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BIO-POLYMERS AS STONE PROTECTIVES

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Abstract

In the last decades, natural organic products have been substituted by synthetic products in the field of Conservation of Cultural Heritage. Unfortunately synthesized products have sometimes some drawbacks, due to the fact that they have high costs of synthesis, or they are soluble in toxic solvents for man or environment, or they become irreversible once applied on the substrate. As a consequence, it appears clear that the use of new polymers derived from natural sources as protectives for lapideous materials would be very welcome.

Lactic acid is produced starting from 100% annually renewable resources. Moreover, under appropriate conditions, polymers of lactic acid can be completely biodegraded. They are widely used in packaging and medical devices, and in this work they were proposed as stone protectives. They were tested on samples of two Apuan Marbles having different conservation state: one of them was specifically quarried for this experimentation, while the other one was obtained by an ancient front quarry, probably used in Roman Age.

Samples of the two marbles were characterised and treated with an homopolymer of lactic acid and two co-polymers between lactic acid and Fluorolink D-10H, a low weight perfluoropolyether, with the aim to improve hydrorepellence properties.

Treated materials were subjected to artificial ageing, both with thermohygrometric cycles and UV exposure.

Colour changes and protective efficacy were evaluated after treatment and monitored during the artificial ageing cycles.

Keywords: poly(lactic acid), renewable resource, protective treatment, marble

1. Introduction

In the last years, several treatments have been used to protect and/or consolidate deteriorated stones, using both inorganic and organic products (Dohene and Price 2010; Borgioli 2002; Amoroso 2002). Among the latter ones, polymer-based materials obtained from animals or plants were substituted in course of time by synthetic polymers, mostly petrochemical-based, which have unfortunately some disadvantages, like high costs of production, often high toxicity for man or environment, and so on.

Nowadays, in the approach of the green chemistry, polymers from renewable sources would be very attracting potential substitutes petrochemical-based materials, even in the field of Conservation Science like in many other.

Among these compounds, poly(lactic acid) (PLA) has raised particular attention. The starting material, lactic acid, is produced using 100% annually renewable sources and the polymer is biodegradable and compostable (Stevens 2002). Furthermore structure and molecular weight of the polymer can be easily controlled and modified through the synthesis to obtain tailored products. PLA is widely employed in packaging and biomedical devices (Ljungberg and Wesslen 2005), and it may also represent an appealing alternative to synthetic polymers commonly employed in Conservation of Cultural Heritage. Recent studies showed indeed that PLA may have a good long-term photo-stability, making it particularly appealing for Conservation applications.

In this study PLA and fluorinated PLA (in order to enhance the water repellence effect) were tested on two different marbles. Stone properties were tested before and after application by means of water absorption and colour variation measurements, in order to evaluate the performance of the polymers as protective products. Moreover, treated stones were subjected to accelerated ageing in Climatic Chamber and in Solar Box, with the aim to verify the durability of such treatments behind thermo-hygrometric conditions variations and UV irradiation. During ageing cycles, stone properties were tested at scheduled intervals.

2. Experimental procedures

2.1 Stone materials and products

The stone samples used for testing PLA and modified PLA were two calcitic marbles characterised by different total open porosity and water accessible porosity. The first, named MVB, is a medium-fine grained (150-200 µm) white marble with many gray veins. The marble become from an ancient front of Gioia quarry (Carrara, Tuscany, Italy), from a block probably extracted in the Roman age. This lithotype is characterised by a total open porosity of 2.8% and a water accessible porosity of 1.1%. The second one, named MG, is a white commercial calcitic marble, medium-fine grained, with total open porosity < 1% and water accessible porosity < 0.5%.

The samples were cut into 5 x 5 x 2 cm specimens.

