Effects of Artificial Weathering on the Mechanical Properties of Paper-Based Materials Consolidated with Polymeric Materials

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ABSTRACT: The study of polymer behavior over time represents the crucial stage in the setup of innovative methodologies for paper restoration. In this research, a series of laboratory simulations by accelerated aging and characterization tests by chemical and physical measurements were carried out on paper samples consolidated both by grafting polymerization with acrylic copolymers and by coating with waterborne polyurethanes with the aim of determining their harmlessness and long-term effectiveness. In this way, our purpose was not only to verify possible risks for the paper materials but also to determine the advantages and potentialities of new restoration methods through an appropriate and essential working plan of investigations. From our evaluation, both the selected consolidation methods appeared unsuitable to be used in paper restoration because of the damage that they could cause on the paper materials because of their limited durability over time. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 3529–3536, 2009

Key words: ageing; coatings; degradation; mechanical properties; polyurethanes

INTRODUCTION

The use of polymeric materials for the consolidation and protection of paper or, in general, of cellulose-based materials is uncommon and, until now, only a small number of studies have been carried out.[1,2] Polymers have been applied in a few cases when traditional restoration methods have not been sufficient to improve the mechanical resistance of degraded artworks, but the materials employed have usually been commercial products with properties not tailored for the conservation of these items. Currently, no polymeric products exist with suitable characteristics for the conservation of paper because of their irreversibility treatment, which can damage materials.

Starting from these considerations, in our laboratory, we investigated new acrylic products and an innovative technique for the conservation of paper to study the effects of other methods of intervention: the grafting polymerization of acrylic monomers in the vapor phase photoinduced by UV radiation and coating with waterborne polyurethanes (PUs).

At first, graft polymerization can induce chemical changes in cellulose, and the introduction of polymer chains can confer different structural characteristics to the raw material. The properties of the grafted copolymer can be tailored by the chemical structure of the monomers, the length of the grafted segment, and the grafting level.[3] In this way, new cellulose-based products can be obtained with mechanical properties better than those of conventional cellulose. Acrylic monomers appear particularly suitable for grafting onto cellulose because of their characteristics, such as water repellence, transparency, and good filmability. Grafting directly from the vapor phase results in enhanced mechanical resistance of the degraded paper without the alteration of its typical flexibility, and importantly, no superficial coatings are formed on the grafted samples.[4,5]

In this research, the grafting polymerization of an acrylic copolymer expressly tailored for cellulose-based materials, 75/25 wt % ethyl acrylate (EA)/methyl methacrylate (MMA), was performed on different paper samples. In a previous article, we reported a complete study concerning the synthesis and characterization of the best acrylic copolymer to be used for the grafting process.[6] This study indicated that 75/25 wt % EA/MMA could be

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successfully used in the grafting polymerization onto cellulose because the introduction of EA units leads to a low-glass-transition-temperature material (10°C), which makes the product more efficient as a consolidating product. Moreover, because of the generally hydrophobic nature of acrylics, it can also perform a protective function for the paper.

Another way to encourage the use of polymers in the conservation of paper artwork is to find appropriate polymeric materials to be used as coatings and adhesives. In our study, we considered two commercial waterborne PUs: a polyester-based product (PES 995) and a polycarbonate one (PC 954).

Waterborne PUs have been synthesized by the well-known process known as prepolymer mixing, in which first the prepolymer is produced and, then, water is added.[7,8] It is a step process, in which a diisocyanate is mixed, with a polyol forming in each step, with a polyaddition mechanism in bulk (without solvent), and a prepolymer. The polyol can be polyester-, polyether-, or polycarbonate-based, depending on the nature of the final material.[8]

Waterborne PUs form films at ambient temperature and exhibit excellent adhesion to many surfaces, such as wood, concrete, leather, cellulose, metal, and some polymers.[7] Generally, films from waterborne PUs show high toughness, excellent adhesion, good hardness/elasticity relationships, remarkable mechanical and abrasion resistances, gloss, and water repellence. With the modulation of these properties and the choice of suitable reagents, it is possible to have a good product to consolidate and protect paper.

