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Stability and ageing behaviour of a polysiloxane-based titania protective coating on terracotta samples

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ABSTRACT
This study investigates the performance of a protective coating composed of a commercial polysiloxane mixed with titanium dioxide nanoparticles (P25), applied onto terracotta samples via airbrushing. The coating was characterized through colorimetric analysis, static contact angle (SCA) measurements, and infrared spectroscopy to evaluate its aesthetic impact, wettability properties, and chemical stability under UV exposure. Results indicate that both polysiloxane alone and the polysiloxane-titania formulation altered the appearance of terracotta samples, with a ΔE^* value of approximately 3. Polysiloxane alone induced a yellowing effect, while the addition of titanium dioxide led to surface whitening. Accelerated aging did not cause significant aesthetic degradation, suggesting good visual durability. As expected, the strong artificial aging process induced the loose of superhydrophobic coating and its water repellency from 136° to 16° SCA values, changing to a hydrophilic state due to increased surface energy. ATR infrared spectroscopy revealed UV-induced polymer aging (segment scission or crosslinking) which may have contributed to these changes. These characteristics make the polymer more suitable for indoor surfaces, characterized by low-irradiance environments, or as a temporary protective treatment for artifacts requiring subsequent restoration intervention. These limitations observed with the commercial product have guided ongoing research in our group toward an eco-friendly formulation with significantly improved UV resistance, tailored for long-term heritage conservation needs.

Section: RESEARCH PAPER

Keywords: coating; titania; hybrid-composite; nanomaterial; UV-aging

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1. INTRODUCTION

The conservation of cultural heritage stone-based materials relies on consolidation and protection treatments to ensure their long-term preservation. However, selecting the most suitable treatment requires a thorough understanding of both the products used and the factors responsible for material deterioration. These factors include physical [1] and chemical weathering [2], biodeterioration [3], and anthropogenic damage [4]. Moreover, evaluating the potential side effects, mechanisms of action, and long-term stability of conservation treatments is crucial to make informed decisions [5], [6]. Among the various challenges faced by monuments exposed to outdoor environments, soiling is a significant concern. This process leads to surface darkening due to the accumulation of fine carbonaceous particles, rich in carbon black [7]. While natural weathering processes can only be mitigated indirectly [8], anthropogenic pollution can often be controlled through regulations and preventive measures. In this regard, a promising approach to preserving architectural surfaces is the development of materials with self-cleaning properties, which prevent soiling through photocatalytic activity.

Protection treatments for stone materials aim to enhance water repellency while preserving their natural vapor permeability. Effective protective coatings must meet several key criteria, including chemical stability, reversibility, strong adhesion to the substrate, and the absence of film formation [9], [10]. Currently, polymer-based products and resins with strong hydrophobic properties, particularly those containing polymeric alkyl siloxane, are widely used [11]–[14]. These compounds penetrate the porous structure of materials due to their low viscosity and ability to polymerize spontaneously via a sol–gel process. This polymerization, combined with their organic moieties, reduces surface energy and prevents water infiltration [15]. Inspired by natural structures such as lotus leaves and water strider legs, researchers have explored the combination of hierarchical micro- and nanoroughness with low surface energy to create superhydrophobic surfaces [16]. These surfaces exhibit the Cassie–Baxter state, in which air pockets form and are kept in the spaces between water droplets and the solid surface, resulting in high hydrophobicity and repellence [17]. Such property can be exploited to make surfaces self-cleaning [18] and for other applications. One of the simplest methods to achieve this effect is the use of hydrophobic nanoparticle dispersions in a solvent. As the solvent evaporates, the nanoparticles self-assemble, creating a Cassie–Baxter surface with enhanced superhydrophobic performance [15]. The most popular, non-toxic, and cost-effective nanoparticles are made up of titanium dioxide (TiO_2, titania), and, thanks to their intrinsic ability to be self-cleaning, biocidal, and smog-eating through surface photocatalytic activity, are widely used [19]–[21]. In this study, a polymeric coating was obtained by mixing a commercial alkyl siloxane formulation with commercial titania nanoparticles (P25) to obtain a self-cleaning coating with photocatalytic properties. The coating was tested for its aesthetic and UV-resistance performances, aiming to serve as a basis for the formulation of a future, new, biodegradable, polymeric coating incorporating titania nanoparticles synthesized through a solvent-free process [22], [23]. This innovative approach seeks to improve the sustainability and reversibility of conservation treatments, contributing to the advancement of protective solutions for cultural heritage materials.

