

An Innovative Fluorinated Polyacrylic Coating for the Protection of the Cultural Heritage

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Abstract – A novel water-repellent methyl methacrylate (MMA)-based resin was prepared via free radical polymerization adopting 1H,1H-heptafluoro-n-butyl methacrylate (F7) as co-monomer at 1% mol/mol. Both macromolecular and wettability features of the as-synthesized polymeric resin were finely studied. Subsequently, it was easily applied by air-brushing on Candoglia marble, a widely used substrate in historical buildings. Hydrophobic properties, water capillary rise and vapor permeability alongside with color variation assessment of coated marbles were investigated both before and after outdoor exposure in a real polluted environment (Monza Cathedral). This work highlights that a polymeric protective prepared from a co-monomer bearing a medium-length (seven fluorine atoms) fluorinated pendant chain is characterized by satisfactory hydrophobic and durability features to be potentially applied for the preservation of the Cultural Heritage.

I. INTRODUCTION

Nowadays, the conservation and restoration of the Cultural Heritage are important issues to be solved, especially in the case of historical buildings and monuments, which are seriously affected by environmental conditions and atmospheric pollution [1,2]. Deterioration phenomena are mainly natural and unrestrainable decay processes arising from water absorption and percolation into stone building materials. Once water attacks and penetrates stone surfaces, several chemical, physical and biological degradation processes can occur altering the properties of the stone themselves [1].

In order to overcome these problems, hydrophobic coatings have been applied on the materials surfaces

hindering the water penetration whilst preserving the natural stones transpirability and external appearance [1,3]. An optimal protective coating should also exhibit high durability and ease of application and removal. Up to now, lots of different polymers (as siloxane- [4], silane- [4] and acrylic-based [5,6] ones) have been studied and adopted for this purpose even if some of them still possess some drawbacks, especially related to the scarce durability and water vapor permeability [5,6]. Among the latter, polyacrylates play a key role, thanks to their broad range of useful features, such as transparency, easy film-forming capability, good mechanical properties, cheapness and flexible synthesis processes [7]. However, either them or their fluorinated derivatives still show some problems and have to be optimized.

In this respect, the present work is a step forward with respect to our previous study [8] in which we finely investigated the preparation of highly stable and durable fluorinated co-polymers based on methyl methacrylate (MMA) and a fluorinated methacrylic monomer, *i.e.* 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-octyl methacrylate (POMA). The presence of a great number of fluorine atoms (13 for each pendant chain) does improve the final coating features, especially concerning the hydrophobicity and durability. Nevertheless, due to the high cost of fluorinated precursors, herein, we decided to slightly reduce the fluorine amount by using 1H,1H-heptafluoro-n-butyl methacrylate (F7) instead of POMA at its same concentration of 1 % mol/mol. Wettability features, water vapor permeability and colorimetric assessment were investigated both before and after outdoor exposure at Monza Cathedral.

II. MATERIALS AND METHODS

A. Polymer synthesis and its characterization

Starting from our previous works [8,9], a polymeric protective resin based on methyl methacrylate (MMA) and 1H,1H-heptafluoro-n-butyl methacrylate (F7) was synthesized via free radical polymerization, adopting F7/MMA at 1% mol/mol. Figure 1a shows the synthetic reaction. Specifically, in a 100 cm³ one-necked flask equipped with a magnetic stirring bar and a reflux condenser, MMA, F7, the initiator α,α' -azoisobutyronitrile (AIBN, mol_{AIBN} = 1% of mol_{MMA+F7}) and cyclohexane (20 cm³) were added and the flask was placed into a thermostatic oil bath under nitrogen atmosphere (see Figure 1a).

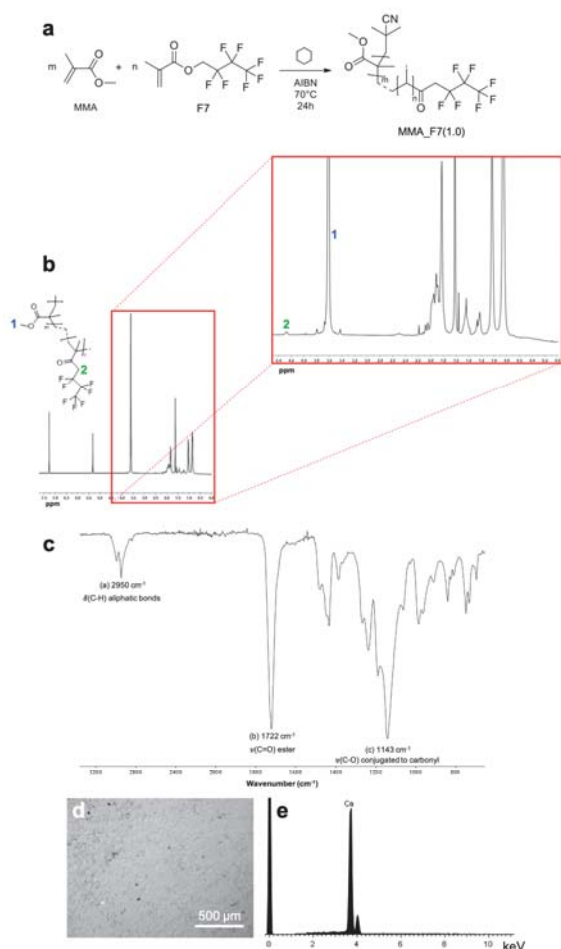


Fig. 1. (a) Synthetic route for the preparation of MMA_F7(1.0) polymeric coating. (b) ¹H-NMR of MMA_F7(1.0) (inset: magnification of 0-4 ppm region to highlight the main peaks). (c) FTIR spectrum of the MMA_F7(1.0) polymer with the main modes highlighted. (d,e) SEM/EDX images relative to bare Candoglia marble.