The choice of the best polymer to apply on paper depends not only on its properties but also on the film characteristics, such as flexibility and transparency; it is clear that no products exist with all these features. Moreover, over the course of time, polymers degrade; thus, their raw properties change their performances.

The tailoring of suitable polymeric materials to be used in paper conservation is actually one of the main goals in the field of chemistry for cultural heritage. Before the introduction of new methods for paper restoration based on polymers, it is essential to evaluate their suitability, stability, and durability from the point of view of conservative aims.[9] In the literature, many investigations on the thermal aging of grafted systems,[10–12] PU stability[13,14] and UV degradation of cellulose[15,16] have been reported.

Polymers useful as consolidating and protective products should have well-defined characteristics and specific properties, such as efficacy, reversibility, and permanence. Moreover, no changes in the paper appearance (yellowing, darkening, etc.), thickness, or handling should be observed after their application.

In our research, with regard to both destructive and nondestructive methodologies, the efficacy and durability of the selected conservative treatments were monitored in the laboratory by

- Colorimetric tests to detect any variation in the paper appearance.[17]
- Mechanical measurements to verify changes in specific mechanical characteristics, such as folding endurance and tearing resistance.[18] The normal use of paper includes its handling; therefore, the evaluation of the mechanical properties should be one of the principal focuses of all stability studies.

Measurements were performed before and after artificial aging on some model paper samples consolidated both by the grafting polymerization of acrylics and by coating with waterborne PUs to evaluate the long-term effect of these polymeric materials when they were used to consolidate and protect paper artwork.

EXPERIMENTAL

Materials

Three different types of paper were selected to set up the conservative treatments:

- Whatman N 1 chromatographic paper (Carlo Erba, Milano, Italy; grammage = 70 g/m^2). This was manufactured from high-quality cotton linters (minimum α-cellulose content = 98%) without additives.
- Newsprint paper (Cartiere Burgo, Toring, Italy; grammage = 65 g/m^2). This was made largely from mechanical pulp and/or waste paper; it contained bleached cellulose, recycled fibers after deinking, starch, a noticeable amount of fillers (≅ 20%) as calcium carbonate, kaolin, and magnesium carbonate.[19] It was one of the least expensive printing papers.
- Paper coming from an Austrian book dated 1903, in which the printed sheets showed evident traces of oxidation on the borders. It contained cellulose, kaolin, and barium sulfate as fillers and an organic ink for printing.[19]

Reagents were commercial products supplied by Aldrich (Milano, Italy). Monomers (MMA and EA) contained an inhibitor (hydroquinone monomethylether), which was removed by being passed through an Aldrich Inhibitor Removers column; the purified monomers were subsequently stored at low temperature (4°C) in the dark. Acetone and methanol were laboratory-grade products and were used without further purification.

Grafting polymerization

The photoinitiated grafting reaction was carried out on Whatman paper previously oxidized with sodium metaperiodate to create photosensitive sites (aldehyde groups) on the cellulose; UV radiation transformed the carbonyl groups in the radical sites where the radical polymerization subsequently started.[4–6]

Cellulose samples, after they were dried in an oven, were swollen in deionized water for 10 min to open up the fibrous structure of cellulose and encourage the homogeneous uptake of the monomers during grafting. Next, the wet samples were placed in a steel reaction vessel (volume = 30 L), which was evacuated for a short time so that the paper was still damp; then, the liquid monomers mixture, 75/25 wt % EA/MMA, was loaded, vaporized, and diffused into the reactor. Subsequently, the whole unit was exposed at room temperature to UV radiation from a mercury vapor lamp (400 W, with complete spectrum emission from 180 nm to visible light); we stopped the polymerization after 20 min by bringing the reactor up to room pressure. Details on the setup of the grafting process were reported elsewhere.[20]

We removed nonreacted monomer by washing the fibers with a methanol–water mixture (30/70 vol %), which was a good solvent for acrylic monomers but not for the corresponding polymers. The drawback of the graft polymerization was the simultaneous and inevitable formation of homopolymer; this was removed from the grafted material by extraction with acetone for 72 h at room temperature.[6]

The quantity of grafted monomer was evaluated as the weight increase of the sample after extraction of the homopolymer:

$$\text{Graft yield (\%)} = [(W_2 - W_1) \times 100]/W_1$$

where W_1 is the initial weight of the sample and W_2 is the grafted weight of the extracted sample.