2. MATERIALS AND METHOD

2.1. Coating formulation

The commercial product Bio Estel New (CTS srl, Italy) was used as received. According to the technical data sheet, this product consists of an isopropanol-based solution with ethoxysilane oligomers, biocidal products, and preservative additives. The product is ready to use and suitable for application on any type of absorbent mineral substrate subject to degradation by biodeteriogenic agents. The surface to be treated must be dry, clean, and free from any efflorescent salts. Such conditions are typically achieved through cleaning or restoration procedures carried out by restorers, as protective treatments are generally applied following appropriate cleaning or restoration. The formulation being tested was prepared by mixing the polymer with P25 titania nanoparticles (Merck srl, Germany), with an average size of 21 nm and a BET surface area of 35–65 m^2/g. The mixture was sonicated for 10 minutes and sprayed on the brick sample by using a low-pressure spray gun [24], [25].

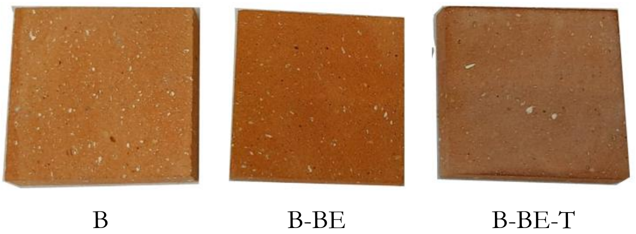

Figure 1. Terracotta samples B (uncoated sample), B-BE treated with polysiloxane polymer, and B-BE-T treated with a mixture of polysiloxane and P25 (commercial titania nanoparticles).

2.2. Terracotta samples

Three porous terracotta samples were fabricated through traditional methods with a dimension of $5 \times 5 \times 1$ cm^3 and purchased from local wholesalers. The sample kept uncoated throughout the study was named B (brick), whereas the ones treated with the sols were named B-BE and B-BE-T, treated with the Bio Estel New polymer alone and with the same polymer containing 0.1 wt/v % TiO_2 nanoparticles, respectively (Figure 1).

2.3. Application and artificial aging of commercial and nano-filled polymer

A low-pressure spray nebuliser (a mini paint spray gun with a gravity cup, FIAC Air Compressors, Casalecchio di Reno (BO), Italy) was used for the application. The samples were placed horizontally, and the surfaces were sprayed until saturation, as indicated by the wetting condition of the stone surface, which persisted for over 1 minute, simulating the procedure used by restorers. The distance between the nozzle and the sample was approximately 20 cm. Only one surface of each sample was treated. The samples were then left curing for one week, during which mass variation was measured until the equilibrium moisture content (EMC) (Table 1). Coating treatment and characterization were in accordance with national and international standard regulations EN 15802: 2009 [26], UNI EN 15886:2010 [27].

2.4. Characterisation techniques

In order to assess the aesthetic properties, hydrophobicity/hydrophilicity, chemical features, and UV-induced changes of the applied coatings, the samples were characterized by using colour, static contact angle, and spectroscopic measurements. For each of the three terracotta samples, measurements were thus performed considering three stages: before treatment (t_0), after applying the coating treatment (t_1), and after UV-induced aging of the treated surface (t_2). Colorimetric measurements were carried out using a handheld Eoptis CLM-194 digital colorimeter, in accordance with ASTM E 1164 and CIE15:2004 recommendations. The devices used the CIE D65 illuminant (daylight simulation with LEDs) and a standard 10° viewing angle, operating in reflective and contact mode. The chromatic coordinates L^*, a^*, and b^* of the CIELab color space were collected for each sample both before and after

Table 1. Weight measurements of samples before and after treatment. Mass 1: untreated sample; Mass 2: treated sample at reached polymerization.

Sample	Treatment	Mass 1 (g)	Mass 2 (g)	Coating mass (g)
B	-	41.8423 ± 0.0021	41.9297 ± 0.0001	-
B-BE	ethoxysilane oligomers	39.3407 ± 0.0016	39.9100 ± 0.0001	0.5700
B-BE-T	ethoxysilane oligomers and P25	41.4843 ± 0.0012	42.0406 ± 0.0001	0.5560

treatment, with a series of measurements taken at multiple points on the surface. Specifically, each measurement was obtained as the average of 3 flashes on 10 different points, preceded by black and white calibration. Color differences (ΔE^*) were calculated by comparing untreated samples with the treated ones after drying, see equation (1). Additionally, to determine the colour alteration caused by TiO_2 coatings, according to the UNI EN 15886:2010, the color differences were assessed not only in the CIELab colour space but also in the CIELCh space, which better represents human eye sensitivity. The colorimetric analysis considers ΔE^* (color difference), ΔH^* (hue variation equation (2)), and ΔC^* (chroma variation, equations (3) and (4)), which describe changes in the chromatic distance, colour purity or saturation, and hue of the corresponding saturated colour, respectively [28].