Three different polymers of lactic acid were studied and tested: an homopolymer of LL-lactide (named PLLA), and two A-B-A block copolymers between lactic acid (A) and Fluorolink D-10H (FLK) (B), that is a low weight perfluoropolyether. One of them was a copolymer of LL-lactide and FLK (named PLLA-FLK), and the other was a copolymer of LD-lactide, that is the rac-lactide, and FLK (named PDLA-FLK). All polymers were synthesized through ROP (Ring Opening Polymerization) technique, that permits a good control of structure and molecular weight of obtained products. The T_g (glass transition temperature) of the products were determined through DSC measurement technique, while their Mw (molecular weight) were evaluated through GPC technique.

GPC (Gel Permeation Chromatography) was performed using a GPC Waters system equipped with a pump Waters model Binary HPLC 1525, a refractive-index detector Waters model 2414 and three columns Shodex KF-803 (length: 300 mm; diameter: 8.0 mm). Analysis was performed at 30°C using chloroform as eluent, with a flow rate of 1.0 mL/min. Chloroform solutions (1 mg of polymer in 1 mL of solvent) were injected.

Weight-average molar mass (Mw)/retention time was calibrated against polystyrene standards.

DSC (Differential Scanning Calorimetry) was performed with a Perkin Elmer instruments Pyris 1 DSC model equipped with an Intracooler 2P cryogenic system. A heating rate of 20°C/min was used. Traces were recorded in the temperature range from 0 to 200°C under a nitrogen atmosphere. To eliminate any effect of thermal history, measurements were made from a second heating cycle, after heating the sample to 200°C at 20 °C/min, followed by quenching to 0°C.

The stability of the polymers was studied in previous works, and they proved an interesting ageing behaviour, with a very slight decrease of molecular weight after 750 hours of UV irradiation and FT-IR spectra generally unchanged up to 1,000 hours of irradiation (Giuntoli *et al.* 2012a, 2012b).

2.2 Treatment procedure and performance evaluation

The products were applied on samples of the two marbles. Two ml of a 13% (w/w) solution of the polymer in chloroform were applied on one of the 5 x5 cm^2 surface of each sample. The amount of product applied for each treatment was determined by weighing the specimens before and after the treatment (after complete evaporation of the solvent). The amount of product is expressed as the weight of product per surface unit (g/m^2).

The treatments were evaluated by measuring colour variations and capillarity water absorptions.

Colour variation measurements were performed with a portable instrument MINOLTA Mod. Chromameter CR200 comparing the colour of the samples before and after treatment, according to the method adopted by the UNI-EN commission (UNI EN 15886:2010).

The water absorption tests were carried out before and after treatment, according to the capillarity test method adopted by the UNI-EN commission (UNI EN 15801:2010).

2.3 Artificial ageing

The durability of the performance of PLA and fluorinated PLA was tested with accelerated ageing.

Treated and untreated samples of both marbles were submitted to thermohygrometric cycles in an Angelantoni Challenge 500 Climatic Chamber. Temperature and Relative Humidity changed according to the cycle represented in the Figure 1. This cycle has been repeated for 15 times and colorimetric measurements were repeated after 5, 10 and 15 cycles, while water absorption tests were carried out after 5 and 15 cycles.

In order to evaluate the performances of products after UV irradiation, treated and untreated samples of both marbles were submitted to artificial ageing in a CO.FO.ME.GRA Solar Box model 3000e up to 1,000 hours, according to the adopted by the UNI-EN commission (UNI EN 10951:2001). Irradiance was kept at 500 W/m^2. Colorimetric measurements were carried out after 250, 500, 750 and 1,000 hours of irradiation, while water absorption tests were repeated at the end of the 1,000 hours (750 hours for MG).

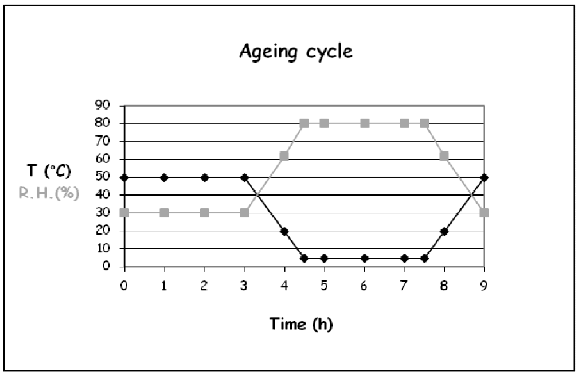

Figure 1. Temperature and Relative Humidity variation cycle

3. Results and discussion

3.1 Chemical-physical characteristics of polymers

The most important chemical-physical parameters for a polymer to be used as a protective of a stone material are reported in Table 1.