The grafting process did not induce any variation in the paper thickness; thus, this method can be considered as one of the most promising for paper restoration.

Coating with waterborne PUs

The coating process was performed with two commercial waterborne PUs coming from ICAP-SIRA Industries (Milano, Italy): the polyester-based PES 995 and the polycarbonate-based PC 954; both are typical examples of water dispersion. Because they are commercial products, no complete information on their composition was available, except that they contained isophorone diisocyanate as isocyanate and, as polyols, poly(butane diole adipate) in PES 995 and aliphatic polycarbonate glycol in PC 954.[21]

A preliminary investigation allowed us to establish the waterborne PUs by brushing to better check the amount of applied product on the sheet. After application on one side, the coated paper was dried in air.

The coating treatment slightly modified the paper thickness; this negative effect could be avoided by application of the same dispersion after a further dilution with water.

Artificial aging

All the samples before and after the consolidating treatments were submitted to artificial aging in a climatic box at 80°C and 65% relative humidity without light radiation and air pollution (ISO 5630/3). The procedure consisted of three phases of aging (12, 30, and 60 days).

Mechanical characterization

In this research, two mechanical tests specific for paper to evaluate the folding endurance and the tearing resistance were performed.

Folding endurance is the paper's capability to withstand multiple folds before breaking. It is very useful in the measurement of the deterioration of paper after aging and/or consolidation. Folding endurance is defined as the number of double folds that a strip 15 mm wide and 102 mm long can withstand under a specified load before breaking. An harmonic Schopper-type tester (Enrico Toniolo, Milano, Italy) was used on strips of paper according to the procedural standards described in the TAPPI test method T423 cm-98, the folding endurance of paper (Schopper-type tester). To perform a correct experiment, each sample was analyzed both in a right-angled orientation according to the machine direction (MD) and in an orientation according to the cross direction (CD). The results are expressed in terms of the folding number converted into the logarithmic form (Log_{10} MD and Log_{10} CD) and related to the corresponding standard deviation (SD).[22]

Tearing resistance represents the force required to tear a paper sheet. As reported in the TAPPI test method T414 om-98, the internal tearing resistance of paper (Elmendorf-type method), the right-angled dimensions of every specimen must be rigorously 63 × 53 mm^2; the tester was a pendulum-type instrument (TMI Testing Machines, Inc., Elmendorf tear tester; Milano, Italy), which measured the force perpendicular to the plane of paper required to tear the paper through a fixed distance. As for the folding endurance test, also in this case, the samples were orientated according to both the MD and CD, even when the results are related only to the former case. The tearing resistance (mN) was calculated by the following equation:[23]

$$\text{Average tearing resistance (mN)} = (16 \times 9.81 \times \text{Average reading})/\text{Number of plies}$$

Colorimetric measurements

Chromaticity was characterized by a point in the three-dimensional L^*, a^*, and b^* coordinates space (CIE*Lab system), where L^* is the lightness factor and ranges between 0 (black) to 100 (white), a^* is the red–green coordinate and ranges from -60 (green) to $+60$ (red), and b^* is the yellow–blue coordinate and ranges from -60 (blue) to $+60$ (yellow).[24]

We determined the chromatic coordinates with a Minolta Chroma Meter CR221 by averaging the values of three spot analyses. Color differences, which are very important for evaluating the relationships between visual and numerical analyses, were calculated as the Euclidean distance between two points in the three-dimensional space defined by L^*, a^*, and b^*:

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

where ΔE^*_{ab}, also defined as ΔE, is referred to as the $L^*a^*b^*$ system.