$$\Delta E^* = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2}\,, \tag{1}$$

$$\Delta H^* = \sqrt{\Delta E^2 - \Delta C^2 - \Delta L^2}\,, \tag{2}$$

$$\Delta C^* = C_f^* - C_i^*\,, \tag{3}$$

$$C_f^* = \sqrt{a_f^2 + b_f^2}; C_i^* = \sqrt{a_i^2 + b_i^2}\,, \tag{4}$$

where C_i^* and C_f^* are the chroma of the uncoated and coated samples, respectively. Changes in C^* and H^* are more sensitive to changes of a^* or b^* coordinates, depending on the original color of the material. The wettability of the terracotta sample surfaces, resulting after the application of different coatings, was assessed through static contact angle (SCA) measurements. For these tests, 5 water droplets, each one with a volume of approximately 5 µL, were placed on the terracotta surface using a Gilson micropipette at room temperature. After 10 seconds, each droplet was imaged using a Dino-Lite Edge Digital Microscope, equipped with a high-resolution 5.0 Megapixel CMOS camera mounted on a stand for precise positioning.

Chemical changes were monitored in the coatings alone (without terracotta substrates) after UV exposure using Attenuated Total Reflectance Fourier Transform infrared (ATR-FTIR) spectroscopy analysis (ThermoFisher® Nicolet iS50, Waltham, MA, USA) in the range of 4000÷400 cm^{-1} with 60 scans and a resolution of 4 cm^{-1}.

2.5. Artificial aging

UV-accelerated aging was performed in a non-reflective, dark chamber equipped with four Hg UV lamps at 20 W power each, emitting in the wavelength range of 290÷315 nm with a maximum peak at 310 nm. The samples were fixed symmetrically around a central point P in the irradiated area to ensure homogeneous irradiation for 14 days. The irradiance (E) at point P was 17 Wm^{-2}, calculated by the Keitz equation, see equation (5) [29]:

$$E = \frac{I \cos^2\theta\ (\alpha + \sin\alpha \cos\alpha)}{2\ h\ \pi^2\ L/2}\,, \tag{5}$$

where:
I is the UV flux of the lamp (Watt);
h is the distance of the point P from the lamp (m);
L is the length of the lamp (m);
θ is 0° in the case of standard geometry (radians);
α is the half angle under which the source is observed in all its extension at point P (radians).

3. RESULTS AND DISCUSSION

The three terracotta samples were prepared before being tested for coating application. The samples were dried in an oven at 100 °C for 4 hours in order to remove any physisorbed moisture from the pores. Subsequently, the mass variation of the samples was measured both upon the coating application and after polymerization (about 7 days after). Sample B served as the untreated reference, while sample B-BE was treated with the polymer and sample B-BE-T was treated with a mixture containing polymer and 0.1 wt/v % of P25. Each mass value was determined as the average of 3 measurements. These measurements were used to quantify the amount of coating retained within the porosity of the terracotta sample (Table 1). Such an amount of coating was estimated around 1.4 wt %.

Color coordinates a^* and b^* are listed in Table 2, whereas total (ΔE^*) and partial (ΔC^*, ΔL^*) color differences are reported in Figure 2. In order to evaluate the preservation or variation of the original appearance of samples B-BE and B-BE-T after treatment, the total colour difference (ΔE^*) is over 3 (Figure 1a). This is above the threshold at which a noticeable difference is observed and exceeds the limit in the field of cultural heritage. [30], [31]. In particular, B-BE shows a ΔE^* value of 3.50 with a decrease of the lightness (ΔL^*) and color saturation (ΔC^*) (Figure 1b, 1c). Analysing the behaviour of the colour coordinates, it can be observed that the colour change is due to the increase of the b^* parameter indicating a slight yellowing of the stone, from 25.63 to 27.39. On the other hand, B-BE-T coating gives a higher ΔE^* of about 4 with similar ΔL^* and ΔC^*, probably due to the presence of titanium dioxide nanoparticle agglomerates entailing visual interference. Following the accelerated aging, the B-BE sample exhibited reduced colour variation ($\Delta E^* = 3.12$), with no changes observed following the application of the protective coating. Specifically, the results indicate a slight decrease in saturation (ΔC^*) and increase in brightness (ΔL^*) (Figure 1b, 1c). In contrast, the B-BE-T sample exhibited a slight increase in colour variation ($\Delta E^* > 4$), as illustrated in Figure 1. The increase in ΔE^* is primarily attributed to an increase in brightness, resulting in a noticeable whitening effect on the surface.

