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PHOTOSTABILITY OF INNOVATIVE FORMULATIONS FOR ARTWORKS RESTORATION

Innovative formulations and products, which may satisfy the requirements imposed by legislation (i.e. water based formulations) and/or use in the field of artworks conservation (i.e. improved photostability), were selected through the study of their photostability to a sun-like irradiation.

Some classes of polymers, and in particular synthetic polymers such as acrylics, fluoroelastomers, silicon based polymers, polyolefin, are materials which find favour with operators in the field of conservation and restoration of works of art in consequence of their transparency, water repellence, cohesive property, easy availability on the market, etc. For these characteristics they are particularly employed as protective or consolidation agents for stone assets or as varnishes and binders for paintings [1-4].

Although these macromolecules have numerous advantages in comparison to natural polymers and inorganic compounds, it must be pointed out that they are designed, produced and commercialized for different purposes than restoration and preservation of works of art, and therefore they often do not satisfy the requirements imposed by this use, first of all the photostability [5-9]. On the other hand the design of new specific molecules, suitable for the limited market of conservation, requires great efforts, mainly by the industries because the required performances, mainly in terms of stability, are generally obtained with highly fluorinated compounds, which are expensive and often soluble in non common and environmentally benign solvents. In fact, it is known that perfluoropolymers show high resistance to UV irradiation, acids, bases and heat.

In addition the wide variety of cultural assets and their degradation pathways requires products with specific properties for each problem, including polymer average molecular weight, cohesive and adhesive properties, and solubility in suitable solvents. Since the great number of synthetic polymers available on the market, it is possible to find the products which fulfil the required mechanical and physical characteristics, but they must be properly formulated for their application on works of art. Moreover, it must be pointed out that flammable and toxic organic solvents are often employed for the application of polymers. In consequence of the legislation on the reduction of the VOC (Volatile Organic Compounds) emissions on the atmosphere [10, 11], many commercial products are recently proposed as water based polymer formulations rather than organic solvent based ones. However, in the case of the new water based formulations, as well as in the new solvent based ones, the evaluation of the photostability is of primary importance before their application on cultural assets.

Tab. 1 - Details of the materials selected for the test

Product	Polymer Composition	Solvent	Conc. (% w/w)	Use
Acril ME	Poly (butyl methacrylate)	Water based micro emulsion	41	Plaster and stone consolidation
Fluoline HY	Poly (hexafluoropropene-co-vinylidene fluoride)	Acetone/butyl acetate	3	Plaster and stone protection with a consolidation effect
Regal varnish gloss	Polyolefin with plasticizer (2% Kraton) and an UV stabilizer (0.5% Tinuvin 292)	Petroleum ether 141-166 °C	25	Paintings varnish containing a stabilizer
Regalrez 1094	Polyolefin	Heptanes	20	Paintings varnish
Aquazol 500	Polyoxazoline	Water	10	Paint layers consolidation
Paraloid B72 (PB72)	Poly(ethyl methacrylate-co-methylacrylate) (EMA-MA)	$CHCl_3$	10	Multi purpose
PB 72/Aquazol 200 (80/20)	EMA-MA and polyoxazoline	$CHCl_3$	10	Paint layers consolidation with protection effect

A series of innovative products or formulations, prepared from different commercial polymers to be used as restoration products (protective or consolidation agents, varnishes) for stone artefacts or mural and easel paintings, has been tested and the photostability of the polymers to a sun-like artificial irradiation (λ>280 nm) has been detected. In particular, the chemical and physical behaviour of the products has been investigated during artificial ageing in order to verify mainly their solubility and colour over time. The stability of these two parameters is, in fact, a crucial condition for a good reversibility of the treatment and for maintaining the initial chromatic characteristics of the artwork surface.