Polymerization degree (DP) evaluation

The determination of DP was carried out by viscosity measurements performed at 25°C with a 0.5*M* solution of cupriethylendiamine in water as a solvent according to ASTM D 1795-90.

Because of the insolubility of filled papers in cupriethylendiamine, the viscosity measurements were performed only on the raw Whatman paper.

RESULTS AND DISCUSSION

Mechanical tests and colorimetric measurements were carried out on Whatman paper, newsprint paper, and the Austrian book as follows:

- The sample was submitted to UV irradiation.
- The sample was grafted with 75/25 wt % EA/MMA (only Whatman paper; % graft yield = 40).
- The sample was coated with the waterborne PUs: PC 954 and PES 995.

These were compared with the original samples as references.

Original UV-irradiated samples

Before the investigation on the durability of grafted paper was approached, a specific study on the effects occurring on paper due to the UV irradiation necessary for the polymerization process was deemed necessary.

The grafted polymerization procedure consisted of 20 min of UV irradiation that, undoubtedly, induced a certain degradation on cellulose, immediately detectable by the material yellowing. The exact evaluation of the degradative action of UV radiation represented an essential step, in which we looked at the future possible applications of this technology on real artwork. In addition, the UV-irradiated papers were also submitted to artificial aging to monitor how temperature contributed to damaging the samples and how they underwent this next degradative step.

The folding endurance and tearing resistance of the UV-irradiated Whatman and newsprint before artificial aging were comparable with that of the original material, as shown in Tables I and II. However, during the progressive artificial aging up to 60 days, a bigger decrease in the resistance values was observed for the UV-irradiated samples, whereas the reduction for the original materials was smaller. Therefore, UV light had a negative effect on paper, with a slight decay of the paper mechanical properties determined. Only the artificial weathering of the Austrian book samples determined a so strong embrittlement of paper that no folding endurance measurements were carried out. For the tearing resistance tests, the artificial aging led to a MD decrease for both the original and the UV-irradiated samples (Table II).

UV irradiation led to a very slight yellowing of the Whatman paper, as detectable from the low ΔE value equal to 1.2; where ΔE is the color difference between two samples, one of which is taken to be standard. Accelerated aging determined a noticeable color change in both the samples, as evident from the ΔE values, which clearly indicated a progressive increase in the yellowing degree with prolonged weathering time (Table III). The colorimetric tests emphasized a more marked yellowing for the irradiated paper after artificial aging as compared with the original one (Table III). On the other hand, the UV irradiation determined a noticeable color change in the newsprint paper ($\Delta E = 5.2$). The effect of UV irradiation on the color of the original Austrian book was slight, as highlighted from the small ΔE value, equal to 2.6. Accelerated aging caused a noticeable decrease in the lightness in all of the samples, especially in the UV-irradiated paper aged for 60 days (Table III). The evaluation of DP was another way to detect in the Whatman paper the effects of the UV

TABLE I
Schopper Folding Endurance Variations [Expressed as Log_{10}(Double Folds)] for the Whatman Paper and Newsprint Paper Before and After UV irradiation During Artificial Aging

Sample	0 days of aging				12 days of aging				30 days of aging				60 days of aging			
	MD	SD	CD	SD	MD	SD	CD	SD	MD	SD	CD	SD	MD	SD	CD	SD
Original Whatman paper	1.96	0.26	0.99	0.11	1.87	0.09	1.02	0.11	1.76	0.20	1.03	0.13	1.55	0.11	0.80	0.11
UV-irradiated Whatman paper	2.08	0.10	1.17	0.10	1.58	0.16	0.97	0.10	1.57	0.17	0.81	0.05	1.34	0.16	0.8	0.16
Original newsprint paper	2.26	0.12	1.82	0.10	2.13	0.15	1.73	0.12	1.82	0.22	1.65	0.1	2.0	0.1	1.61	0.1
UV-irradiated newsprint paper	2.34	0.12	1.75	0.14	1.59	0.13	1.64	0.28	1.37	0.14	1.53	0.16	1.4	0.2	1.5	0.2