The results of the SCA measurements are summarized in Table 3. The untreated sample exhibited rapid water absorption

Table 2. Colorimetric coordinates a^* (green-red axis) and b^* (yellow-blue axis).

Samples	Untreated (t_0)		Treated (t_1)		Aged (t_2)	
	a^*	b^*	a^*	b^*	a^*	b^*
B	15.92 ± 0.29	26,41 ± 0.40	15.82 ± 0.43	25.42 ± 0.54	15.64 ± 0.43	25.31 ± 0.60
B-BE	15.81 ± 0.38	25.63 ± 0.43	16.87 ± 0.30	27.39 ± 0.42	16.56 ± 0.39	27.01 ± 0.51
B-BE-T	14.39 ± 0.59	24.00 ± 0.59	13.96 ± 0.42	20.09 ± 0.66	14.99 ± 0.49	20.86 ± 0.69

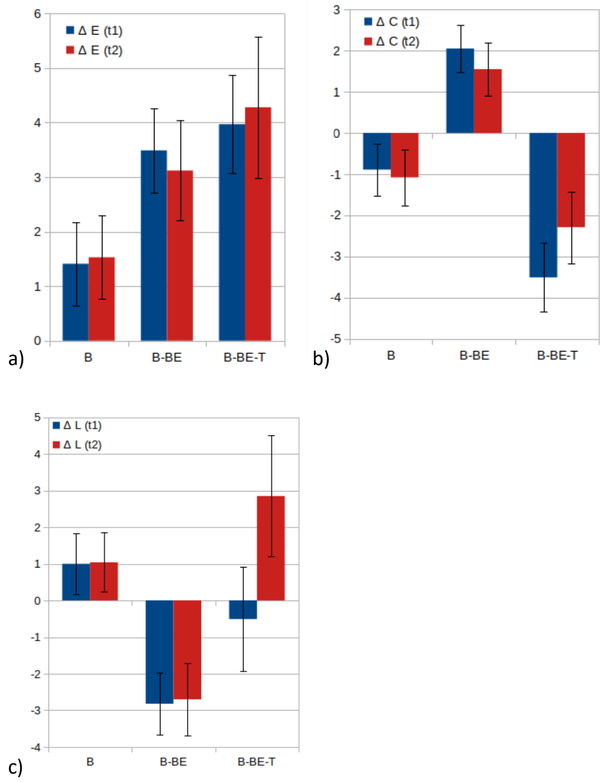

Figure 2. Colour differences for the treated samples, unaged (t_1) and aged (t_2).

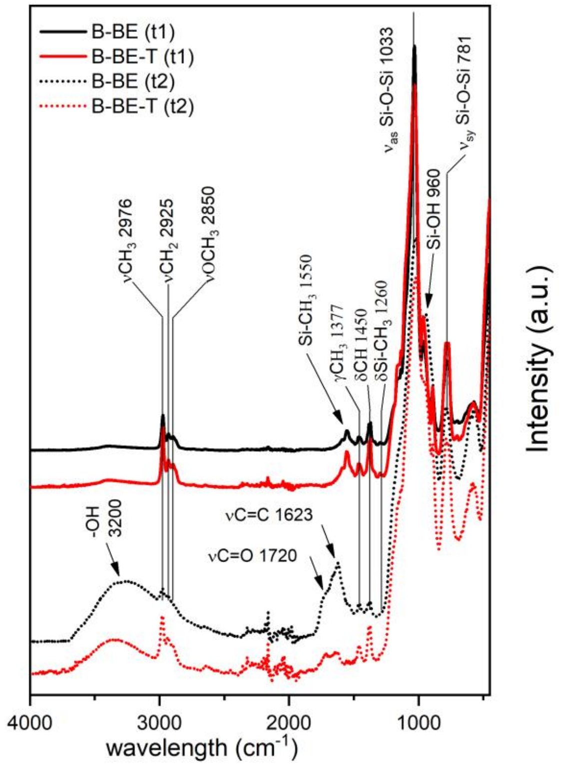

Figure 3. ATR-FTIR spectra of polysiloxane at t_1 (black line) and t_2 (red line).