Innovative materials

Four classes of compounds have been selected as suitable materials for stone and plaster consolidation and protection (acrylic and perfluorinated polymers), for paint layers consolidation (polyoxazoline) and for paintings varnishing (polyolefin). Two polymers (acrylic polymer and polyoxazoline) may be employed as water based formulations, while the others may be applied only as solvent based solutions. Paraloid B72 [poly(ethyl methacrylate-*co*-methyl acrylate)] has been used as reference material since its wide use both in the field of stone and painting conservation. Details of the employed products and formulations are reported in Tab. 1.

Samples preparation and investigation techniques

Each product was deposed on glass slide for Gel Permeation Chromatography (GPC) and Differential Scanning Calorimetry (DSC) measurements, as well as mass and solubility determinations. KBr disks and marble specimens (sivec marble, 5cmx5cmx1cm dimensions) were used as support for Fourier Transform Infrared (FTIR) analysis and colour determinations, respectively.

The UV irradiation (λ>280 nm) has been performed by a solarbox Cofomegra mod. 3000e. The irradiation was 500 W/m^2, while the Black Standard Temperature (BST) was maintained below 70 °C.

The molecular weight determinations were carried out by a HPLC-SEC system equipped with a Perkin Elmer mod. Series 200, a Rheodyne 7010 injector with a 200 μl injection loop, and a Perkin Elmer LC-30 refraction Index detector. Two PL Gel linear columns (30 cm length, 5 μm gel particle size, Polymer Lab, GB) with an eluent flow of 1 ml/min were employed. Chloroform was used as eluent for PB72, Regal varnish gloss, Regalrez 1094, Aquazol 500 and PB72/Aquazol 200, while THF was used for Acril ME and Fluoline HY.

The FTIR spectra were recorded by a Perkin Elmer mod. System 2000 FTIR spectrometer.

The colour determinations were carried out in accordance to NORMAL 43/93 [12] using the L*a*b* (CIE 1976) system (Minolta CR200 colorimeter). In this system L* is the lightness, while a* and b* the chromatic coordinates. The L* value ranges between 100 (white) and 0 (black), while the a* and b* values ranges between +60 and -60 (+a* and +b* indicate red and yellow, respectively, while -a* and -b* indicate green and blue). The chromatic changes are reported as $\Delta E = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2}$, where ΔL^*, Δa^* and Δb^* are the difference between the chromatic values after UV irradiation and before the treatment.

The glass transition temperature (Tg) were determined by a Perkin Elmer Pyris 1 differential scanning calorimetry equipped with a cryogenic system (Intracooler 2P). The heating rate was 20 °C/min.

Photostability of polymers

Mass changes

All products decrease their mass after irradiation, however only Aquazol 500 has a progressive loss of material up to 3000 h of irradiation (Tab. 2). For Acril ME and PB72/Aquazol 200, the progressive mass decrease is observed only during the first 1000 h, while for further irradiation (up to 3000 h) the value is maintained more or less constant. A

Tab. 2 - Percentage of the polymer mass change after different times of UV irradiation

Product	Mass change of polymer (%)* during UV irradiation					
	238 h	497 h	982 h	1580 h	2034 h	3000 h
Acril ME	-1,5	-3,0	-3,5	-3,5	-3,5	-4,0
Fluoline HY	-1,5	-1,5	-2,0	-1,5	-1,5	-1,0
Regal varnish gloss	-4,0	-4,5	-5,5	-4,5	-4,5	-4,0
Regalrez	-2,0	-1,5	n.d.	-7,0	n.d.	-3,0
Aquazol 500	-7,0	-10,0	-20,0	-21,0	-23,0	-29,0
Paraloid B72 (PB72)	-6,0	-6,5	-9,5	-11,5	-10,5	-6,5
PB 72/Aquazol 200 (80/20)	-6,5	-6,5	-11,5	-10,5	-11,0	-12,0

***The mass change was determined as (m_1-m_0)/m_0·100, where m_1 and m_0 are the mass of polymer after and before irradiation, respectively.**

