 DOI: 10.1002/masy.200650611

Durability of Protective Polymers: The Effect of UV and Thermal Ageing

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Summary: This paper aimed at studying thermal contribution to the UV ageing process, trying to understand which decisive changes reduce the protective effectiveness of polymer coatings. In this paper the effects on the shielding efficacy of different protective polymers, applied on different low porosity stones have been studied, comparing ageing of a 1000 h simulated solar UV radiation with thermal ageing at about 50 °C, which is the temperature usually reached in UV chambers. The aim of the study has been the evaluation of a possible thermal contribution: the testing methods have been suggested by UNI-Normal Italian protocol and include capillary water absorption, static contact angles and colour variation measurements. A reduction in protective efficacy has been highlighted, probably due to both oxidation and a surface rearrangement of the polymeric material; in most cases chemical degradation of the macromolecules did not occur.

Keywords: coatings; stone conservation; thermal ageing; UV ageing; water repellency

Introduction

Polymeric materials have been tuned and developed in the last decades with the aim of protecting stone materials from the environment; acrylic, silicones and fluorinated resins are among the most widely used resin in this field, thanks to their chemical-physical properties [1].

Durability and long-term efficacy of these products are often evaluated through ageing tests in a UV chamber. This approach is also suggested by Italian standards [2] and it is definitely correct in the case of considering the performances of a polymer exposed to solar irradiation in outdoor conditions; it should also be considered that even the temperature, in some cases, could affect the shielding behaviour of protective polymers. Superficial film modifications, both chemical or morphological, are decisive factors for the treatment efficacy, especially in the case of low porosity stones in which the polymer lays on the surface and is directly exposed to the simulated ageing. Some of these modifications are induced not only by UV energy, but by even a slight increase in temperature. This paper aims at studying the thermal contribution to the UV ageing process, trying to understand which decisive changes reduce the effective protection of the polymeric coating.

Actually, important surface modifications cannot be totally attributable to photo-oxidation phenomena, but also to some coating rearrangements, which are induced by the energy provided to the stone/polymer system both as photonic and as thermal irradiation.

Undoubtedly chemically degraded treatments lead to lower protective performances; nevertheless a chemically sound polymer, which has been exposed to irradiation or heating, does not, necessarily, mean an efficient coating.

Starting from the results obtained in a preceding paper, [3] regarding two experimental fluorinated acrylic copolymers

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tailored as stone protective, both showing a reduction of shielding efficacy after accelerated solar UV ageing and low temperature (50 °C) thermal ageing, a similar experimental work has been extended to four commercial products in order to verify their behaviour.

The effects of a thermal ageing at about 50 °C on the shielding efficacy of different polymeric materials, applied on low porosity stones, have been studied and compared with the effects obtained after simulated solar UV irradiation. 50 °C is a temperature easily reached for outdoor exposed surfaces during the summer period.

Experimental Details

The Copolymers

The tested commercial products for the stone protection tested are:

a fluorinated cationic polyurethane water emulsion supplied by Syremont (PC), ready to use;
a commercial fluorinated copolymer (difluoroethylene/exafluoropropene) in acetone and buthyl acetate supplied by Syremont (CC) ready to use;
a commercial dimethylsiloxane in white spirit supplied by Rhodia (SC) ready to use;
a commercial acrylic copolymer (ethyl methacrylate/methylacrylate, 2:1) supplied by Rhom & Haas (CP). The chosen concentration is 7% in ethyl acetate.

The treatment was applied over 8h by capillarity absorption; treated specimens were dried at room temperature on glass beads for 24h and then at 40°, 24h. In Table I the amount of product absorbed has been reported; finally they were dried at 50 Pa for 24h at room temperature and stored in silica gel desiccators.