Table 1. Principal chemical-physical parameters of polymers

	M_w (g/mol)	**PD**	**T_g (°C)**
PLLA	68,000	2.0	60
PLLA-FLK	34,000	1.5	46
PLDA-FLK	18,000	1.1	30

Data on Table 1 show that the co-polymers containing a fluorinated moiety have smaller molecular dimensions, in addition to a lower T_g, especially for PLDA-FLK: this last datum is coherent with the supposed stereochemistry of the sample obtained using rac-lactide, which should be amorphous. Moreover, PLDA-FLK has a low polydispersity, near to the ideal value (PD = 1), that means that all the molecules of the polymer have the same Mw.

3.2 Amount of product absorbed

Data reported on Table 2 show that in all cases, the amount of product absorbed by the stone is lower than the expected one (16 g/m^2), this is due to the general low porosity of a lithotype like an Apuan Marble. Anyway, a greater amount of the three polymers is able to penetrate inside the porous structure of MVB, while the lower porosity of MG makes the penetration of the polymers more difficult. In contrast with expectations, PLDA-FLK is the least absorbed product on both marbles, although it has the smallest molecular dimensions.

Table 2. Amount of product absorbed by stone samples

Amount of product absorbed (g/m^2)			
	PLLA	PLLA-FLK	PLDA-FLK
MBV	12.8	14.2	11.8
MG	12.4	9.6	8.8

3.3 Colour variation and water absorption

In Figure 2 the colour variations for the stone samples treated with the polymers are reported.

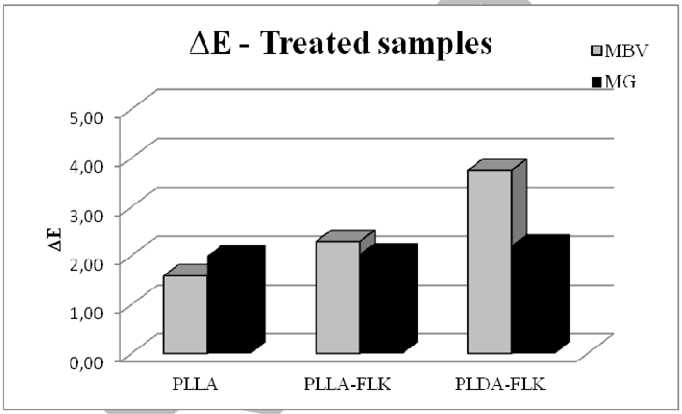

Figure 2. Colour variations (in terms of ΔE) of the treated marble samples

For all treated stones, ΔE values are lower or very close to the limits of the human eye (~ 2), except for PLDA-FLK treatment applied on MBV (3.75). The more relevant contribution to ΔE comes from ΔL, that is lightness. The samples were darkened (a decrease in L) after treatment.

The presence of the fluorinated moiety in the polymers seems to give to the treatment the desired increase of the hydrorepellent effect (Fig. 3): Protective Efficacy of PLLA-FLK and PLDA-FLK treatments is consistently higher than the one of PLLA.