Tab. 3 - Solubility of the polymers after different times of UV irradiation

Product	Solvent	Mass change of polymer (%)* during UV irradiation					
		238 h	497 h	982 h	1580 h	2034 h	3000 h
Acril ME	Acetone	100	42	28	27	28	12
Fluoline HY	Acetone	100	100	n.d.	100	100	100
Regal varnish gloss	Chloroform	100	100	100	100	100	100
Regalrez 1094	Chloroform	100	100	n.d.	100	n.d.	82
Aquazol 500	Chloroform	100	100	92	91	89	60
Paraloid B72 (PB72)	Chloroform	100	100	100	100	100	100
PB 72/Aquazol 200 (80/20)	Chloroform	100	100	100	100	100	100

special case is represented by the fluoroelastomer (Fluoline HY) that shows a small and approximately constant decrease for all the detected ageing steps. PB72, Regal varnish gloss and Regalrez 1094, on the contrary, show an initial progressive decrease followed by a reversing trend of the decrease. The mass decrease of the polymers is usually justified with depolymerization reactions occurring during irradiation, but the evaporation of the residual solvent used for the deposition of the polymer, or water absorbed by the polymer during the casting, must be considered. The FTIR spectra of film of Acril ME, Fluoline HY, PB72 and PB72/Aquazol 200 in fact show weak peaks due to water (i.e. Acril ME and Fluoline HY) and chloroform (i.e. PB72 and PB72/Aquazol 200). Moreover it was found that these signals disappear after 1000 h (Acril ME) or 250 h (Fluoline HY, PB72 and PB72/Aquazol 200) of irradiation, which are in good agreement with the percentage of mass changes reported in Tab. 2 for these compounds. The presence of solvent in Aquazol 500, Regal varnish gloss and Regalrez 1094 was not detected by FTIR since their signals are overlaid by those of the polymers, however a similar behaviour with the other polymers is expected. In the case of PB72, Regalrez 1094 and, in a much lesser extent, Regal varnish gloss, oxidation reactions may occur after 1000 h of irradiation (reversing trend of mass decrease), and they may be competitive with the depolymerization ones (Tab. 2).

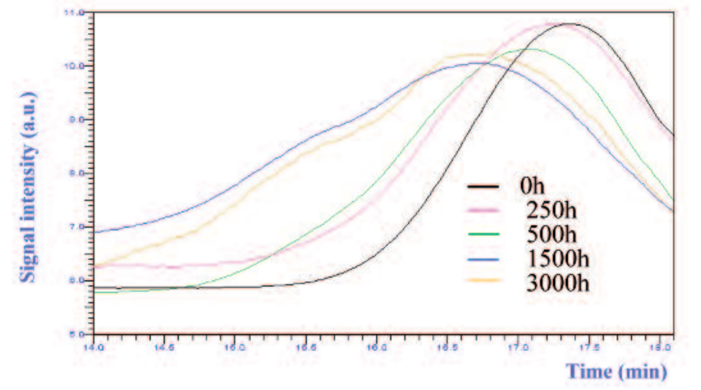

Fig. 1 - Gel Permeation chromatograms of Regalrez 1094 after different times of UV irradiation

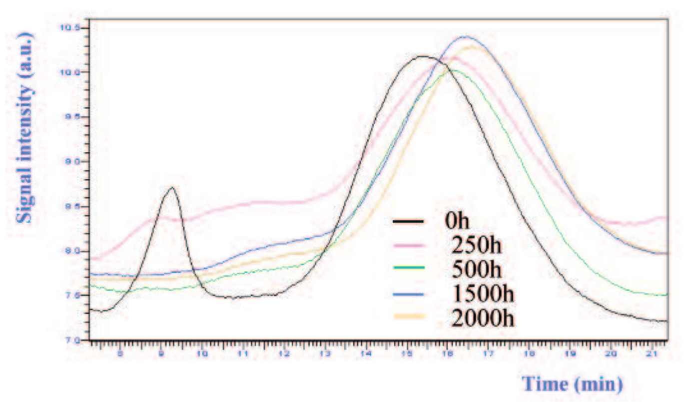

Fig. 2 - Gel Permeation chromatograms of Acril ME after different times of UV irradiation