Table 3. Static contact angle values for the commercial syloxane polymer (B-BE) and commercial syloxane polymer filled with nanotitania (B-BE-T)

Samples	Average SCA (°)		
	Untreated (t_0)	Treated (t_1)	Aged (t_2)
B	ND	ND	ND
B-BE	ND	136.5 ± 2.0	28.5 ± 1.4
B-BE-T	ND	137.2 ± 2.0	16.5 ± 1.6

ND: not detected

into the pores of the material, making the contact angle undetectable. According to the NORMAL guidelines [32] (NORMAL 33/89: Measurement of Contact Angle, 1989), the minimum acceptable contact angle for a protective coating on stone materials is 90°, which indicates an initial water-repellent surface. Surfaces with a contact angle greater than 150° are classified as superhydrophobic [33]–[35]. In this study, all treated samples demonstrated excellent hydrophobization, with SCA values around 136°. These results indicate superior water repellency and performance comparable to that of similar systems containing titania nanoparticles [36]. After accelerated aging, the SCA values drastically decreased, suggesting that the UV radiation affects the structure of the polysiloxane-based coating. To better understand the long-term efficacy of the polysiloxane coating alone, ATR-FTIR analysis was performed after UV-accelerated aging.

As shown in Figure 3, the polymeric coating before (solid line) and after (dot line) UV-induced aging exhibited the characteristic peaks of siloxane groups both for samples treated with polymer alone and polymer filled with P25. The peak at 790 cm^{-1} can be assigned to the symmetric stretching of Si−O−Si, while the peak at 1032 cm^{-1} corresponds to the asymmetric stretching. The shoulder around 960 cm^{-1} is associated with the angular deformation of Si−OH in the silanol group. Additionally, the weak peaks at 1260, 1377, and 1450 cm^{-1} correspond to Si-CH_3 bending vibration, -CH_3 out-of-plane bending, and –CH bending in CH_3 groups, respectively. The peaks at 2850, 2925, and 2976 are responsible for OCH_3, CH_2, and CH_3 deformation related to the aliphatic group in the polymer [37]. After accelerated aging, the siloxane groups remained at the same peak positions. However, new signals were detected at 1720 and 1626 cm^{-1}, corresponding to C=O [38] and C=C [39]–[42], respectively. Moreover, a broad peak was present around 3200 cm^{-1} suggesting an increase of hydroxyl group at the surface of the siloxane coating. This may indicate that the branched chains present on the silicons and polymeric additives were degraded during the photochemical oxidation process [43]. This process can lead to various effects, including the oxidation of double bonds with oxygen, polymer segment scission, and crosslinking, as well as the high temperatures and moisture that contribute to thermal degradation and hydrolysis [44]. The resulting oxidation products contain highly polar functional groups (e.g., OH or CO) and tend to form strong hydrogen bonds, leading to additional inter-chain crosslinking [44]. As a macroscopic result, the surface undergoes cracking. These findings are in line with the SCA results, which indicated increased hydrophilicity and, consequently, higher surface energy for both samples treated with the coating.

4. CONCLUSIONS

The study evaluated a protective coating composed of a commercial polysiloxane mixed with commercial titanium dioxide nanoparticles (P25) and applied to terracotta samples via airbrushing. Colorimetric, SCA, and ATR-FTIR measurements were conducted to assess the aesthetic and chemical stability of the coating, as well as the structural modifications of the polymer upon UV exposure. Results showed that both the pure polysiloxane and the formulation containing titanium dioxide altered the appearance of terracotta samples surfaces, with a ΔE^* value around 3 in both cases. The polysiloxane alone induced a yellowing effect, whereas the addition of titanium dioxide led to a whitening of the surface. After UV-accelerated aging, no marked deterioration was observed (ΔE^* of about 4), suggesting good aesthetic durability. Regarding wettability, the coated surfaces initially exhibited superhydrophobic properties. However, after aging, the surface energy increased, leading to a transition from superhydrophobic to hydrophilic behaviour. This loss of water-repellency highlights a critical limitation of the treatment in the context of conservation for stone-based cultural heritage materials. Additionally, infrared spectroscopy analysis provided insights into the structural changes of polymer due to UV exposure, giving evidence of polymer segment scission and crosslinking [37], [45]. These modifications may contribute to the observed changes in surface properties over time. Therefore, while the coating demonstrates promising initial properties, its inability to maintain long-term hydrophobicity and structural susceptibility to UV-induced alterations suggest that further optimization is required for its application in the conservation field. These modifications could cause the progressive loss of hydrophobicity observed under prolonged UV exposure. While this commercial polysiloxane-based coating, both alone and filled with P25, shows limited long-term stability, identifying these constraints is essential for guiding material selection in conservation practice. It should be noted that one specimen per condition was tested; consequently, the reported variability reflects intra-sample measurements and does not account for potential inter-sample differences. The findings have motivated our group to focus on the design of alternative, eco-sustainable formulations with improved UV resistance and durability, aiming to better meet the requirements of heritage conservation [46].

