Fluoro-Functionalized PLA Polymers as Potential Water-Repellent Coating Materials for Protection of Stone

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ABSTRACT: A series of sixteen fluoro-functionalized poly (lactic acid)s were synthesised using two commercial fluorinated alcohols [3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octanol and 4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)benzyl alcohol] as co-initiators in the ring-opening polymerization of L-lactide and rac-lactide (the racemic mixture of L- and D-lactide) catalyzed by Tin(II) 2-ethylhexanoate. The polymers were characterized by NMR, IR, GPC, DSC and tested as potential protective coating for stone. The performances were comparatively evaluated in terms of water protection efficacy and colour changes of the treated stone. Furthermore, the photo-stability of nine selected polymers under Solar Box condition was also investigated. It has been shown that the presence of fluorine makes the stone more water-repellent. The polymers showed also interesting photo-stability and some of them provided a behavior close to PLA-FLK-PLA block copolymers recently reported in the literature, in spite of their lower fluorine content © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 3125–3133, 2012

Key words: ageing; coating; fluopolymers; functionalization of polymers; synthesis

INTRODUCTION

The use of synthetic polymers having water-repellent properties is a common practice in the conservation of historic building and ancient stone surfaces exposed to the open air.[1–4] In fact, the direct and/or indirect activity of water is generally accepted to play a relevant role in stone weathering, improving both chemical and physical/mechanical decay.[2,3]

The Italian Committee for Stone Material Normalization has suggested the basic requirements which a protective coating material for Cultural Heritage should fulfill. These are impermeability to liquid water, permeability toward water vapor, chemical, and photochemical stability, reversibility, and suitable optical properties.[5] However, scientific community is still far from the development of a material having these requirements.

Acrylic resins (e.g., Paraloid B-72-Rohm & Haas), silicone resins (e.g., Rhodorsil RC 11309 Rhône-Poulenc), microcrystalline waxes (e.g., Cosmolloid 80H-Astor), and perfluorinated polymers (e.g., Fomblin Y-Montedison) are the synthetic materials more widely used as protective for stone. Fluorinated polymers are considered the most suitable products. In fact, the formal substitution of hydrogen by fluorine atoms into polymer structure has the effect of improving resistance to chemical and physical degradation agents (C—F bond energy = 116 kcal/mol at 25°C) and of inducing higher water-repellence.[6,7] Perfluoropolyethers (PFPE) were applied in the '80s on some Florentine buildings as stone protective.[2] The properties of these polymers are very close to those of an ideal coating material. Nevertheless, one of their main drawbacks is the poor solubility in common organic solvents. Indeed, solubility is high in halogenated solvents, like chlorofluorocarbons (CFC). Furthermore, because of their inertness, they are not able to graft to stone substrates, which results in a migration inside of the coated material after a few time deposition.[1,2,4] On this basis, the preparation of fluorinated polymers or blends with additional features has been the subject of research. In particular, the possibility of synthesizing copolymers or functionalized polymers with a specific microstructure is of primary importance. In fact, the covalent bond among chemical groups prevents macroscopic phase separation and provides greater control of the properties of the material. Some examples of modification are represented by fluorinated polyether-amides and fluorinated acrylic polymers.[2]

Recent studies[8] have also been devoted to joining the special properties of the fluorine chemicals with the use of polymers from renewable feedstocks, like poly(lactic acid) (PLA).[9] This research has evidenced

the possibility of synthesizing PLA-FLK-PLA block copolymers, coming from a commercial PFPE with two hydroxyl telechelic functionalities, Fluorolink D-10H (FLK).[8] These copolymers were soluble in typical organic solvents and showed encouraging performances as stone protective coating, that is, impermeability to liquid water, chemical and photochemical stability, and negligible short- and long-term modification of the appearance of the substrate. Finally, fluorine atoms preferentially disposes at the polymer/air interface, due to the typical low surface energy of PFPE, as shown by the analysis performed by an environmental scanning electron microscope-energy dispersion spectroscopy (ESEM-EDS) system.[8]

In this article, we present the results of a research devoted to synthesizing and testing innovative fluo-functionalized PLA polymers as protective for stone. The major feature of the polymers is the lower fluorine content with respect to PLA-FLK-PLA. A series of polymers were synthesized using two commercial fluorinated alcohols as coinitiators in the ring-opening polymerization (ROP) of L-lactide and rac-lactide (the racemic mixture of L-lactide and D-lactide) catalyzed by Tin(II) 2-ethylhexanoate [Sn(Oct)$_2$]. The samples were comparatively evaluated in terms of water protection efficacy and color changes on stone substrates. Furthermore, the photostability of nine selected polymers was investigated by artificial ageing tests.