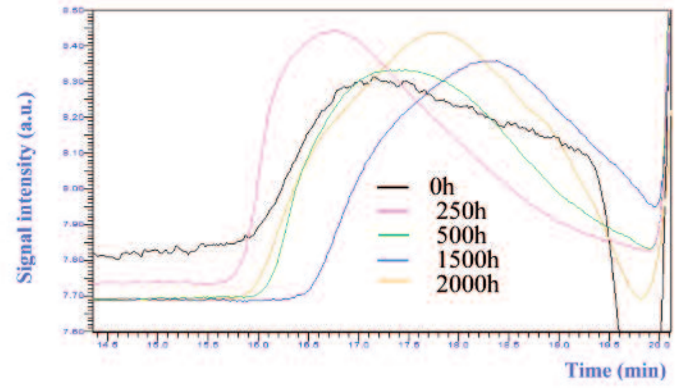

Fig. 3 - Gel Permeation chromatograms of Aquazol 500 after different times of UV irradiation

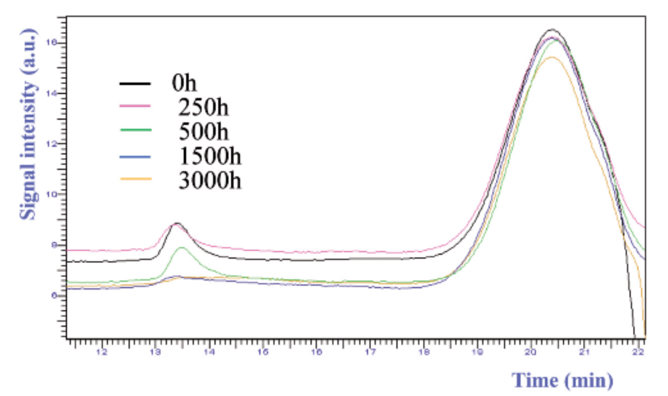

Fig. 4 - Gel Permeation chromatograms of Regal Varnish Gloss after different times of UV irradiation

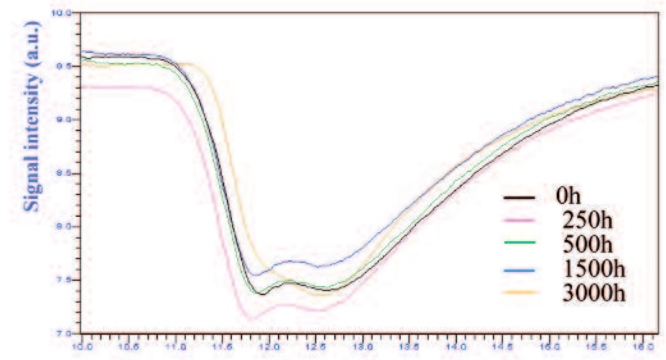

Fig. 5 - Gel Permeation chromatograms
of Fluoline HY after different times of UV irradiation