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REFERENCES

[1] F. Vidal, R. Vicente, J. Mendes Silva. J., Review of environmental and air pollution impacts on built heritage: 10 questions on corrosion and soiling effects for urban intervention, J. Cult. Herit. 37 (2019), pp. 273–295.
DOI: 10.1016/j.culher.2018.11.006

[2] C. Cardell-Fernández, G. Vleugels, K. Torfs, R. Van Grieken., The processes dominating Ca dissolution of limestone when exposed to ambient atmospheric conditions as determined by comparing dissolution models, Environ. Geol. 43 (2002), pp. 160–171.
DOI: 10.1007/s00254-002-0640-x

[3] A. C. Pinheiro, N. Mesquita, J. Trovão, F. Soares, I. Tiago, C. Coelho, H. P. de Carvalho, F. Gil, (+ 3 more authors), Limestone biodeterioration: A review on the Portuguese cultural heritage scenario, J. Cult. Herit. 36 (2019), pp. 275–285.
DOI: 10.1016/j.culher.2018.07.008

[4] R. Hamilton, V. Kucera, J. Tidblad, J. Watt, The Effects of Air Pollution on Cultural Heritage Eds.; Springer US: Boston, MA, 2009; ISBN 978-0-387-84892-1.
DOI: 10.1007/978-0-387-84893-8

[5] T. Fistos, I. Fierascu, M. Doni, I. E. Chican, R. C. Fierascu, A Short Overview of Recent Developments in the Application of Polymeric Materials for the Conservation of Stone Cultural Heritage Elements, Materials 15 (2022) 18, 6294.
DOI: 10.3390/ma15186294

[6] A. Casanova Municchia, M.R. Fidanza, G. Caneva, Advances in testing the interference of biocides on stone materials: A comparative analysis and guidelines for a standardised approach, J. Cult. Herit. 64 (2023), pp. 23–41.
DOI: 10.1016/j.culher.2023.08.001

[7] M. F. La Russa, V. Comite, N. Aly, D. Barca, P. Fermo, N. Rovella, F. Antonelli, E. Tesser, M. Aquino, S. A. Ruffolo, Black crusts on Venetian built heritage, investigation on the impact of pollution sources on their composition, Eur. Phys. J. Plus 133 (2018), 370.
DOI: 10.1140/epjp/i2018-12230-8

[8] G.C. Institute, Plant Biology for Cultural Heritage: Biodeterioration and Conservation, Getty Publications, 2008.

[9] M. Zucchelli, G. Mazzon, L. Bertolacci, R. Carzino, E. Zendri, A. Athanassiou, Stone sustainable protection and preservation using a zein-based hydrophobic coating, Prog. Org. Coat. 159 (2021), 106434.
DOI: 10.1016/j.porgcoat.2021.106434

[10] M. Sadat-Shojai, A. Ershad-Langroudi, Polymeric coatings for protection of historic monuments: Opportunities and challenges, J. Appl. Polym. Sci. 112 (2009), pp. 2535–2551.
DOI: 10.1002/app.29801

[11] K.-H. Haas, S. Amberg-Schwab, K. Rose, G. Schottner, Functionalized coatings based on inorganic–organic polymers (ORMOCER®s) and their combination with vapor deposited inorganic thin films, Surf. Coat. Technol. 111 (1999) 1, pp. 72–79.
DOI: 10.1016/S0257-8972(98)00711-7

[12] H. Ni, A.D. Skaja, M.D. Soucek, Acid-catalyzed moisture-curing polyurea/polysiloxane ceramer coatings, Prog. Org. Coat. 40 (2000) 1–4, pp. 175–184.
DOI: 10.1016/S0300-9440(00)00116-8

[13] A. Privitera, S. Tuti, U. Pasqual Laverdura, L. Duranti, E. Di Bartolomeo, A. R. Taddei, A. Sodo, One-step nanoencapsulation of essential oils and their application in hybrid coatings: A sustainable long-lasting treatment of stone materials against biodeterioration, Prog. Org. Coat. 196 (2024), 108759.
DOI: 10.1016/j.porgcoat.2024.108759

[14] L. Ruggiero, M. R. Fidanza, M. Iorio, L. Tortora, G. Caneva, M. A. Ricci, A. Sodo, Synthesis and Characterization of TEOS Coating Added With Innovative Antifouling Silica Nanocontainers and TiO2 Nanoparticles, Front. Mater. 7 (2020).
DOI: 10.3389/fmats.2020.00185

