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Reversible fluorinated PLA/SiO_2 nanocomposites as hydrophobic coatings for stone

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SUMMARY: The synthesis of reversible hydrophobic nanocomposite coatings was carried out by mixing SiO_2 nanoparticles with a fluorinated polylactide and applied by a simple procedure on stone surfaces. The coating showed hydrophobic properties, reaching a maximum static contact angle of 137° on stone. This behavior was ascribed to an increase of surface roughness (as confirmed by AFM). Water vapour permeability and capillary water absorption confirmed the efficacy of the hydrophobic treatment. Finally, we have been able to remove the coating applied on stone surfaces by using an organic solvent. Therefore, these coatings may be used for temporary and reversible applications on building materials.

KEY-WORDS: reversible, hydrophobic, polylactide, silica, fluorinated.

INTRODUCTION

Biopolymers are replacing synthetic ones in many applications because they are biodegradable and reversible [1]. Polylactic acid (PLA) can be obtained from sources such as corn, and once it is obtained, it can be recycled in order to produce lactide and lactic acid, through hydrolysis or pyrolisis. It also is biodegradable and the products generated do not present toxicity.

However, PLA polymers have some disadvantages, such as low mechanical resistance toughness and scarce hydrophobicity. These disadvantages may be overcome by incorporating fillers such as silica nanoparticles [2] and hydrophobic groups [3-4]. Similar strategies have been used to improve the hydrophobicity of siloxane polymers, by incorporating SiO_2 nanoparticles into a silica-PDMS (polydimethylsiloxane) matrix. In these nanocomposites, the size and shape of the SiO_2 nanoparticles contributes to minimize the contact area between the water droplets and the surface. Moreover, the surface modification of the silica matrix with PDMS reduces surface energy [5].

In previous studies, we have reported the synthesis of PLA hydrophobic materials with the aim of applying them to buildings. Our main focus was to produce a coating with reduced surface energy. Both the photochemical stability and the hydrophobicity of the polylactide polymers were greatly enhanced by including a fluorine-derivative into the PLA polymer backbone [6].

In this paper, increasing amounts of SiO_2 nanoparticles were added to a fluorinated polylactide polymer in order to obtain a surface with lower surface energy and with increased rugosity. The nanocomposites were obtained by mixing SiO_2 nanoparticles with a fluorinated PLA polymer dissolved in an organic solvent. The novel nanomaterials were applied on marble surfaces for their characterization and the evaluation of their hydrophobic properties. The surfaces of the treated samples were evaluated through SEM-EDX, AFM, and water contact angle measurement. Hygric properties were also evaluated. Finally we carried out a test to confirm the reversibility of the treatments.

EXPERIMENTAL

Fluorinated PLA-SiO_2 nanocomposites were prepared by mixing a solution of a fluorine-containing PLA (PLDA-FLK-PLDA copolymer) in chloroform with colloidal silica nanoparticles AEROSIL® OX50 from Evonik (hereafter OX50) under magnetic stirring. OX50 is a hydrophilic fumed silica with an average particle diameter of 40 nm. PLDA-FLK-PLDA is a block copolymer (Mw = 13790 g/mol) composed of a central block of Fluorolink D-10H perfluoropolyether (FLK) and two side blocks of PLDA chains (the rac, or, racemic mixture, of PLA). More details about polymer synthesis and characterization can be found in a previous work [6].

Solutions of PLA-SiO_2 were prepared according to the following procedure:

(1) About 100 mg of PLDA-FLK-PLDA were dissolved in 5 mL of chloroform,

(2) Between 1 and 80 mg of OX50 was added to the solution under magnetic stirring; and,

(3) The solution was kept under magnetic agitation for 5 minutes to avoid aggregation of the nanoparticles.

The products were called P (fluorinated PLA) followed by S (silica particles) and a number referring to the SiO_2/polymer weight ratio used in the formulation (e.g., P-S20 contained 20 mg of SiO_2 and 100 mg of polymer).