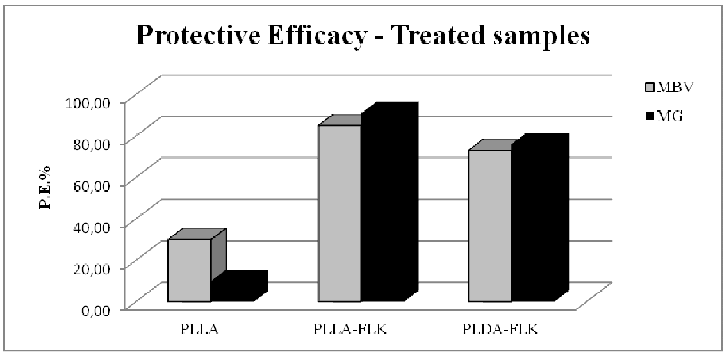

Figure 3. Protective Efficacy (P.E.%) of the treated marble samples

3.4 Artificial ageing

In Figure 4 the colorimetric variation of treated samples subjected to thermohygrometric cycles are reported. The measures were repeated after 5, 10 and 15 cycles.

In Figure 5 the Protective Efficacy of the treated samples is reported: in this case the water absorption tests were carried out after 5 and 15 cycles.

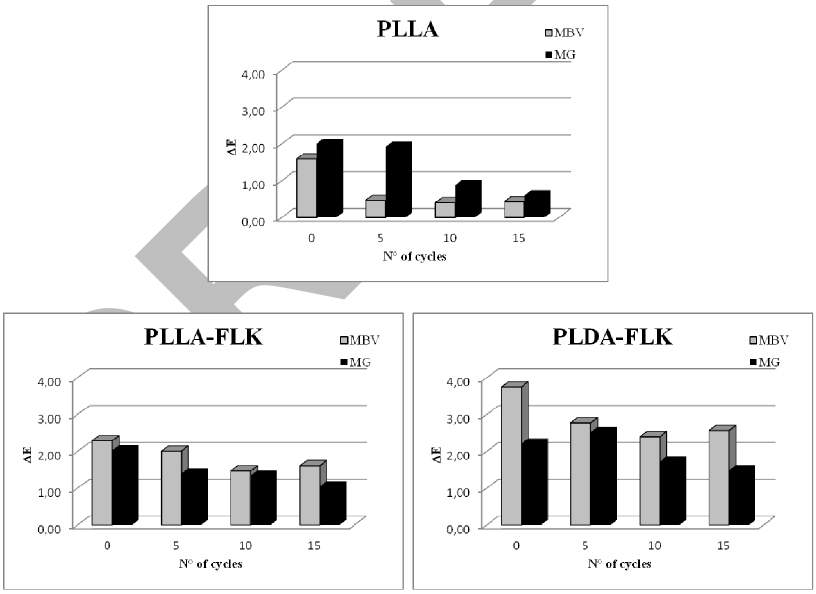

Figure 4. Colour variations (in terms of ΔE) of the treated marble samples after 0, 5, 10 and 15 cycles of thermohygrometric ageing