The Stone Materials

Candoglia marble, is a xenoblastic metamorphic carbonatic stone, with a very low open porosity (<1 vol-%), coming from the quarries of Candoglia (Verbania), in northern Italy, and used in the building and maintenance of the gothic Cathedral of Milan. The stone specimens were cut in squared blocks of $5 \times 5 \times 2$ and $5 \times 5 \times 1$ cm size. The surface of each specimen was smoothed with abrasive carborundum paper (No. 180). The specimens were then accurately washed with deionised water and dried 24h at 40 °C followed by 24h under vacuum (50 Pa) at room temperature; they were finally weighed and stored in silica gel desiccators before treatment. [4]

The Testing Methodologies

Water repellency (evaluated by static contact angle measurements), water capillary absorption and colorimetric tests were carried out on the stone specimens, according to UNI Cultural Heritage Protocol, [4] before and after application of the polymer coating and after each step of the ageing procedure. The capillary absorption results are reported as Relative Capillary Index (ICr) [4,5] to give a prompt evaluation of the amount of water absorbed. ICr is calculated from the ratio of the areas described by the capillary absorption curves before and after treatment. Color changes were measured with a CR-200 Minolta colorimeter, based on the $L^*a^*b^*$ coordinates of the CIE Lab space. Static contact angle measurements [4] were performed with a Lorentzen & Wettre instrument.

The treated specimens were aged and tested after 500 and 1000 hours.

Photooxidation experiments were carried out with Suntest CPS+ apparatus (Heraeus, Germany) equipped with a 1500W Xenon lamp light source and a cutoff filter for wavelengths below 295 nm, [2] irradiation was kept constant at 750 W/m^2. The maximum temperature on the samples during irradiation was 50 °C. Thermal ageing was carried out, for 500 and 1000 hours, in a climatic chamber Mazzali Thermair at the temperature of 50 °C. PC1, CC1, SC1, CP1 specimens were thermally aged while PC2, CC2, SC2, CP2 were UV aged.

Results and Discussion

The Table I shows the amount of product that each specimen absorbed during the treatment by capillary absorption. This value, for a given stone substrate, depends on the characteristics of product, the molecular weight, the solution concentration and the nature of solvent.

CC penetrates in reduced amount to the specimens, twice less than PC and SC and three times less than CP; this is probably due to its high molecular weight (around 350000), the high volatility of the solvent (acetone/butylacetate) and its low affinity with the stone. The high water repellency of the fluorinated structure does not favour the penetration of the polymer into the hydrophilic structure of the marble.

After the application of the polymer coatings, an alteration in the appearance of the treated marble surfaces resulted in a slight darkening for all products. In Table II the colour changes are reported as differences in brightness values (L^*) before and after treatment and before and after ageing. When applied to marble all treatments cause a similar decrease of L^* values ($\Delta L^* \sim -2$), only in the case of SC ΔL^* values are near -3. During UV and thermal ageing PC and CP suffer a slight increase of darkening while CC and SC tend to keep the values unaltered. For the a^* and b^* coordinates no significant variations were observed, that is, neither yellowing or reddening were measured. Therefore, it can be stated that all polymers substantially do not induce color variations to the marble surfaces, as previously tested coatings. [6,7,8,9] Definitely the behaviour has to be considered really satisfactory, bearing in mind that human eye can detect differences lower than 2 points in colour coordinates only with difficulty. Moreover, no differences have been highlighted between the two ageing procedures.

As regards the static contact angle measurements, CP offers the poorest water repellency behaviour among the products, before and after ageing. The best performing polymer is siloxane (SC) which maintained a static angle around 100 degrees even after 1000 hours of ageing. Generally speaking, analysing Table III, it is clear that the effect of UV ageing, with its oxidising capability, induces heavier damage than thermal ageing. The effect of the low temperature ageing (50 °C) is, nevertheless, evident. Actually, if in the case of UV photooxidative ageing it is possible to justify the loss of water-repellency with the formation of hydrophilic compounds, [10,11] this is not possible in the case of mild thermal ageing (50 °C), which is not able to provide enough energy to break the copolymers' bonds. It is clear that some physical rearrangement occurred to the polymers, which was able to modify the coating efficacy.