EXPERIMENTAL

Materials

L-lactide, rac-lactide, 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octanol (**F**), Sn(Oct)$_2$, n-hexane, and deuterated solvent (CDCl$_3$) were purchased by Aldrich. 4-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)benzyl alcohol (**B**) was purchased by Fluka. Acetone and chloroform were purchased by Normapur. 2-Butanone was purchased by Merck. Tetrahydrofuran was purchased by Riedel-De Haën.

The monomers (i.e., L-lactide and rac-lactide) were purified from lactic acid impurities by sublimation under reduced pressure and stored under nitrogen atmosphere. n-Hexane, acetone, chloroform, 2-butanone, and tetrahydrofuran were laboratory-grade products and used without any further purification. Distilled water was used throughout the work.

Synthesis of polymers

Polymers were synthesized introducing the appropriate amount of monomer (L-lactide or rac-lactide), fluorinated alcohol (**F** or **B**) and Sn(Oct)$_2$ into a 50 mL glass vial. Fluorinated alcohol and lactide, in different molar ratios, with 0.5 : 100 catalyst : lactide

molar ratio were employed. The vial was heated for 3 h under stirring in an oil bath at 130°C. The polymers were purified by dissolution-precipitation method (chloroform and n-hexane) and dried under reduced pressure overnight to remove any residual solvent.

Nuclear magnetic resonance (NMR) spectroscopy

^{1}H, ^{13}C, and ^{19}F-NMR spectra were obtained using a Varian VXR 200 MHz spectrometer, working at 199.958 MHz for ^{1}H, 50.294 MHz for ^{13}C, and 188.114 for ^{19}F, using CDCl$_3$ as solvent. Chemical shifts were referred to tetramethylsilane for ^{1}H-NMR and ^{13}C-NMR spectra and to CFCl$_3$ for ^{19}F-NMR spectra.

Fourier transform infrared (FTIR) spectroscopy

FTIR analysis was performed with a Shimadzu FTIR spectrometer IRAffinity-1 model, using either NaCl disks or a Specac Golden Gate single reflection diamond attenuated total reflectance (ATR) accessory. Polymeric film was casted on NaCl disks using chloroform as solvent. ATR accessory was used to acquire the infrared spectra directly on the neat polymer.

Gel permeation chromatography (GPC)

GPC 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 (M$_w$)/retention time was calibrated against polystyrene standards.

Differential scanning calorimetry (DSC)

DSC was performed with a Perkin Elmer instruments Pyris 1 DSC model equipped with a 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.

Stone samples and glass slides treatment

White dolomitic Shivec marble's samples (5 × 5 × 2 cm) were used for testing polymers as stone protective. The samples were washed with water, dried in an oven at 60°C, and brought to constant weight in

a drier. One of the wider surfaces was treated with 2 mL of a 13% (weight/weight) solution of the polymer in chloroform using a pipette. After evaporation of the solvent, the samples were kept in a drier until constant weight was reached. The average amount of polymer applied was 33 (± 5) mg (determined by weight difference). To evaluate solubility, weight, and molecular weight changes of the polymers after artificial ageing, polymers were casted on glass slides (38 × 26 mm) preliminarily washed with acetone and brought to constant weight. Afterwards 270 µL of a 10% (weight/weight) solution of polymers in chloroform were casted on the glass surface. After the evaporation of the solvent, the slides were kept in a drier up to constant weight and the amount of polymer applied was determined by weight difference.

Artificial ageing of polymers

Artificial ageing tests were performed using a CO.FO.ME.GRA Solar Box model 3000e, equipped with a Xenon-arc lamp. An outdoor type UV filter with cut-off <290 nm was used to eliminate radiation not present in the external sunlight. According to the ISO 1134/2004 protocol,[10] irradiance was kept at 550 W/m^2, and black standard temperature (BST) at 65 ± 2°C. Stone samples, NaCl disks and glass slides coated with the polymeric film were placed with untreated stone samples as control in the plate of the chamber and exposed for 750 h to the same conditions. FTIR spectra of polymers placed on NaCl disks were recorded after 24, 72, 125, 250, 500, and 750 h of exposure. Chromatic data, solubility, weight, and molecular weight changes were determined after 250, 500, and 750 h.

Weight loss, solubility, and molecular weight test

After exposure in Solar Box, the treated glass slides were stored under controlled humidity in a drier until a constant mass was reached and the weight loss between before and after ageing was determined. The slides were washed with chloroform to dissolve all soluble polymers and weighted again. The amount of polymer eventually remaining on the slides was calculated by weight difference. To confirm these data, chloroform solutions were evaporated and the polymeric residues were weighed. The soluble fraction was used for molecular weight determinations using GPC.