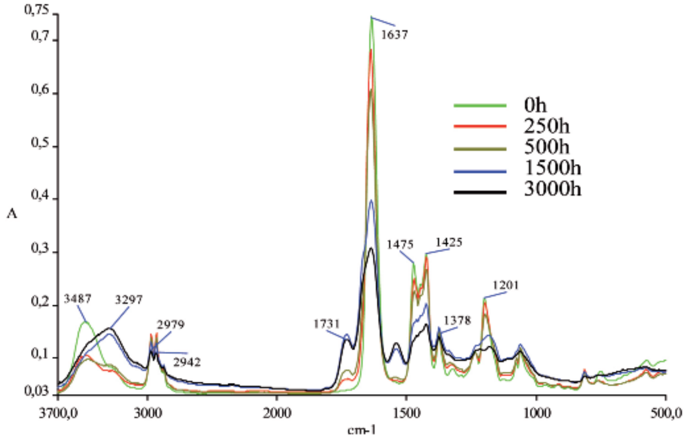

Fig. 7 - FTIR spectra of Aquazol 500 after different times of UV irradiation

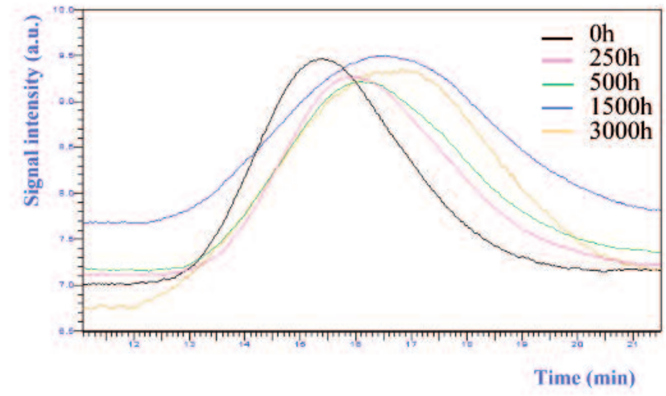

Fig. 6 - Gel Permeation chromatograms
of PB72 after different times of UV irradiation

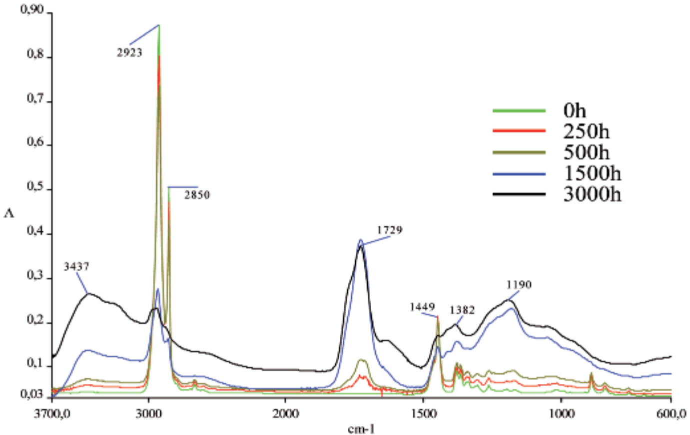

Fig. 8 - FTIR spectra of Regalrez 1094 after different times of UV irradiation

Solubility and Average Molecular Weight

One of the effects of the UV irradiation on polymers is the change of their solubility which is mainly related to the molecular weight variation. The tested innovative materials show, in general, an excellent solubility up to 3000 h of ageing (Tab. 3). Only Acril ME drastically reduces its solubility already at short times of irradiation (42% of soluble polymer at 500 h of irradiation), while Aquazol 500 and Regalrez 1094 show an appreciable reduction of solubility at long times of UV exposition (60% and 82% of soluble polymer after 3000 h of ageing, respectively for Aquazol 500 and Regalrez 1094). This characteristic is usually in accordance with the molecular weight increase; the gel permeation distributions of Regalrez 1094, in fact, show a decrease in the retention time of the irradiated polymer in comparison to the not irradiated one's, indicating an increase in the molecular weight of the polymer (Fig. 1). The same trend was not found for Acril ME (Fig. 2), but only the soluble fraction was here analyzed.

Aquazol 500, on the contrary, does not show a trend in the retention times of the gel permeation distributions (Fig. 3) with the irradiation time, but a random behavior; this may be explained by the formation of oxidized compounds in competition with depolymerization reactions. Regal varnish gloss seems more stable than Regalrez 1094 because only at 500 h of irradiation a small amount of a higher molecular weight product (lower retention time) is found (Fig. 4). The UV stabilizer added to the polyolefin seems to improve the photo-stability of the polymer. On the other hand, the fluoroelastomer (Fluoline HY) maintains its solubility up to 3000 h of irradiation and its molecular weight is practically unchanged after ageing (Fig. 5).