irradiation and the progressive artificial aging. DP values were measured only on these samples (Table IV) because no viscosity measurements could be carried out both on the filled papers (because of the presence of fillers) and on the consolidated samples (because of the presence of polymers). Twenty minutes of UV irradiation treatment did not determine immediate damage on the Whatman paper, as highlighted from the comparable DP values for the original and the UV-irradiated samples. During the accelerating aging, a considerable gradual decrease of DP values occurred, especially in the irradiated paper. This result demonstrated that the accelerated aging performed on a paper already submitted to the damaging action of UV light was more sensitive to degradation in respect to the raw material.

Grafted samples with acrylic monomers

After the preliminary tests performed on the Whatman paper after UV irradiation, artificial aging was also carried out on the grafted Whatman paper to evaluate the durability of this treatment and the stability of acrylics under the actions of temperature and relative humidity.

Experiments carried out on the irradiated samples demonstrated that the UV irradiation performed during the grafting process to allow the initiation and the propagation of polymerization determined a worsening in the mechanical resistance of paper. This was due to the damaging action of UV light on the cellulose fibers, which caused a lowering of DP. Moreover, the UV radiation also altered the appearance of the paper by darkening or yellowing the paper, depending on the paper grade.

With these preliminary considerations taken into account, it is clear that, during the polymerization, two antagonistic events occurred: the consolidative action due to the grafting of acrylic chains onto the cellulose and the damaging action of UV irradiation. This evidence was responsible for the low resistance to the accelerated aging of grafted paper. Indeed, the grafted Whatman paper (% grafting yield = 40) aged for 60 days was unsuitable for the folding endurance test: the data were null. With regard to tearing resistance, a decrease from 191.84 (original Whatman paper) to 98.1 was observed after 60 days of weathering; after this aging time, a strong browning occurred in the Whatman paper, which corresponded to a chromatic alteration equal to 34.3 (Table III).

Samples coated with waterborne PUs

When the Whatman paper was coated with PC 954 and PES 995, the folding endurance considerably

TABLE II
Elmendorf Resistance Variations [MD Average Tearing Force (mN)] for the Whatman Paper, Newsprint Paper, and Austrian Book Samples Before and After UV Irradiation During Artificial Aging

Sample	0 days of aging	12 days of aging	30 days of aging	60 days of aging
Original Whatman paper	575.52	575.52	523.20	366.24
UV-irradiated Whatman paper	758.64	758.64	680.16	549.36
Original newsprint paper	226.72	209.28	191.84	191.84
UV-irradiated newsprint paper	244.16	261.6	244.16	209.28
Original book sample	156.96	141.26	78.48	47.09
UV-irradiated book sample	125.57	109.87	78.48	47.09

TABLE III
L^*, a^*, b^*, and ΔE Values for Whatman Paper, Newsprint Paper, and Austrian Book Samples Before and After UV Irradiation During Artificial Aging