Similar considerations apply when water absorption by capillarity and the ICr values are considered (Table III and Figure 1, 2). The specimens treated with the different protective treatments show similar curves of water absorption, independently of the type of ageing. This behavior is highlighted by the ICr values which confirm the similar response of the copolymer to the two different stimulations. So, part of the decreased performances of copolymers usually connected to the UV ageing have to be linked, in some way, to the temperatures reached in the chamber and not to the energy of the radiation, i.e. to the photooxidative damage. The low ageing temperature (50 °C) , is enough to induce some

Table I.
Amount of absorbed product

Product	sample (thermally aged)	mg	mg/cm^2	sample (UV aged)	mg	mg/cm^2
Polyurethane	PC1	0,0184	0,000736	PC2	0,0132	0,000528
Perfluoropolyether	CC1	0,0076	0,000304	CC2	0,0079	0,000316
Polysiloxane	SC1	0,0176	0,000704	SC2	0,0150	0,000600
Acrylic resin	CP1	0,0340	0,001360	CP2	0,0347	0,001388

Table II.
Stone color evaluation after treatment and after 1000h of ageing.

	Color differences treated/untreated			Color differences aged 1000h/untreated		
	ΔL^*	Δa^*	Δb^*	ΔL^*	Δa^*	Δb^*
PC1	−1,94	0,57	0,94	−3,13	0,60	0,69
PC2	−1,26	0,58	1,35	−3,53	0,62	0,74
CC1	−1,40	0,61	1,17	−1,42	0,68	0,67
CC2	−1,12	0,57	1,25	−1,69	0,65	0,74
SC1	−2,93	0,56	1,21	−2,54	0,73	0,91
SC2	−3,06	0,47	1,59	−2,32	0,50	0,96
CP1	−1,89	0,20	1,04	−2,17	0,49	1,03
CP2	−2,22	0,26	0,95	−2,66	0,63	1,10

modification in the coating properties, probably modifying the surface arrangement of the macromolecules and changing the distribution, particularly in the case of products containing fluorinated groups.[12,13]

Regarding these last, dynamic contact angle measurements [14,15] by the analysis of the thermodynamic potentials of treated surfaces carried out with the Wilhelmy balance technique, confirmed a modification of the surface hydrophobic homogeneity after UV ageing, with the formation of partly segregated highly fluorinated micro-zones and the consequently appearing of other micro-zones with partial hydrophilic character, that could favour the contact and the penetration of water. The results reported in this paper suggest that a similar effect probably occurs when the energy is supplied as heat. The two not fluorinated polymers (SC and CP) show similar but distinctive behaviours. The siloxane, SC, with its remarkable performances as water repellent coating for stone materials, seems to be slightly affected by the two ageing processes, so the performances appear similar. In the case of the acrylic copolymer (CP), the UV ageing [11] heavily affects the performances as evinced both by water repellency and by water absorption by capillarity, while the thermal ageing shows a slightly lower effect. Although the structure of the acrylic polymer is surely weaker than that of the fluorinated ones, probably the absence of fluorine and a higher affinity to the stone nature for the acrylic backbone reduce the rearrangement potential of the coating.

Conclusions

It is clear that the changes in the shielding efficacy and water-repellency of the copolymers have to be correlated to modifications of the surface coating arrangement, after energy has been supplied (UV or thermal). These superficial modifications are a decisive factor for the protective

Table III.
Static contact angle and ICr values after treatment (0h) and after 500h or 1000h of ageing.