Colorimetric test

Colorimetric measurements were performed according to the UNI EN 15886/2010 protocol,[11] using a tristimulus Minolta Chroma Meter (CR 200) instrument operating with the CIE-L*a*b* system. The calibration was carried out with a white, bright standard plate (L* = 97.83, a* = −0.52, and b* = 2.39). The measuring head was positioned on the stone sample on the same area, using a positioning mask. Color changes were expressed in term of ΔL*, Δa*, Δb*, and ΔE*, where:

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

The chromatic difference is defined as:

$$\Delta x^* = x^*_i - x^*_0 \quad (2)$$

where x_i^* is the chromatic value (L*, a*, b*, or E*) of the treated stone sample (either before or after ageing) and x_0^* is the colorimetric value of the untreated sample. For each polymer, determinations were performed three times on three different stone samples and the average ΔL*, Δa*, Δb*, and ΔE* were reported.

Capillary water absorption test

Capillary water absorption measurements were performed according to the UNI EN 15801/2010 method.[12] The dried samples were placed on a multilayer pack of filter paper soaked in distilled water. The amount of water absorbed by capillarity forces was determined by weighing samples before and after keeping them on the soaked filters for 60 min. The amount of absorbed water M_i at 60 min contact time per surface unit, is defined as:

$$M_i = \frac{m_i - m_0}{S} \quad (3)$$

where m_i is the wet sample mass (g) at 60 min contact time, m_0 is the dry sample mass (g), and S is the contact surface (cm^2).

The water protection efficacy (%E) is defined as:

$$\%E = \frac{A_0 - A_i}{A_0} \quad x \quad 100 \quad (4)$$

where A_0 is the capillary water uptake of the untreated stone sample (g) and A_i is the capillary water uptake of the treated sample (g) ($A_i = M_i \times S$). For each polymer, determinations were performed three times on three different stone samples and the average M_i and %E were reported.

RESULTS AND DISCUSSION

Synthesis and characterization of polymers

Commercially available fluorinated alcohols **F** and **B** were used as coinitiators in the ROP of L-lactide and

TABLE I
Selected Chemical and Physical Characteristics of the Polymers

Sample	Lactide	Alcohol/lactide (%)[a]	M_w (g/mol)[b]	PDI[b]	T_g (°C)[c]	T_m (°C)[c]	T_c (°C)[c]
PLLA	L-	0.0	18,863	1.3	54.0	162.2	104.7
PLDA	rac-	0.0	11,732	1.2	44.2	–	–
PLLA_F$_{1.5}$	L-	1.5	8506	1.3	44.4	151.0	106.7
PLLA_F$_{2.5}$	L-	2.5	3505	1.4	36.6	137.0	105.2
PLLA_F$_5$	L-	5.0	3214	1.4	34.7	135.6	105.1
PLLA_F$_{20}$	L-	20.0	1458	1.5	–	–	–
PLDA_F$_{1.5}$	rac-	1.5	10,120	1.2	33.6	–	–
PLDA_F$_{2.5}$	rac-	2.5	9772	1.3	29.4	–	–
PLDA_F$_5$	rac-	5.0	4725	1.2	28.4	–	–
PLDA_F$_{20}$	rac-	20.0	1253	1.7	-	–	–
PLLA_B$_{1.5}$	L-	1.5	22,027	1.3	55.7	163.8	97.4
PLLA_B$_{2.5}$	L-	2.5	11,836	1.1	50.4	157.2	94.9
PLLA_B$_5$	L-	5.0	6258	1.1	40.2	141.8	94.7
PLLA_B$_{20}$	L-	20.0	1058	1.4	–	–	–
PLDA_B$_{1.5}$	rac-	1.5	14,984	1.3	44.7	–	–
PLDA_B$_{2.5}$	rac-	2.5	9143	1.2	41.6	–	–
PLDA_B$_5$	rac-	5.0	1957	1.2	25.2	–	–
PLDA_B$_{20}$	rac-	20.0	929	1.4	–	–	–

Readings "F" and "B" in sample's nomenclature indicates polymers containing alcohol F or B, respectively. Catalyst/monomer molar ratio = 0.5%
[a] Molar ratio.
[b] Measured by GPC.
[c] Measured by DSC.

rac-lactide catalyzed by Sn(Oct)$_2$. The alcohols were selected for their different distance between fluorinated moiety and terminal hydroxyl group. A series of fluoro-functionalized PLA polymers was obtained, as listed in Table I. Figure 1 shows the synthetic reaction employed to obtain the modified PLAs.

The growth of the polymer chain was monitored by NMR analysis (^{1}H, ^{13}C, and ^{19}F-NMR) on the basis of the signal of $-CH_2O$ group for the fluorinated alcohol and the signal of $-CH_3$ group for PLA moiety (Fig. 2).