PB72 also maintains its solubility over UV irradiation (up to 3000 h), however a decrease in the molecular weight is observed (Fig. 6).

Chemical changes (FTIR spectroscopy and DSC)

FTIR spectroscopy is, in general, an efficient and fast technology for monitoring chemical changes in polymer films. The registration of the FTIR spectra on the same film of polymer, deposed on KBr disk, before and after different times of UV exposure allows us to detect oxidation reactions, as well as the elimination of small molecules due to decomposition or depolymerization reactions. Aquazol 500 is a relevant example, in fact, in accordance with the mass decrease (Tab. 2), the FTIR spectra of the polymer after different irradiation times (Fig. 7) show a moderate formation of new peaks compatible with ester-lactones groups (1730 cm^{-1}, C=O stretch) and secondary amides (1541 cm^{-1} NH bending, 3297 and 3080 cm^{-1} NH stretch) due to oxi-

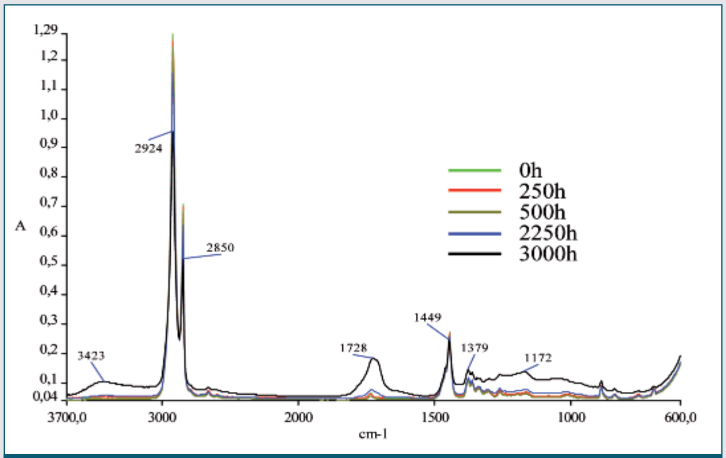

Fig. 9 - FTIR spectra of Regal varnish gloss after different times of UV irradiation