Aging (days)	L^*	a^*	b^*	ΔE
Original Whatman paper				
0	95.5 ± 0.3	−0.4 ± 0	2.4 ± 0.3	—
12	92.1 ± 0.4	−0.1 ± 0.1	8.6 ± 0.4	7.1
30	90.1 ± 0.3	0.3 ± 0.1	11.5 ± 0.4	10.6
60	88.9 ± 0.6	0.8 ± 0.1	13.3 ± 0.3	12.8
UV-irradiated Whatman paper				
0	95 ± 0.3	−0.6 ± 0.1	3.5 ± 0.8	—
12	90.8 ± 0.5	0.1 ± 0.2	10.3 ± 0.7	8.0
30	89.4 ± 1.1	0.6 ± 0.3	11.4 ± 1.4	9.8
60	87.2 ± 1.2	1.5 ± 0.4	13.9 ± 1	13.2
Grafted Whatman paper				
0	94.4 ± 1.3	−0.5 ± 0.1	2.06 ± 0.6	—
60	70.1 ± 2.5	6.46 ± 1.2	25.3 ± 2.2	34.3
Original newsprint paper				
0	91.1 ± 0.3	1.1 ± 0.3	3.3 ± 0.1	—
12	89.2 ± 0.1	0.4 ± 0.1	10 ± 0.4	7.0
30	87.7 ± 0.2	0.8 ± 0.2	12.1 ± 0.7	9.4
60	86.7 ± 0.6	1.1 ± 0.2	14.3 ± 1	11.8
UV-irradiated newsprint paper				
0	89.3 ± 0.6	0.4 ± 0.3	8.1 ± 1.5	—
12	87.7 ± 0.7	0.6 ± 0.1	12.9 ± 1.8	5.1
30	86.9 ± 1	0.6 ± 0.3	13.6 ± 1.5	6.0
60	85.4 ± 0.6	1.3 ± 0.3	16.6 ± 1.3	9.4
Original Austrian book				
0	86.4 ± 0.7	1.4 ± 0.3	18 ± 0.7	—
12	79.1 ± 0.9	3.5 ± 0.3	19.3 ± 0.6	7.7
30	76 ± 0.6	4.2 ± 0.2	19.8 ± 0.3	10.9
60	72.7 ± 0.9	4.7 ± 0.2	19.7 ± 0.3	14.2
UV-irradiated Austrian book				
0	87.5 ± 0.7	0.8 ± 0.3	15.7 ± 0.7	—
12	78.9 ± 1.1	3.5 ± 0.5	19.3 ± 1.2	9.7
30	75.8 ± 1.5	4.1 ± 0.5	19.4 ± 1.2	12.7
60	71.5 ± 1.2	4.9 ± 0.4	19.7 ± 0.7	22.3

TABLE IV
DP Values for the Whatman Paper Before and After UV Irradiation During Artificial Aging

	DP	
Aging (days)	Whatman reference sample	UV-irradiated Whatman paper
0	1178	1195
12	1159	861
30	998	798
60	822	620

increased with respect to tearing resistance, as shown form the data collected in Tables V and VI. After 12 days of aging, a fast increasing in the yellowing degree took place in all of the coated samples (Table VII). However, the application of PES 995 caused a more significant color change than the use of PC 954. After 30 days of aging, whereas the mechanical characteristics of the original Whatman paper are substantially unaltered, for the samples coated with PC 954, the mechanical resistance was slightly reduced, which kept the MD/CD conditions balanced. For the samples coated with PES 995, a stronger yellowing was observed ($\Delta E = 24.2$), which was linked to a consequent decrease in the folding endurance. After 60 days of aging, the samples coated with PC 954 continued to yellow, but the mechanical resistance decrease was stopped (Table VII).

For the newsprint paper, after 12 days of aging, the sample showed a chromatic variation (Table VIII), which was not linked to a marked decreased of the mechanical resistance. After 30 and 60 days of weathering, the two consolidation treatments did not cause any significant decrease in the resistance with respect to the original material.

For these aged samples, a typical drawback related to the applications of such products was immediately visible: the brushing carried out on the sheet surface during the coating. Traces of the brush became more evident with prolonged aging time, and consequently, when the yellowing was noticeable, the final paper appearance was characterized by cockling and stiffness.