The ^{1}H-NMR spectrum of the starting alcohol **F** is characterized by the following signals: a multiplet at 2.42 ppm assigned to the $-CF_2CH_2$, a multiplet at 4.01 ppm assigned to the $-CH_2O$ and the hydroxyl proton signal at 1.62 ppm. In the ^{1}H-NMR spectrum of alcohol **B** are present the $-CH$ aromatic signals at 7.33 and 7.21 ppm, a multiplets assigned to $-PhCH_2$ at 2.92 ppm, a multiplet assigned to $-PhCH_2CH_2$ at 2.36 ppm, a singlet assigned to $-CH_2O$ at 4.67 ppm and the hydroxyl proton signal at 1.72 ppm. The ^{1}H-NMR spectra of the fluoro-functionalized polymers are characterized by the shift of the original $-CH_2O$
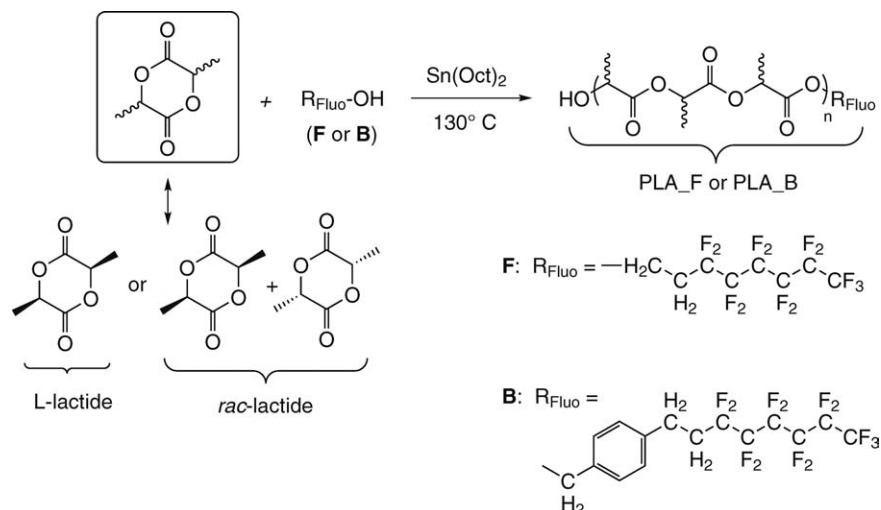

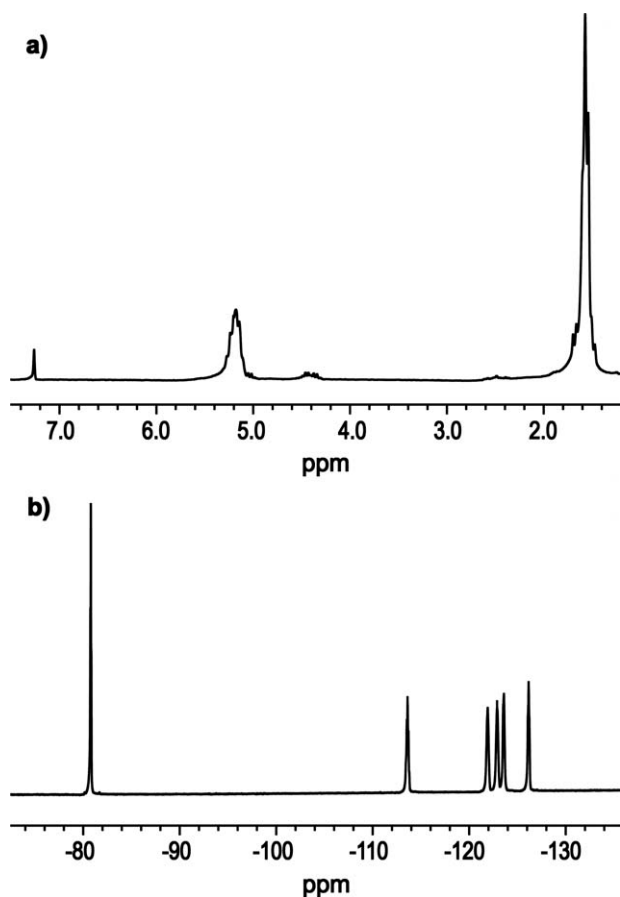**Figure 1** Synthesis of fluoro-functionalized PLA polymers from L-lactide, rac-lactide, and fluorinated alcohols **F** and **B**.