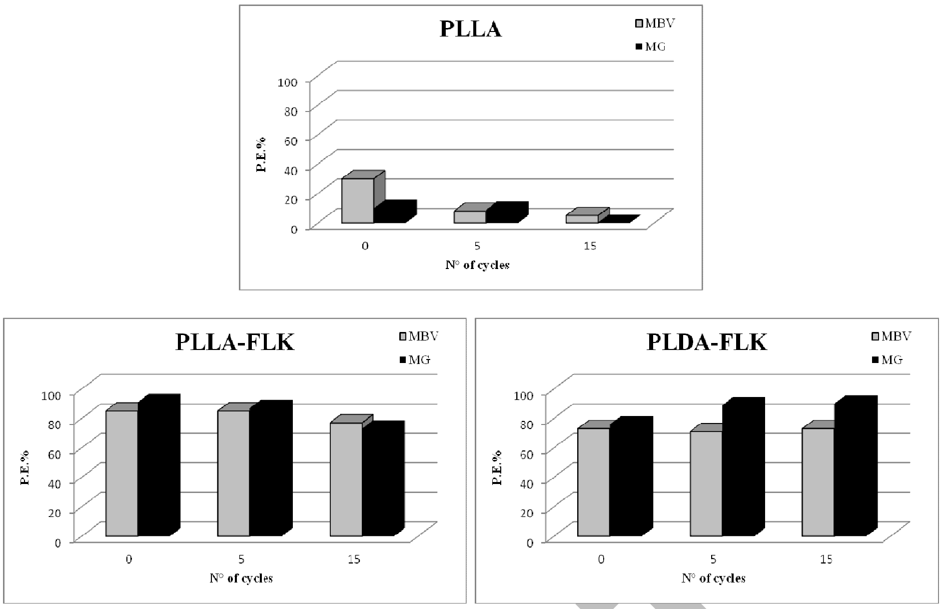

Figure 5. Protective Efficacy (P.E.%) of the treated marble samples after 0, 5 and 15 cycles of thermohygrometric ageing

For all products applied on both marbles, the thermohygrometric cycles don't entail an aggravation of the colour variation of the stone surfaces. On the contrary, L parameter (lightness) in all cases tends to come closer to the initial values, reducing ΔL.

The low Protective Efficacy given by PLLA to both marbles, further decreases after 5 and 15 thermohygrometric cycles. Regarding fluorinated polymers, instead, they maintain very good values of P.E.% on MVB. On the other marble (MG), PLDA-FLK even improves protective performance with thermohygrometric ageing, while P.E.% values for PLLA-FLK slightly decrease going along with cycles.

These behaviours are probably due to the fact that an increase of the temperature can carry to a reorganisation of the polymer structure in the first layers of stone material and a better distribution on the surface: in this way, the colour turns to resemble to the initial one, and the Protective Efficacy is improved or approximately unchanged. In the case of PLLA treatment, the reduction of ΔL, together with the drastic decrease of Protective Efficacy, can suggest the detachment of the product from the surface.

Figures 6 and 7 show respectively the colorimetric variations and the Protective Efficacy of the treated samples subjected to artificial ageing in Solar Box: colour measurements were carried out after 250, 500, 750 and 1,000 (only for MBV) hours of irradiation, while water absorption tests were carried out at the end of the complete ageing period: 1,000 hours for MBV and 750 hours for MG.

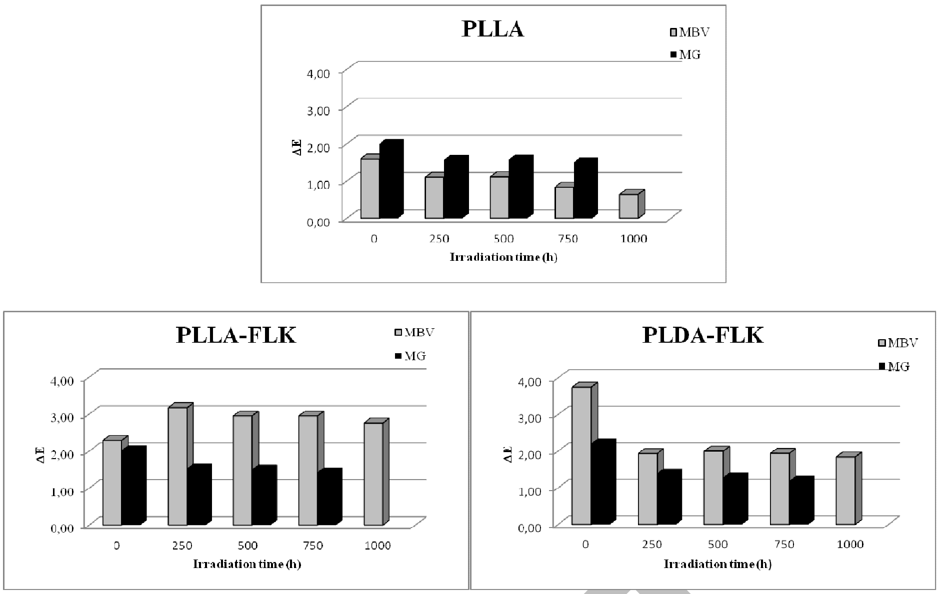

Figure 6. Colour variations (in terms of ΔE) of the treated marble samples after 0, 250, 500, 750 and 1,000 hours of UV irradiation