TABLE V
Schopper Folding Endurance Variations [Expressed as Log_{10}(Double Folds)] for the Whatman Paper and Newsprint Before and After Coating with PC 954 and PES 995 During Artificial Aging

	0 days of aging				12 days of aging				30 days of aging				60 days of aging			
Sample	MD	SD	CD	SD	MD	SD	CD	SD	MD	SD	CD	SD	MD	SD	CD	SD
Original Whatman paper	1.96	0.26	0.99	0.11	1.87	0.09	1.02	0.11	1.76	0.20	1.03	0.13	1.55	0.11	0.80	0.11
Whatman paper coated with PC 954	3.28	0.07	2.91	0.08	2.90	0.11	2.42	0.23	2.69	0.14	2.22	0.10	3.28	0.07	2.91	0.08
Whatman paper coated with PES 995	3.18	0.05	2.79	0.06	1.94	0.05	1.34	0.06	1.40	0.15	1.09	0.11	1.50	0.22	1.12	0.09
Original newsprint paper	2.26	0.12	1.82	0.10	2.13	0.15	1.73	0.12	1.82	0.22	1.65	0.10	2.0	0.10	1.61	0.09
Newsprint coated with PC 954	2.51	0.03	2.28	0.12	2.54	0.06	2.20	0.11	2.28	0.25	2.24	0.19	2.3	0.08	2.2	0.08
Newsprint coated with PES 995	2.51	0.11	2.41	0.10	2.31	0.12	2.35	0.16	2.06	0.10	2.07	0.31	1.8	0.12	1.9	0.10

TABLE VI
Elmendorf Resistance Variations [MD Average Tearing Force (mN)] for the Whatman Paper and Newsprint Before and After Coating with PC 954 and PES 995 During Artificial Aging

Sample	0 days of aging	12 days of aging	30 days of aging	60 days of aging
Original Whatman paper	575.52	575.52	523.20	366.24
Whatman paper coated with PC 954	596.45	470.88	439.49	439.49
Whatman paper coated with PES 995	722.02	596.45	502.27	376.70
Original newsprint paper	226.72	209.28	191.84	191.84
Newsprint paper coated with PC 954	226.72	226.72	209.28	191.84
Newsprint paper coated with PES 995	219.74	204.05	204.05	188.35

TABLE VII
L^*, a^*, b^*, and ΔE Values for the Whatman Paper, Newsprint Paper, and Austrian Book Samples Before and After Coating with PC 954 and PES 995 During Artificial Aging

Aging (days)	L^*	a^*	b^*	ΔE
Original Whatman paper				
0	95.5 ± 0.3	−0.4 ± 0	2.4 ± 0.3	—
12	92.1 ± 0.4	−0.1 ± 0.1	8.6 ± 0.4	7.1
30	90.1 ± 0.3	0.3 ± 0.1	11.5 ± 0.4	10.6
60	88.9 ± 0.6	0.8 ± 0.1	13.3 ± 0.3	12.8
Whatman paper coated with PC 954				
0	95.2 ± 0.3	−0.5 ± 0	3.2 ± 0.4	—
12	89.5 ± 0.7	−0.3 ± 0.2	14.9 ± 0.4	13
30	85.9 ± 0	1.2 ± 0.1	21.8 ± 1	20.9
60	84.5 ± 0.7	1.7 ± 0.2	24 ± 1.4	23.5
Whatman paper coated with PES 995				
0	94.9 ± 0.3	−0.7 ± 0	3.9 ± 0.5	—
12	87.8 ± 0.3	0.5 ± 0.3	18.1 ± 0.7	15.9
30	83.5 ± 0.4	2.2 ± 0.3	25.1 ± 0.6	24.2
60	81.6 ± 0.5	3.6 ± 0.1	27.2 ± 0.8	27.2
Original newsprint paper				
0	91.1 ± 0.3	1.1 ± 0.1	3.3 ± 0.1	—
12	89.2 ± 0.1	0.4 ± 0.1	10 ± 0.4	7.0
30	87.7 ± 0.2	0.8 ± 0.2	12.1 ± 0.7	9.4
60	86.7 ± 0.6	1.1 ± 0.2	14.3 ± 1	11.8
Newsprint paper coated with PC 954				
0	90.7 ± 0.3	1.0 ± 0.1	3.7 ± 0.2	—
12	88.4 ± 0.4	0.3 ± 0.1	11.7 ± 0.3	8.4
30	86.6 ± 0.3	0.6 ± 0.1	15.4 ± 0.5	12.4
60	84.8 ± 0.3	1.2 ± 0.2	17.2 ± 1	14.7
Newsprint paper coated with PES 995				
0	90.6 ± 0.3	0.6 ± 0.2	4.6 ± 0.4	—
12	88.5 ± 0.3	0.1 ± 0.1	11.7 ± 0.8	7.4
30	86.7 ± 0.4	0.4 ± 0.2	15.4 ± 0.7	11.5
60	84.3 ± 0.5	1.2 ± 0.3	19.0 ± 0.7	15.7
Original Austrian book sample				
0	86.4 ± 0.7	1.4 ± 0.3	18 ± 0.7	—
12	79.1 ± 0.9	3.5 ± 0.3	19.3 ± 0.6	7.7
30	76 ± 0.6	4.2 ± 0.2	19.8 ± 0.3	10.9
60	72.7 ± 0.9	4.7 ± 0.2	19.7 ± 0.3	14.2
Austrian book sample coated with PC 954				
0	87.8 ± 0.6	0.9 ± 0.2	15.5 ± 0.8	—
12	80.2 ± 0.5	2.8 ± 0.5	19.7 ± 0.5	8.9
30	76.6 ± 1	3.6 ± 0.3	21.5 ± 0.6	13.0
60	73.0 ± 0.7	4.3 ± 0.3	22.8 ± 0.4	16.8
Austrian book sample coated with PES 995				
0	86.3 ± 0.8	1.3 ± 0.3	17.7 ± 1	—
12	77.5 ± 0.9	3.8 ± 0.3	22.9 ± 0.9	10.6
30	74.1 ± 0.4	4.0 ± 0.2	23.1 ± 0.6	13.6
60	70.1 ± 0.6	5.3 ± 0.2	24.3 ± 0.7	17.9