Figure 2 (a) ^{1}H-NMR and (b) ^{19}F-NMR spectra of fluoro-functionalized polymer PLDA_F$_5$ in CDCl$_3$.

signals respectively from 4.01 to 4.45 ppm in **F** and from 4.67 to 5.09 ppm in **B**, indicating the formation of the new ester linkage. The signals assigned to —CH$_3$ and —CH groups of PLA segment were observed at 1.58 and at 5.16 ppm, respectively, according to the literature for other PLA polymers.[13]

^{19}F-NMR spectra of fluoro-functionalized polymers showed the presence of signals due to fluorine
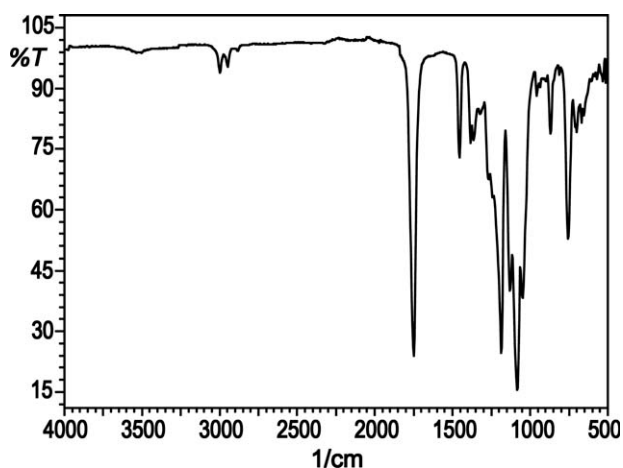

Figure 3 FTIR-ATR spectrum of fluoro-functionalized polymer PLDA_F$_5$.

atoms, having chemical shift very close to those detected in the original alcohols. Since no signals due to terminal carboxyl group of PLA were detected in ^{13}C-NMR spectra of polymers, the signals present in ^{19}F-NMR spectra are referred to fluorinated alcohol incorporated in PLA chain-end.

C—F bonds were also detected in FTIR spectra: the bands between 1350 and 960 cm^{-1} are more intense (using the same —C=O intensity as reference) in the fluoro-functionalized PLAs with respect to unfluorinated ones, due to the presence, among the other signals, of the bands due to C—F stretching (Fig. 3).

The weight-average molar mass (M_w) and the molecular weight distribution of polymers were determined by GPC. Comparatively higher M_w were measured for polymers obtained using lower alcohol : monomer ratio. The values decrease with an increase in alcohol content. Only for polymers prepared with 1.5 : 100 alcohol **B** : lactide monomer ratio (PLLA_B$_{1.5}$ and PLDA_B$_{1.5}$), molecular weights slightly increase with respect to unfluorinated PLAs (PLLA and PLDA, respectively; Table I). Polymers obtained using alcohol **B** generally showed higher molecular weights than polymers obtained using alcohol **F**. This behavior may be ascribed to a different influence of alcohol **B** on melt viscosity in bulk polymerization.

Monomodal distributions with a narrow polydispersities (PDI) were always observed (Fig. 4).

GPC chromatograms of PLLA_F$_{20}$, PLLA_B$_{20}$, PLDA_F$_{20}$, and PLDA_B$_{20}$ show also a reversed, negative signal with respect to PLA polymers. These signals, according to the literature,[8,14] are due to the disparity of refractive indices between the solvent and the fluorinated moiety, confirming the presence of large amount of fluorine moiety in the polymers.

DSC data show that samples obtained using L-lactide are semicrystalline, showing both glass transition temperatutre (T_g), melting temperature (T_m), and crystallization temperature (T_c) while samples obtained using rac-lactide are amorphous, showing only T_g. This finding is in agreement with their
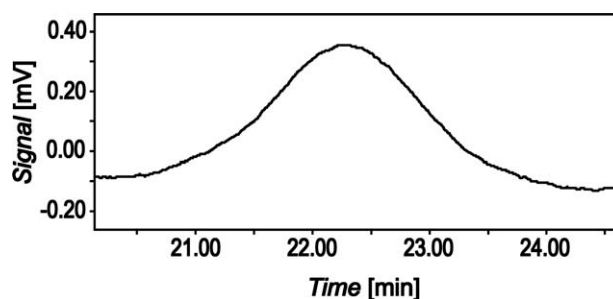

Figure 4 GPC chromatogram of fluoro-functionalized polymer PLDA_F$_5$.