[15] L. A. M. Carrascosa, R. Zarzuela, N. Badreldin, M. J. Mosquera, A simple, long-lasting treatment for concrete combining hydrophobic performance with photo-induced superhydrophilic surface for easy removal of oily pollutants, ACS Appl. Mater. Interfaces 12 (2020), pp. 19974–19987.
DOI: 10.1021/acsami.0c03576

[16] S. Moradi, P. Englezos, S. G. Hatzikiriakos, Contact angle hysteresis: surface morphology effects, Colloid Polym. Sci. 291 (2013), pp. 317–328.
DOI: 10.1007/s00396-012-2746-3

[17] L. Gao, T. J. McCarthy, Wetting 101°, Langmuir 25 (2009) 24, pp. 14105–14115.
DOI: 10.1021/la902206c

[18] D. S. Facio, L. A. M. Carrascosa, M. J. Mosquera, Producing Lasting Amphiphobic Building Surfaces with Self-Cleaning Properties, Nanotechnology 28 (2017) 26, 265601.
DOI: 10.1088/1361-6528/aa73a3

[19] L. Tortora, G. Di Carlo, M. J. Mosquera, G. M. Ingo, Editorial: Nanoscience and Nanomaterials for the Knowledge and Conservation of Cultural Heritage, Front. Mater. 7 (2020).
DOI: 10.3389/fmats.2020.606076

[20] E. Marconi, I. Luisetto, L. Tortora, Green synthesis and characterization of titanium dioxide nanoparticles and their photocatalytic activity, Acta IMEKO 13 (2024) 3, pp. 1–7. DOI: 10.21014/actaimeko.v13i3.1775

[21] E. Marconi, L. Tortora, Synthesis of titania nanoparticles in W/O microemulsion: Moving the production toward a green approach, Proc. of IMEKO TC4 Int. Conf. on Metrology for Archaeology and Cultural Heritage MetroArchaeo 2023, Rome, Italy, 19-21 October 2023, pp. 479–484. DOI: 10.21014/tc4-ARC-2023.091

[22] A. Buzarovska, PLA Nanocomposites with Functionalized TiO2 Nanoparticles, Polym.-Plast. Technol. Eng. 52 (2013), pp. 280–286. DOI: 10.1080/03602559.2012.751411

[23] E. Marconi, A. Lopez, F. Bertelà, C. Meneghini, C. Battocchio, D. Mirabile Gattia, G. Vanga, T. Skála, (+ 9 more authors), Ecofriendly Synthesis of Titanium Dioxide for Glyphosate Adsorption, Eur. J. Inorg. Chem. 28 (2025), e202400496. DOI: 10.1002/ejic.202400496

[24] A. M. Ferrari, M. Pini, P. Neri, F. Bondioli, Nano-TiO2 Coatings for Limestone: Which Sustainability for Cultural Heritage?, Coatings 5 (2015) 3, pp. 232–245. DOI: 10.3390/coatings5030232

[25] E. Quagliarini, F. Bondioli, G.B. Goffredo, C. Cordoni, P. Munafò, Self-cleaning and de-polluting stone surfaces: TiO2 nanoparticles for limestone, Constr. Build. Mater. 37 (2012), pp. 51–57. DOI: 10.1016/j.conbuildmat.2012.07.006

[26] EN 15802:2009 Conservation of cultural property - Test methods - Determination of static contact angle.

[27] UNI EN 15886:2010 Conservation of cultural property—test methods— colour measurement of surfaces, 2010, UNI Ente Nazionale Italiano di Unificazione, 2010.

[28] L. Bergamonti, G. Predieri, Y. Paz, L. Fornasini, P. P. Lottici, F. Bondioli, Enhanced self-cleaning properties of N-doped TiO2 coating for Cultural Heritage, Microchem. J. 133 (2017), pp. 1–12. DOI: 10.1016/j.microc.2017.03.003

[29] A. De Carlo, V. Graziani, A. Privitera, A. Sodo, P. Branchini, P. Antici, L. Tortora, Artificial aging of monoazo and isoindoline yellow pigments, Acta IMEKO 13 (2024) 3, pp. 1–9. DOI: 10.21014/actaimeko.v13i3.1791

[30] F. Gherardi, A. Colombo, M. D’Arienzo, B. Di Credico, S. Goidanich, F. Morazzoni, R. Simonutti, L. Toniolo, Efficient self-cleaning treatments for built heritage based on highly photo-active and well-dispersible TiO2 nanocrystals, Microchem. J. 126 (2016), pp. 54–62. DOI: 10.1016/j.microc.2015.11.043

[31] W. S. Mokrzycki, M. Tatol, Color difference Delta E - A survey, Mach. Graph. Vis. 20 (2011) 4, pp. 383–411.