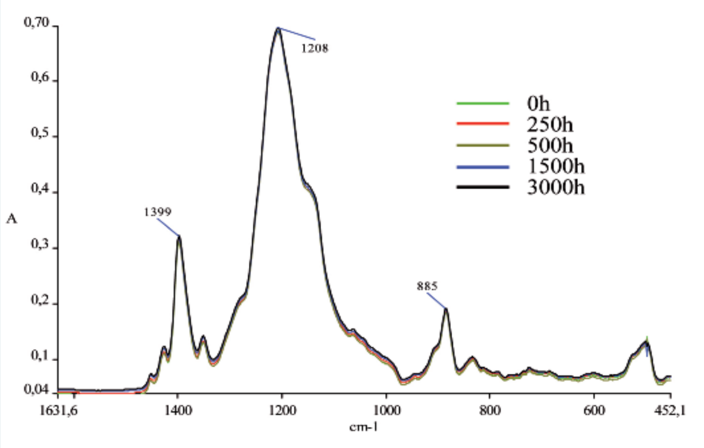

Fig. 10 - FTIR spectra of Fluoline HY after different times of UV irradiation

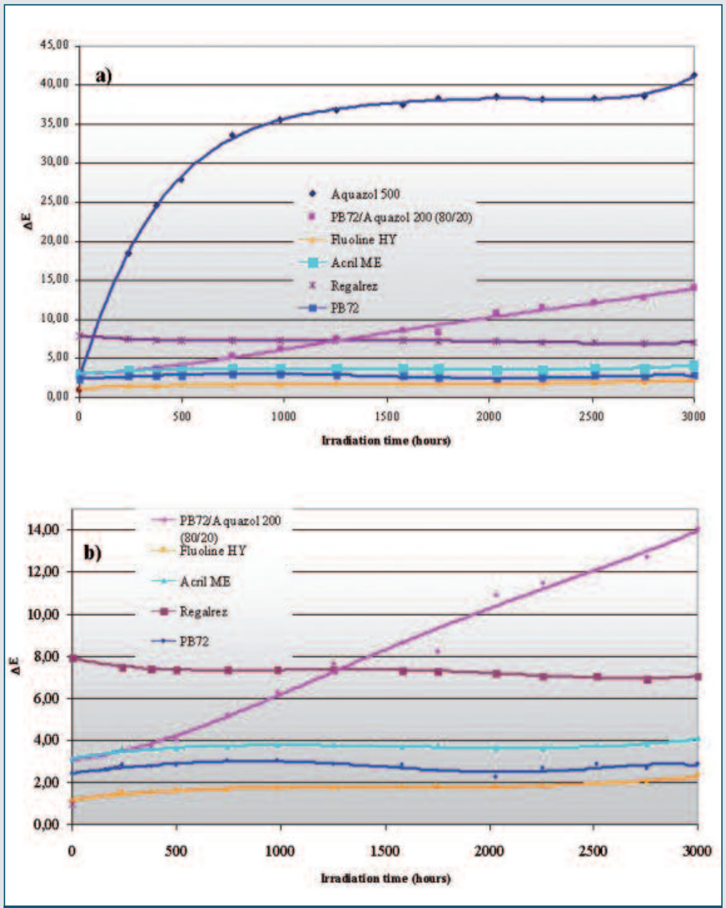

Fig. 11 - Total chromatic change (ΔE) of marble specimens after different irradiation times: a) all products; b) without Aquazol 500. The total change is referred to the corresponding untreated sample

dation and depolymerization reactions. A contemporary relevant decrease of the signal intensity of the more important peaks corresponding to C=O stretch of Amide I (1637 cm^{-1}), CH stretch (range 2800-3000 cm^{-1}) and bending (1300-1500 cm^{-1}) is also observed. The ester-lactones groups and the secondary amides may be the responsible in the reduction of solubility and molecular weight variability. Evident changes in the FTIR spectra of the irradiated polymer are also observed for Regalrez 1094. In this case, the oxidation reactions are competitive with the decomposition (elimination of small molecules) of the polymer (Fig. 8); the FTIR spectra are in accordance with the gravimetric data (Tab. 2), solubility (Tab. 3) and molecular weight distributions (Fig. 1).

Better photo-stability than Regalrez 1094 has been found for Regal varnish gloss, a formulation based on the polyolefin Regalrez 1094, where a plasticizer (Kraton) and an UV stabilizer (Tinuvin 292) were added. No decomposition of the polymer is observed up to 3000 h, and moderate oxidation reactions are detected starting from 2250 h of ageing (Fig. 9). No relevant changes in the FTIR spectra have been detected for Fluoline HY (Fig. 10), PB72 and Acril ME, but while for Fluoline HY the gravimetric data, the solubility determinations and the molecular weight distributions confirmed the stability of the polymer, for PB72 and Acril ME depolymerization reactions and cross-linking may be supposed, respectively, without oxidation reactions. Additional information about chemical changes due to molecular variations are found by DSC analysis. The Tg of Acril ME and PB72 after different times of UV irradiation show, in fact, a contrary behaviour (Tab. 4), in accordance with an increase and decrease of molecular weight, respectively.

Chromatic changes (colour determinations)

Oxidation reactions of polymers usually influence the chromatic values (mainly the a* and b* parameters in the CE Lab system) of the surface where the product is applied in consequence of the yellowing of the polymer. The total chromatic change of marble specimens treated with Aquazol 500, one of the most oxidized polymers, shows in fact high values (30-40) also after short times of UV exposure (500 h) (Fig. 11). In addition the high values are mainly due to the b* value which turns on yellow (Tab. 5). On the contrary, the other compounds, except Regalrez 1094 not detected, show very low chromatic changes with ΔE values less than 3, which is the threshold sensitivity of the human eye. These results confirm the absence or very low oxidation reactions in PB72 and Acril ME.