TABLE II
Color Changes (ΔL^*, Δa^*, Δb^*, and ΔE^*), Amount of Absorbed Water at 60 min
Contact Time per Surface Unit (M_i) and Water Protection Efficacy (% E) of the
Treated Stone Samples

Treatment	ΔL^*	Δa^*	Δb^*	ΔE^*	M_i (g/cm^2)	% E
PLLA	−4.38	−0.02	−0.68	4.46	0.004	37
PLDA	−4.57	−0.15	0.06	4.61	0.004	33
PLLA_F$_{1.5}$	−1.54	0.03	−0.59	1.69	0.002	68
PLLA_F$_{2.5}$	−4.79	0.05	−0.88	4.89	0.002	69
PLLA_F$_5$	−2.67	−0.01	−0.41	2.72	0.001	78
PLLA_F$_{20}$	−3.24	0.00	−0.32	3.35	0.002	66
PLDA_F$_{1.5}$	−3.47	0.00	−0.32	4.18	0.004	34
PLDA_F$_{2.5}$	−5.87	−0.13	0.28	5.87	0.004	36
PLDA_F$_5$	−4.51	−0.07	−0.10	4.51	0.004	37
PLDA_F$_{20}$	−7.56	−0.00	0.14	7.57	0.002	60
PLLA_B$_{1.5}$	−2.11	−0.09	−0.07	2.12	0.003	58
PLLA_B$_{2.5}$	−3.11	0.16	−0.81	3.27	0.001	73
PLLA_B$_5$	−2.15	0.02	−0.80	2.75	0.001	84
PLLA_B$_{20}$	−5.91	0.06	0.12	5.92	0.002	62
PLDA_B$_{1.5}$	−2.59	−0.08	−0.18	2.61	0.002	64
PLDA_B$_{2.5}$	−4.30	−0.01	−0.41	4.37	0.003	51
PLDA_B$_5$	−6.61	−0.07	0.18	6.61	0.003	45
PLDA_B$_{20}$	−8.02	0.03	−0.12	8.03	0.002	64
Untreated	0.46	0.02	−0.10	0.47	0.006	0

supposed stereochemistry.[15,16] Neither T_g nor T_m nor T_c were observed for the oligomers prepared using 20 : 100 alcohol : lactide molar ratio (PLLA_F$_{20}$, PLLA_B$_{20}$, PLDA_F$_{20}$, and PLDA_B$_{20}$).

The presence of fluorinated alcohol in the polymer significantly decrease T_g and (when present) T_m (Table I). For instance fluoro-functionalized samples with 5 : 100 alcohol : lactide molar ratio (PLLA_F$_5$, PLLA_B$_5$, PLDA_F$_5$, and PLDA_B$_5$), T_g is lowered of 15–20°C than that one of the unfluorinated PLA (PLLA or PLDA, respectively). These changes may be attributed to the decreasing of molecular weight due to the inclusion of the alcohol in the polymer chain.[17,18] For most of the fluoro-functionalized polymers (PLLA_F$_{1.5}$, PLLA_F$_{2.5}$, PLLA_F$_5$, PLLA_B$_5$, PLDA_B$_{1.5}$, and PLDA_B$_{2.5}$) T_g values are in the range from 35 to 44°C that is slightly upon room temperature, improving the flexibility of the polymer.

Furthermore, all the samples were soluble in typical organic solvents (i.e., acetone, chloroform, 2-butanone, and tetrahydrofuran), that allows for an easy film deposition. Solubility in these solvents is higher than PLA-FLK-PLA copolymers, due to the lower fluorine amount.

Evaluation of polymers as protective for stone surfaces

To evaluate the performances of polymers as stone protective, they were applied on Shivec marble samples by solution-casting. Afterwards color changes and water protection efficacy were measured.

Color changes

The lightness difference ΔL^* resulted the most significant parameter when analyzing the color changes in the CIE-L*a*b* system (Table II). All the treatments produced a darkening of the stone sample, as L^* values were always decreasing. Instead, the variation of the parameter a^* (indicating the displacement of chromaticity from red to green) and b^* (indicating the displacement of chromaticity from blue to yellow) were almost negligible. A similar trend in the variation of $L^*a^*b^*$ parameters has been reported for PLA-FLK-PLA copolymers.[8]

The global differences in color, indicated by ΔE^* values, are in a limited range (from 1.69 for PLLA_F$_{1.5}$, to 8.03 for PLDA_B$_{20}$). Small differences in ΔE^* values were detected varying the type of alcohol employed. Stereochemistry of PLA seems to have a slight effect. In fact comparatively lower ΔE^* values were measured for polymers obtained from L-lactide. This may be attributed to the high crystallinity of PLLA polymers, which form a film having a low visible light-absorbing property.[19] Among these, PLLA_F$_{1.5}$, PLLA_F$_5$, PLLA_B$_{1.5}$, and PLLA_B$_5$, showed ΔE^* values lower than 3, so the chromatic variation are not detectable by human eye.