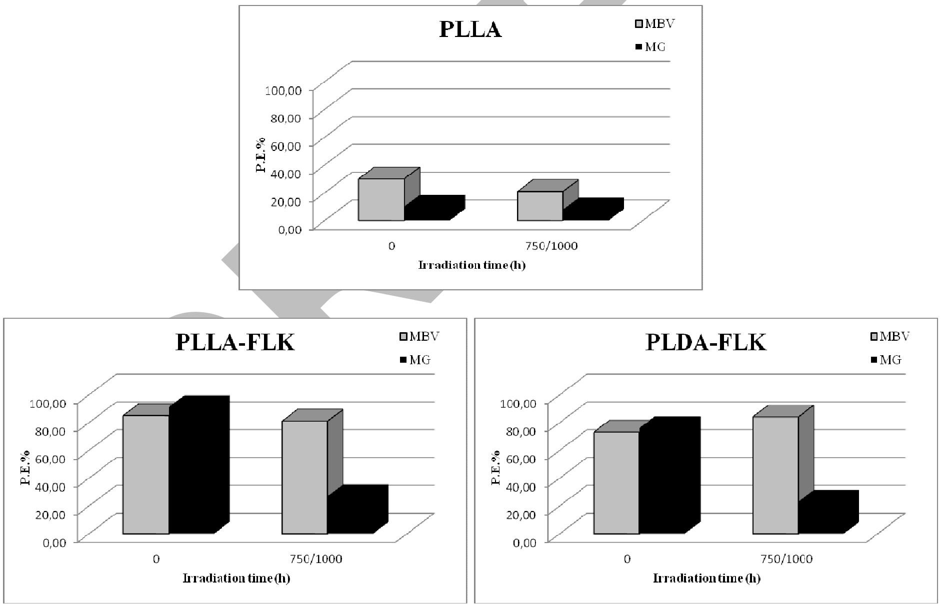

Figure 7. Protective Efficacy (P.E.%) of the treated marble samples after 0 and 750 (for MG) or 1,000 (for MBV) hours of UV irradiation

As well as for thermohygrometric ageing, UV irradiation brings to a decrease of ΔE on the treated samples too. Again, L parameter (lightness) turns back towards the initial values, except for PLLA-FLK on MBV. In this case, it can be noted an increase of ΔE after the first 250 hours of irradiation and then a slight decrease up to 1,000 hours.

Protective effect of PLLA treatment on both marbles decreases after 750 or 1,000 hours of UV irradiation in Solar Box. The fluorinated polymers have instead a different behavior on the two marbles: both polymers maintain a very good P.E.% on MBV after 1,000 hours of irradiation, while they drastically decrease their protective performance when applied on MG.

This different trend of treated MG subjected to UV irradiation can be due to its lower open porosity: the polymers irradiated can be more easily lost from a very compact stone like MG, because they don't penetrate in deep but remain on the surface.

4. Conclusions

The application of polymers from a monomer produced starting from renewable resources in the field of Cultural Heritage represents an attracting alternative to traditional petrochemical-based materials.

In this work, the properties of innovative homopolymers and block fluoro-functionalised co-polymers of lactic acid for the protection of stone having a low open porosity have been reported. As wished, the presence of a fluorinated group in the polymer chain gives an enhancement of the water-repellent effect with respect to the unfluorinated PLAs.

Such property is maintained even when the treated stone is subjected to thermohygrometric variations cycles.

On the contrary, treated samples submitted to UV irradiation show a different behaviour: the marble with the lower porosity (MG) seems to lose P.E.% as a consequence of the detachment of the applied product. The other marble (MVB) instead maintains unaltered the water-repellence given by the fluorinated products.

Taking account of the promising results of such fluorinated co-polymers as stone protective products, it can be useful to test different applying methods (ie more diluted solutions, iterated application, etc.) in order to reach a better penetration of the product even in lithotypes having a very low porosity.

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