), (7C) Heat-moist aged treated sample (Magn. 1000), (7D) Heat aged treated sample (Magn. 900)

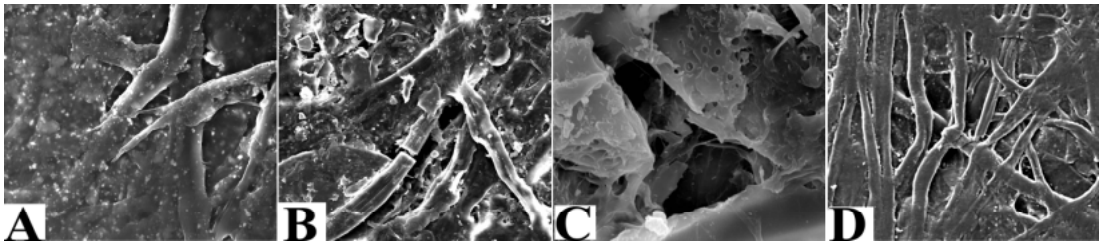

Fig. 8: Scanning electron micrographs of the treated and aged treated of the Rivista de Diritto Commerciale paper with cellulose acetate at the second concentration: (8A) Treated sample (Magn. 1000), (8B) Heat-moist-light aged treated sample (Magn. 1000), (8C) Heat-moist aged treated sample (Magn. 2000), (8D) Heat aged treated sample (Magn. 1000)

CONCLUSIONS

1. The first and second concentrations of cellulose acetate and chitosan succeeded to treat Austrian Book paper and "Rivista di Diritto Commerciale" paper. The third and fourth concentrations should be rejected. The results obtained show that the mechanical properties (tensile strength and elongation) of Austrian Book papers treated with cellulose acetate and chitosan were better than tensile strength and elongation of "Rivista di Diritto Commerciale" treated with the same polymers.
2. The results confirmed that the treatment of the Austrian Book paper samples with polymers decreased the color difference (ΔE). ΔE values of the treated and aged treated samples were better than the ΔE of the aged untreated samples.
3. For the Austrian Book paper, the heat ageing cycle slightly affected the peak positions. Some peaks increased and the other decreased the crystallinity dimension. It can be added that the increasing or decreasing in the crystallinity dimensions was considered very low. This indicates that the untreated or treated paper had good stability towards ageing method.
4. By the study of the crystallinity index, it was clear that the use of cellulose acetate increased the crystallinity of the Austrian Book paper before and after heat ageing cycle. The use of chitosan increased the crystallinity before ageing and decreased the crystallinity after heat ageing.
5. The crystallinity of cellulose fibers of the Rivista de Diritto Commerciale was affected by the use of polymers. The crystallinity of the sample treated with cellulose acetate was better than the crystallinity of the untreated sample. The crystallinity of the aged sample treated with cellulose acetate, treated and aged treated samples with chitosan was lower than the crystallinity of the untreated sample;
6. The surface morphology of the papers treated with cellulose acetate was better than the papers treated with chitosan at the second concentration. The surface morphology of the Austrian Book paper treated with the polymers used was better than the Rivista de Diritto Commerciale papers treated with the same polymers. The second concentration was the best concentration for the papers treated with cellulose acetate and chitosan.

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