	Static contact angles			Relative capillary indexes	
	0h	500h	1000h	ICr after tretment	ICr after 1000h
PC1	114	92	89	0.58	0.87
PC2	112	98	96	0.74	0.85
CC1	110	99	83	0.87	0.94
CC2	110	108	102	0.86	0.96
SC1	128	106	100	0.24	0.56
SC2	126	116	99	0.24	0.55
CP1	86	60	44	0.26	0.92
CP2	86	71	69	0.38	0.82

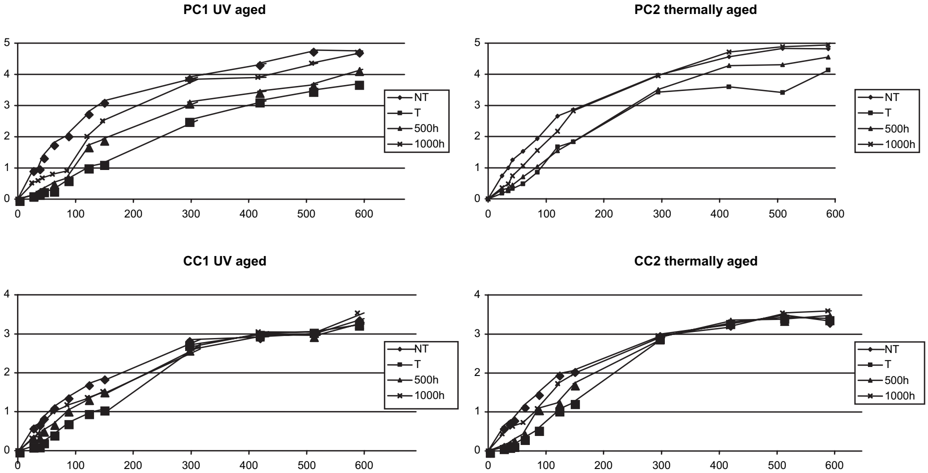

Figure 1.
The capillary absorption curves of PC and CC treated specimens: before and after treatment; after 500h and 1000h of ageing. On the left are the curves of UV aged specimens, on the right the thermally aged ones.

efficacy in a low porosity stone, in which most of the polymer is lying on the surface, directly exposed to ageing stimulations and with greater possibilities for mobility. It has been important to demonstrate that the protective efficacy of a polymeric coating can be weakened not only by a chemical oxidation, but also by a small increase of the system energy. This general conclusion is well-grounded, independently of the chemistry of polymeric material, even if each class shows its own sensitivity to ageing.

Further studies are necessary to characterize thermally aged copolymers (by FTIR and SEC analysis) in order to exclude chemical modifications and to analyze

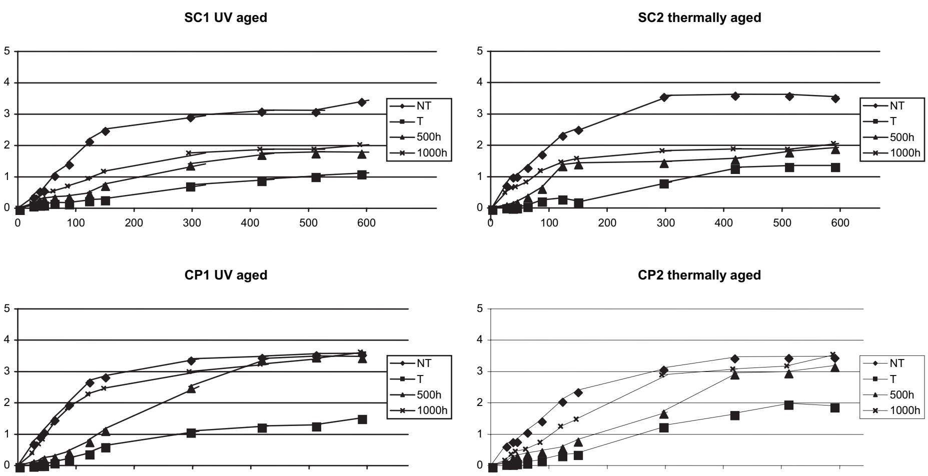

Figure 2.
The capillary absorption curves of SC and CP treated specimens: before and after treatment; after 500h and 1000h of ageing. On the left are the curves of UV aged specimens, on the right the thermally aged ones.

thermally and UV aged surfaces by a dynamic contact angle technique to produce a fair comparison.