On the contrary, the Austrian book samples showed the opposite behavior; neither of the coating treatments induced any improvement in the mechanical resistance of the paper before and after artificial aging. Indeed, the Austrian book already underwent a natural weathering, which determined an evident degradation of the cellulose matrix; therefore, the paper, which was already deteriorated at the test starting point, after 12, 30, and 60 days of aging was unsuitable for the mechanical measurements and gave null data. Also, the color measurements (Table VIII) indicated that the initial yellowish color progressively darkened with prolonged aging time; also in this case, PES 995 determined the highest chromatic alteration.

CONCLUSIONS

After the setup of an innovative method for paper conservation with polymeric materials, the evaluation of the durability of consolidated papers was deemed. In our study, we investigated the stability, durability, and performances of grafted and PU-coated paper-based materials after artificial aging in a climatic box (80°C and 65% relative humidity).

The increase of folding endurance and tearing resistance during artificial aging was observed only in the case of Whatman paper, manufactured with good quality cellulose, whereas the filled papers showed no improvement in the mechanical properties.

Both the acrylics and PUs showed a low stability when submitted to artificial aging. Generally, after 60 days of artificial aging, all of the samples coated with waterborne PUs showed a strong yellowing, which was linked to the worsening of the mechanical resistance and to a change in the paper thickness and appearance. However, PC 954 imparted to the paper a relatively higher stability then PES 995.

With regard to the grafting polymerization, the UV irradiation caused an appreciable decrease in the mechanical resistance that did not balance the effect due to the grafted acrylic chains.

In the collected results, both consolidating methods appeared unsuitable for use in paper restoration because of the damage that they can caused to the samples and to the limited durability of the treated paper over time, as demonstrated by the aging experiments. Indeed, both the acrylics and the waterborne PUs did not increase the stability of paper, as required from a correct preservation technique.

In addition, our research suggested a method for the elaboration of a specific and essential working plan for the determination of a long-term effect of a polymer-based preservation technique from the point of view of a safe final application of real paper restoration. This approach should be always followed to determine the possible risks for the paper when a new restoration method is proposed, also through appropriate comparisons with other commonly techniques used by restorers nowadays.

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