Capillary water absorption

Fluoro-functionalized PLAs showed a reduction of the amount of water absorbed by capillarity per surface unit at short contact time (60 min), M_i, with respect to the unfluorinated PLAs (Table II). Therefore the introduction of fluorine atoms determined

Changes of Weight-Average Molar Mass (M_w) and Polydispersity (PDI) of Polymers After Different Ageing Time (0, 250, 500, and 750 h)

Treatment	Before ageing		After 250 h ageing		After 500 h ageing		After 750 h ageing	
	M_w (g/mol)	PDI	M_w (g/mol)	PDI	M_w (g/mol)	PDI	M_w (g/mol)	PDI
PLDA	11,732	1.2	11,771	1.1	11,686	1.1	11,109	1.1
PLLA_F$_{1.5}$	8506	1.3	8061	1.3	7939	1.3	7731	1.3
PLLA_F$_5$	3214	1.4	3536	1.4	3069	1.2	3151	1.2
PLDA_F$_{1.5}$	10,120	1.2	9918	1.2	9833	1.2	9869	1.3
PLDA_F$_5$	4725	1.2	4798	1.2	4224	1.2	3982	1.3
PLLA_B$_{1.5}$	22,027	1.3	21,930	1.2	21,326	1.2	19,361	1.3
PLLA_B$_5$	6258	1.1	6222	1.0	6136	1.0	6019	1.1
PLDA_B$_{1.5}$	14,984	1.3	13,953	1.3	13,776	1.6	13,809	1.2
PLDA_B$_5$	1957	1.2	1636	1.1	1349	1.2	1104	1.6

an increment of protective efficacy, %E, in agreement with the achievements reported in previous works.[8] Within each series of polymers various trends of water protection efficacy were detected: the influence of different chemical and physical effects (e.g., fluorine content, stereochemistry, and molecular weight) on the water-repellent properties could be assumed. Generally, polymers obtained from L-lactide showed higher water protection efficacy than polymers obtained from rac-lactide (Table II). This finding should be ascribed to the low hydrophilicity of semicrystalline PLAs with respect to the amorphous ones. Furthermore, polymer obtained from L-lactide generally showed higher molecular weight than polymer obtained from rac-lactide (Table I) and the higher M_w in a homogeneous series of polymers may itself enhance water protection efficacy.

Among fluorinated polymers, the most efficient are PLLA_F$_5$ and PLLA_B$_5$, with a reduction of, respectively, 78 and 84% of the water absorption. These water-repellent performances are very close to those of PLA-FLK-PLA copolymers, in spite of the lower fluorine content.

Artificial ageing

The stability of PLDA and of some fluoro-functionalized polymers selected among those showing the best performances as color changes and water protection efficacy (i.e., PLLA_F$_{1.5}$, PLLA_B$_{1.5}$, PLDA_F$_{1.5}$, PLDA_B$_{1.5}$, PLLA_F$_{1.5}$, PLLA_B$_5$, PLDA_F$_5$, and PLDA_B$_5$) was tested with accelerate ageing up to 750 h in a Solar Box. The polymers were analyzed (by FTIR, color changes, solubility, weight, and molecular weight changes) at various time intervals.

FTIR analysis

The FTIR spectra of the polymers generally remained qualitatively unchanged at different ageing times. The spectra of PLDA, PLDA_F$_5$, and PLDA_B$_5$ only, showed the appearance of a new weak absorption at 1843 cm^{-1}. This band appeared at the beginning of the ageing process (after 24 h in PLDA_B$_5$, 72 h in PLDA_F$_5$, and 125 h in PLDA) and slightly becomes stronger as the ageing time increases. This band could be ascribed to the ─C═O stretching of lactic acid anhydride, originated by solid state reaction of traces of monomeric lactic acid. Lactic acid may be formed into the polymeric matrix from residues of lactide and/or slight depolymerization of main PLA chain, as discussed below.

Solubility, weight loss, and molecular weight changes

At different ageing times, (250, 500, and 750 h) polymers were still completely soluble in chloroform. These data are an indication that crosslinking processes don't take place and strongly support the possibility to remove the polymer at the end of its useful life. GPC data evidenced only a slight diminution of weight-average molar mass after a long-term ageing (Table III). These data confirm the trend in weight change observed for polymers cast on glass slides. In fact, the weight of the polymers slightly decreased during ageing (variation are lower than 10% after 750 h). This behavior may be ascribed to loss of solvent residues accompanied by very low depolymerization processes occurring in PLA chain, as seems suggested by GPC measurements (Table III).