The products were applied onto Macael marble, a common building stone in Andalusia. This stone is composed of more than 99% calcium carbonate and presents an average open porosity of 0.1%. The treatments were applied on 5x5x2 cm surface. Coatings were applied by solution casting with 2 mL of a 20 mg/mL solution of the products using a glass pipette on the surface of the samples in order to minimize product loss.

The effectiveness of the coating materials for hydrophobic protection was tested by water contact angle determination (sessile drop method), using a commercial video-based, software-controlled contact angle analyzer, model OCA 15plus, from Dataphysics Instruments.

The topography of the stone surface after coating with the products under study and its untreated counterpart were examined by Atomic Force Microscopy (AM-AFM, Nanotec Electrónica S.L.) operating in tapping mode. The root mean square (RMS) roughness value was calculated from 5 µm X 5 µm images.

The stone samples were then subjected to a water absorption test by capillarity (WAC) following the UNI EN 15801/2010 protocol. The treated surface of each stone sample was kept in contact for 24 hours with filter paper pads soaked in distilled water. The protective efficiency (E%) was calculated from the weight of absorbed water, according to the following equation: E% = $(E_0\text{-}E_1)$x100/E0, where E0 was the amount of water absorbed before treatment and E1 the amount of water absorbed after treatment.

Water vapour permeability was performed on 4x4x1 cm stone specimens using an automatic setup developed in our laboratory based on the standard cup test.

Color changes of stone surface induced by treatments were evaluated using a total color difference (ΔE*) using a solid reflection spectrophotometer, Colorflex model, from Hunterlab. The conditions used were: illuminant C and observer CIE10^0. CIELa*b* color space parameters were detected and variations in color before and after treatments were evaluated.

A specific test was carried out in order to evaluate the reversibility of the treatment. The sample was placed in a beaker filled with chloroform so that half of the treated surface of the sample was covered by the solvent. The changes in the morphology of the stone surface generated by the eventual elimination of the coating were visualized by SEM working in low-vacuum mode. Energy dispersive X-ray spectroscopy (X-EDS) measurements were carried out in order to elucidate the variations in surface composition after the test. In addition, AFM and water contact angles measurements were also performed.

RESULTS AND DISCUSSION

The hydrophobic effectiveness of the different stone coatings was evaluated by measuring static and dynamic contact angles. The results showed that higher contact angles were obtained with the increase of SiO_2 content. The highest static contact angle obtained was of 137° for P-S80 (Fig. 1). This highly hydrophobic behaviour was ascribed to: 1) the reduction of the free surface energy due to the presence of a fluorinated polylactide polymer coating surrounding the SiO_2 nanoparticles [3-6]; 2) an increase of surface roughness, which was able to minimize the contact area between water droplets, air and treated surface **(**Fig. 2), as confirmed by AFM [2,5].

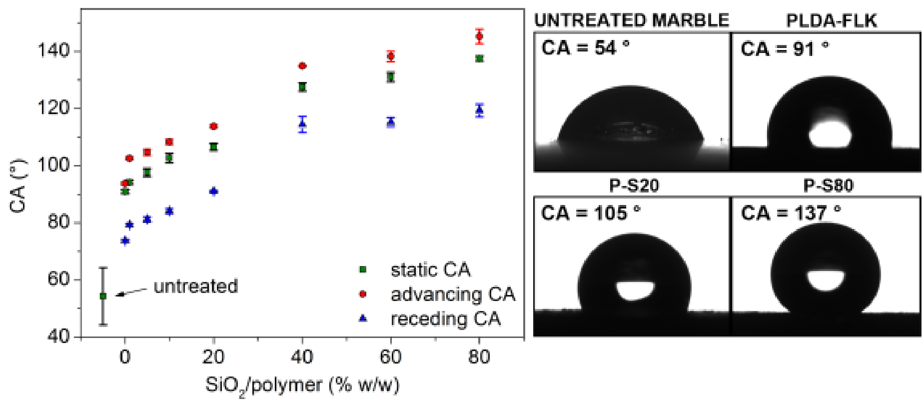

Figure 1. Contact angles obtained on marble with increasing SiO_2 contents in the hydrophobic nanocomposites.