Concluding, this paper has aimed to move the attention, in the field of stone protection, from the study of the chemical and structural degradation of polymers to the study of the superficial behavior and properties of the coatings.

[1] T. Poli and L. Toniolo ''The challenge of protecting outdoor exposed monuments from atmospheric attack: experience and strategy'' in Proceeding of 16th European Conference of Fracture: Failure Analysis of Nano and Engineering Materials and Structrures, Alexandroupolis, Grece, 2006 accepted.
[2] UNI10925 Protocol ''Method for artificial solar light test'' (2001).
[3] T. Poli, L. Toniolo ''Protection efficacy of fluorinated Acrylic Copolymers Applied on Historical Italian Marbles'' in Materials Issues in Art and Archaeology Edited by P.M. Vandiver, J.L. Mass, A. Murray *Mater. Res. Soc. Symp. Proc.* 852, Warrendale, PA, 2005, OO6.3.
[4] UNI10921 Protocol ''Water repellents – Applications on samples and determination of their properties in laboratory'' (2000).
[5] R. Peruzzi, T. Poli, L. Toniolo ''The experimental text for the evaluation of protective treatments: a critical survey of the ''Capillary Absorption Index'', *Journal of Cultural Heritage* 4 (2003) 251–254.
[6] G. Alessandrini, M. Aglietto, V. Castelvetro, F. Ciardelli, R. Peruzzi, L. Toniolo, ''Comparative evaluation of fluorinated and unfluorinated acrylic copolymers as water-repellent coating materials for stone'', *Journal of Applied Polymers Science* 76 (2000), 962–977.
[7] Guidetti V., Chiavarini M., Parrini P., ''Polyfluorourethanes as stone protectives'' in: Proceedings of 7 th International Congress on deterioration and conservation of stone, Lisbon, 1992, 1279–1288.
[8] Piacenti F. et al. Protection of stone by perfluoropolyethers, Proceedings of 7^{th} Int. Congress on deterioration and conservation of stone, Lisbon, 1992, pp. 1223–1230.
[9] Tiano P., Manganelli Del Fa C., Fratini F., Pecchioni E., Lucido V., Piacenti F. Aggrgation and protection by fluorinated elastomers of stones exposed to the atmospheric agents, Proc. VI Int. Cong. On Deterioration an Conservation of Stone, Torun, 1988, 492–500.
[10] O. Chiantore, M. Lazzari, V. Castelvetro, M. Aglietto, ''Photooxidative stability of copolymers containing hexafluoroisopropyl groups'' Proceedings of the Fluorine in Coatings IV, Brussels, 5-7 March 2001, Paper 15.
[11] O. Chiantore, M. Lazzari, ''Photo-oxidative stability of Paraloid acrylic protective polymers'', *Polymer* 42 (2001) 17–27.
[12] T. Poli, ''Protective efficacy and photo-oxidative ageing stability of a new class of fluorinated acrylic polymers for the stone protection. Methodologies and problems'', PhD thesis, University of Turin, Italy (2002).
[13] T. Poli, L. Toniolo, O. Chiantore, M. Lazzari, V. Castelvetro, A. Manariti, ''Tailoring new fluorinated acrylic copolymers as protective coatings for marble'', *Journal of Cultural Heritage* 3 (2002) 309–316.
[14] M. Brugnara, E. Degasperi, C. Della Volpe, D. Maniglio, A. Penati, S. Siboni, L. Toniolo, T. Poli., S. Invernizzi, V. Castelvetro, ''The application of the contact angle in monument protection: new materials and methods'', *Colloids and Surfaces A*, 241 (2004) 299–312.
[15] T. Poli, L. Toniolo, R. Peruzzi, M. Brugnara, C. Della Volpe, ''Partially fluorinated acrylic copolymers as coatings for stone protection: characterization and surface properties'', Symposium II Materials Issues in Art and Archaeology VI, Symposium Proceedings Volume 712, II.3.3, (2002) 91–97.