Color changes

The treated stone samples shows negligible variation of a^* and b^* parameters due to ageing up to 750 h. The color changes are mainly related to an increase of lightness, L^*, so there is a recovery of the brightness that was lost after polymer deposition (Table IV). A similar trends in the variation of $L^*a^*b^*$ parameters has been observed in ageing tests performed on PLA-FLK-PLA copolymers. This apparently strange

TABLE IV
Color Changes (ΔL^*, Δa^*, Δb^*, and ΔE^*) Measured at Different Ageing Time (0, 250, 500, and 750 h)

Treatment	Before ageing				After 250 h ageing				After 500 h ageing				After 750 h ageing			
	ΔL^*	Δa^*	Δb^*	ΔE^*	ΔL^*	Δa^*	Δb^*	ΔE^*	ΔL^*	Δa^*	Δb^*	ΔE^*	ΔL^*	Δa^*	Δb^*	ΔE^*
PLDA	-4.57	-0.15	0.06	4.61	2.40	0.35	-0.79	2.39	4.07	0.31	-0.85	4.06	4.63	0.26	-0.97	4.62
PLLA_F$_{1.5}$	-1.54	0.03	-0.59	1.69	0.59	0.06	-0.54	0.59	2.25	-0.02	-0.67	2.25	2.26	0.06	-0.76	2.26
PLLA_F$_5$	-2.67	-0.01	-0.41	2.72	2.20	0.11	-1.36	2.19	3.35	-0.03	-1.48	3.35	3.66	0.16	-1.54	3.66
PLDA_F$_{1.5}$	-3.47	0.00	-0.32	4.18	3.00	0.12	-1.12	2.99	5.41	0.21	-1.22	5.40	6.31	0.10	-1.24	6.30
PLDA_F$_5$	-4.51	-0.07	-0.10	4.51	2.32	0.05	-0.70	2.31	3.64	0.07	-0.83	3.63	4.10	-0.02	-0.95	4.09
PLLA_B$_{1.5}$	-2.11	-0.09	-0.07	2.12	1.40	0.15	-0.66	1.39	1.64	0.17	-0.51	1.63	1.68	0.07	-0.66	1.68
PLLA_B$_5$	-2.15	0.02	-0.80	2.75	1.16	0.16	-0.76	1.15	2.11	0.02	-0.84	2.10	2.26	0.13	-0.94	2.25
PLDA_B$_{1.5}$	-2.59	-0.08	-0.18	2.61	1.62	0.18	-0.23	1.62	2.70	0.06	-0.30	2.70	3.07	0.18	-0.22	3.07
PLDA_B$_5$	-6.61	-0.07	0.18	6.61	4.06	0.22	-0.80	4.05	5.57	-0.25	-0.94	5.56	5.20	0.15	-0.80	5.19
Untreated	0.46	0.02	-0.10	0.47	0.56	-0.05	-0.22	0.56	1.03	-0.01	-0.26	1.03	0.98	0.00	-0.24	0.98

behavior could be explained in terms of reorganization of the coating material at the polymer-air interface as a result of exposition at a temperature over its T_g (in the Solar Box BST, according to ISO 11341/2004 protocol, temperature is kept at $65 \pm 2°C$). In these conditions, polymer chains can easily undergo conformational rearrangement from a glassy to a rubbery state. Consequently, the coating surface should become smooth, thereby enhancing brightness. Comparatively lower color variations were observed for polymers obtained from L-lactide, irrespective of the type of alcohol employed. Anyway, only for PLDA, PLDA_F$_{1.5}$, and PLDA_B$_5$, ΔE^* values are significantly higher than 3.

CONCLUSION

The application of polymers from renewable feedstocks in the field of Cultural Heritage represents an attracting alternative to traditional petrochemical-based materials.

In this work, the properties of a series of innovative fluoro-functionalized PLA polymers for the protection of stone have been reported. One of the main features of these polymers is the solubility in typical organic solvent having low toxicity (e.g., acetone, 2-butanone, and tetrahydrofuran). These properties allow for an easier and healthier protection of the substrates than PLA-FLK-PLA copolymers.

Of course, the presence of a fluorinated group in the polymer chain gives an enhancement of the water-repellent effect with respect to the un-fluorinated PLAs. The polymers generally prove an interesting stability to artificial ageing, even after a long-term exposition (750 h). No significant differences neither in the structure or composition of the polymers nor in their final performances are evidenced. Nevertheless, polymers obtained from L-lactide are generally more appealing, because they show higher water protection efficacy, lower short-, and long-term color changes and higher stability than polymers obtained using a racemic mixture of L- and D-isomers. Comparing the results obtained in all the experimental tests (i.e., colorimetric test, water protection efficacy, and artificial ageing), PLLA_F$_5$ ($M_w = 3214$ g/mol and $T_g = 34.7°C$) and PLLA_B$_5$ ($M_w = 6258$ g/mol and $T_g = 40.2°C$) show the best performances for coating purposes among all the polymers tested. The performances are due to the overall effect of different parameters such as molecular weight, fluorine content, and stereochemistry of the polymer. Surprisingly, the above cited samples prove protective performances close to PLA-FLK-PLA copolymers, in spite of their lower fluorine content. Nevertheless, it has to be noted that the new polymers lead to interesting advantages with respect

to PLA-FLK-PLA, that is, higher solubility in organic solvents, higher eco-compatibility, and cheapness.

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