[32] UNI EN 15802:2010 Conservazione dei beni culturali - Metodi di prova - Determinazione dell’angolo di contatto statico. [in Italian]

[33] I. S. Bayer, Superhydrophobic Coatings from Ecofriendly Materials and Processes: A Review, Adv. Mater. Interfaces 7 (2020) 13, 2000095. DOI: 10.1002/admi.202000095

[34] A. Hooda, M. S. Goyat, J. K. Pandey, A. Kumar, R. Gupta, A review on fundamentals, constraints and fabrication techniques of superhydrophobic coatings, Prog. Org. Coat. 142 (2020), 105557. DOI: 10.1016/j.porgcoat.2020.105557

[35] V. Renda, M. A. De Buergo, M. L. Saladino, E. Caponetti, Assessment of protection treatments for carbonatic stone using nanocomposite coatings, Prog. Org. Coat. 141 (2020), 105515. DOI: 10.1016/j.porgcoat.2019.105515

[36] C. Li, Y. Sun, M. Cheng, S. Sun, S. Hu, Fabrication and characterization of a TiO2/polysiloxane resin composite coating with full-thickness super-hydrophobicity, Chem. Eng. J. 333 (2018), pp. 361–369. DOI: 10.1016/j.cej.2017.09.165

[37] E. Tesser, F. Antonelli, L. Sperni, R. Ganzerla, N.-P. Maravelaki, Study of the stability of siloxane stone strengthening agents, Polym. Degrad. Stab. 110 (2014), pp. 232–240. DOI: 10.1016/j.polymdegradstab.2014.08.022

[38] S. Wu, X. Zhang, Y. Sun, H. Yang, B. Lin, X. Han, P. Chen, Study on the influence of crosslinking density and free polysiloxan chain length on oxygen permeability and hydrophilicity of multicomponent silicone hydrogels, Colloid Polym. Sci. 299 (2021), pp. 1327–1335. DOI: 10.1007/s00396-021-04850-5

[39] D. Rosu, L. Rosu, C.N. Cascaval, IR-change and yellowing of polyurethane as a result of UV irradiation, Polym. Degrad. Stab. 94 (2009) 4, pp. 591–596. DOI: 10.1016/j.polymdegradstab.2009.01.013

[40] F. Xie, T. Zhang, P. Bryant, V. Kurusingal, J. M. Colwell, B. Laycock, Degradation and stabilization of polyurethane elastomers, Prog. Polym. Sci. 90 (2019), pp. 211–268. DOI: 10.1016/j.progpolymsci.2018.12.003

[41] H. Yu, X. Bai, G. Qian, H. Wei, X. Gong, J. Jin, Z. Li, Impact of Ultraviolet Radiation on the Aging Properties of SBS-Modified Asphalt Binders, Polymers 11 (2019) 7, 1111. DOI: 10.3390/polym11071111

[42] Y. Li, J. Feng, S. Wu, A. Chen, D. Kuang, T. Bai, Y. Gao, J. Zhang, (+ 5 more authors), Review of ultraviolet ageing mechanisms and anti-ageing methods for asphalt binders, J. Road Eng. 2 (2022) 2, pp. 137–155. DOI: 10.1016/j.jreng.2022.04.002

[43] P. P. C. Sartoratto, C. U. Davanzo, I. Valéria, P. Yoshida, Photooxidation studies on branched polysilanes, Eur. Polym. J. 33 (1997) 1, pp. 81–88. DOI: 10.1016/S0014-3057(96)00107-3

[44] S. Mitra, A. Ahire, B. P. Mallik, Investigation of accelerated aging behaviour of high performance industrial coatings by dynamic mechanical analysis, Prog. Org. Coat. 77 (2014) 11, pp. 1816–1825. DOI: 10.1016/j.porgcoat.2014.06.002

[45] M. Frigione, A. Rodríguez-Prieto, Can Accelerated Aging Procedures Predict the Long Term Behavior of Polymers Exposed to Different Environments?, Polymers 13 (2021) 16, 2688. DOI: 10.3390/polym13162688

[46] E. Marconi, F. Visone, V. Graziani, A. De Carlo, N. Ismail, L. Tortora, Polyhydroxyalkanoate/TiO2 nanocomposite as sustainable coating for protection of marble, basalt, and travertine in the conservation of cultural heritage assets, Journal of Cultural Heritage, Volume 80, 2026, pp. 102–109. DOI: 10.1016/j.culher.2026.05.006.