Tab. 4 - Glass transition temperature (Tg) of the polymers after different times of UV irradiation

Product	Tg (°C) during UV irradiation						
	0 h	238 h	497 h	982 h	1580 h	2034 h	3000 h
Acril ME	19	17	22	22	22	24	31
Fluoline HY	-22	-20	-20	-21	-20	-20	-21
Regal varnish gloss	19	15	10	23	22	18	-25
Aquazol 500	63; 115	34; 115	41; 137	-2	6	24	-13
Paraloid B72 (PB72)	39	39	29	20	29	18	-2
PB 72/Aquazol 200 (80/20)	37	39	37	37	35	13	-6

Conclusions

The study of the photostability of polymers by a sun-like artificial irradiation may be considered a good method for selecting the more suitable commercial products to be used in different conservation fields. In fact, the control of various parameters, such as solubility, mass, average molecular weight, chemical composition, glass transition temperature and colour, allows us to follow the degradation path of polymers suggesting the possible application field.

Among the products/formulates studied in this work, the fluoroelastomer Fluoline HY shows the best photostability and, for its physical and mechanical properties, it may be successfully used as protective agent with consolidation effect for indoor and outdoor artefacts.

Acril ME, a water based formulation, in consequence of the cross-linking reactions (loss of solubility) occurring during irradiation, may be proposed as consolidation agent for stone also in outdoor conditions. In addition, the photodegradation is relatively slow, without oxidation reactions and chromatic changes.

On the contrary PB72, a solvent based polymer, undergoes depolymerization with loss of consolidating and, probably, protective properties. Regal varnish gloss, a solvent based formulation containing a polyolefin at low molecular weight and suitable refractive index to be used as varnish for paintings, shows an improved photostability in respect to the pure polyolefin (Regalrez 1094); a moderate oxidation is detected only after long time of UV exposure (2250 h).

Finally, the polyoxazoline Aquazol 500 shows oxidation and depolymerization reactions with evident changes in the FTIR spectra, mass and chromatic properties: this polymer is too sensible to UV for its use on outdoor items, and its only acceptable use is as adhesive. The same degradation effects are found for Aquazol 200, although it is mixed with PB72.

Tab. 5 - Chromatic parameters of marble specimens treated with different polymers after different times of UV irradiation

		Acril ME	Fluoline HY	Regal varnish gloss	Aquazol 500	PB72	PB72/ Aquazol 200
L*	Before ageing	86,38	88,03	81,50	86,69	86,83	85,65
	238 h	85,71	87,38	81,90	76,87	86,36	85,11
	982 h	85,53	87,24	81,97	61,63	86,19	83,39
	3000 h	85,18	86,61	82,28	56,84	86,34	78,88
a*	Before ageing	-0,51	-0,36	-0,38	-0,57	-0,41	-0,66
	238 h	-0,42	-0,24	-0,27	1,55	-0,29	-0,42
	982 h	-0,32	-0,21	-0,28	5,86	-0,36	-0,44
	3000 h	-0,25	-0,18	-0,36	6,23	-0,28	-0,16
b*	Before ageing	2,40	2,34	3,13	2,68	2,19	3,13
	238 h	1,89	1,49	2,43	15,64	1,69	2,38
	982 h	1,58	1,41	2,43	23,70	2,20	5,71
	3000 h	1,50	1,48	2,30	26,77	2,01	12,41

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RIASSUNTO

Fotostabilità di formulazioni innovative per il restauro di opere d’arte

Formulazioni e prodotti innovativi che possono soddisfare i requisiti imposti dalla legislazione (come formulazioni a base acqua) e/o dall’uso nel campo del restauro di opere d’arte (ad esempio fotostabilità) sono stati selezionati attraverso uno studio della loro stabilità ad un irraggiamento tipo solare.