Table 1. Protective Efficacy (E%), water vapour diffusivity and color change (ΔE*) of marble samples treated with the hydrophobic nanocomposites

Treatment	E% [a]	Vapour diffusivity (10^{-6} $m^2 \cdot s^{-1}$)[b]	Δ*E**
Untreated	-	5.20 ± 0.15	0
PLDA-FLK	87	2.52 ± 0.08	2.20
P-S20	90	2.22 ± 0.11	2.35
P-S80	98	2.16 ± 0.13	2.41

[a] E% = $(E_0-E_1)\cdot 100/E_0$ (E_0 and E_1: amounts of water absorbed before and after treatment)
[b] average values with standard deviations

In addition, capillary water absorption measurements (evaluated by measuring protective efficacy, E%) confirmed the hydrophobic properties of our products. Water vapour diffusivity test demonstrated the suitable permeability of our coatings. Total colour change (Δ*E**) measurements demonstrated that the treatments did not significantly change the colour of the samples (Table 1). However, some gloss change was observed when higher amounts of SiO_2 were added to the polymer (Fig. 2).

Finally and most importantly, we have been able to remove the coatings applied on stone surfaces by simply immersing the treated stone surface in an organic solvent (chloroform). The removal of the coating was confirmed by evaluating the following properties of the surfaces (Fig. 2): morphology and composition (SEM-EDX), roughness (AFM) and hydrophobic properties (contact angle measurements).

From the results obtained we can conclude that a new and simple strategy to prepare hydrophobic coatings with great potential for reversible applications on building materials has been developed.

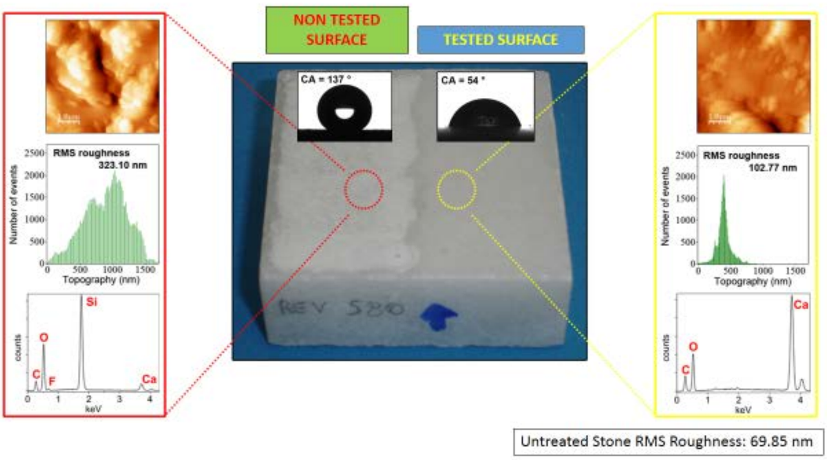

Figure 2. Changes observed in the roughness of a stone sample treated with our bionanocomposites. The roughness obtained after the test is very close to the one obtained for the untreated stone surface.

CONCLUSIONS

This study served to develop simple, low cost and reversible hydrophobic coatings for marble surfaces of civil buildings. The coatings were obtained by mixing a PLDA-FLK-PLDA copolymer with SiO_2 nanoparticles in an organic solution. After applying the solution on the marble surface and once the solvent evaporated, a coatings of silica particles covered by a fluorinated polymer are obtained.

From our investigation on the texture of the nanocomposites, we conclude that addition of SiO_2 nanoparticles is a key factor for improving the hydrophobic properties of the coating on marble surfaces. Silica particles increased the surface average height and roughness and the fluorinated organic component reduced the surface free energy.

Finally, we have demonstrated that the PLDA-FLK-PLDA/nanocomposites applied on a building stone produces a reversible coating. The products did not penetrate in the bulk of the substrate, but forms a superficial coating that was easily removed with a simple solvent treatment.

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