The reaction was stirred at 70 °C for 24 h. Then, large excess of methanol was added to the polymer in order to solubilize the possible unreacted monomers and subsequently removed through filtration. The product was

dried under vacuum at 40 °C to remove traces of solvent and impurities.

The as-obtained polymeric material was characterized by ¹H-NMR, Fourier-Transformed Infrared Spectroscopy (FTIR), Differential Scanning Calorimetry (DSC) and Size Exclusion Chromatography (SEC). NMR spectra were collected at 25 °C with a BRUKER 400 MHz spectrometer. Samples were prepared dissolving 8-10 mg of polymer in 1 cm³ of CDCl₃. DSC analyses were conducted using a Mettler Toledo DSC1; the analyses were performed weighting 5-10 mg of the sample in a standard 40 μL aluminum pan, heating from 25 °C to 125 °C at 10 °C min⁻¹ and using an empty 40 μL aluminum pan as reference. FTIR spectrum was collected on a Spectrum 100 Perkin-Elmer spectrophotometer in attenuated total reflection (ATR) mode using a resolution of 4.0 and 256 scans, in a range of wavenumber between 4000 and 400 cm⁻¹. The number-average molecular weight (\overline{M}_n) was investigated by size exclusion chromatography (SEC), using a refractive index (RI) detector and tetrahydrofuran as eluent. Molecular weight values are expressed in polystyrene (PS) equivalents.

To further study the wettability properties of the polymer itself, Water Contact Angles (WCAs) using a Krüss Easydrop Instrument were determined. WCA values were obtained by depositing a drop (around 5 μL) of Milli-Q water on polymeric films (4×4 cm) obtained via solvent casting deposition. Samples were dissolved in ethyl acetate (21% w/w) and cast onto a polytetrafluoroethylene (PTFE) mold. All the data were averaged over at least five measurements on each sample to guarantee a statistical population.

In order to unravel the long-term properties of the as-prepared resin UV accelerated test was performed for 100 h, at 25 °C, 1 atm and with an Ultra Vitalux lamp characterized by a wavelength of 315-400 nm for UVA rays (UVA radiated power: 13.6 W) and 280-315nm for UVB ones (UVB radiated power: 3.0 W).

B. Coating deposition and characterization techniques

Candoglia (C) marble was adopted as natural stone substrate (see scanning electron micrograph (SEM) and elemental spectrum (by energy dispersive x-ray spectroscopy, EDX) reported in Figures 1d,e). Candoglia calcitic marble (80-85% CaCO₃ and the 15-20% other minerals) shows a characteristic pink to grey colour and a coarse-grained texture (> 3 mm): frequent centimeter-thick dark-greenish silicate layers (mainly represented by diopside and tremolite) characterize the texture of the marble and the porosity is less than 1%. It has been largely used in local rural constructions and historical buildings (for example Monza Cathedral in Italy), but its most famous application has been for the “Duomo di Milano” construction (in 14th century).

4 Candoglia tiles of 5×5×1 cm (two uncoated as references) and 16 of 2×2×2 cm (eight used as references)

were dried in an oven at 60 °C for a week. The application of the prepared polymer on marble surfaces was carried out by using an air-brush system (Asturo airbrush, 700 µm nozzle, see Fig. 2a). The adopted polymer was dissolved in a solution of dichloromethane/toluene (1/2.5 v/v) with a concentration of 4 mg mL⁻¹. The quantity of sprayed coatings was kept constant at 6 mL every 4 cm² of surface area by controlling also the spray pressure (2.5 bar). All the samples were dried under fumehood overnight. Each sample was weighed before and after the deposition obtaining an average deposited amount equal to 18 mg for each sample.

Wetting properties of both bare and coated samples were assessed by Water Contact Angle (WCA) measurements using a Krüss Easydrop Instrument. WCA values were obtained by depositing a drop (around 5 µL) of Milli-Q water. All the data were averaged over at least ten measurements on each sample to guarantee a statistical population.

Colorimetric analyses were carried out, directly on the different areas of the marble surface, before and after the restoration, by means of a Konica Minolta CM 2300D portable spectrophotometer, referring to the CIE L*a*b* chromaticity diagram and to the Normal recommendation 43/93, (1933) [10]. L* is luminosity or lightness, which varies from black (value = 0) to white (value = 100); a* ranges from +a* (red) to -a* (green) and b* varies from +b* (yellow) to -b* (blue). The instrument was calibrated with its white reference (100% reflective) and zero calibration box (0% reference) in the 400–700 nm range. Three measurements were performed on each area and the mean values of colorimetric parameters were calculated as representative for that area.

Capillary water absorption analyses were performed on bare and coated materials, before and after the exposure test, by the gravimetric sorption technique, as described in the standard protocol UNI EN 10895 [11].

Water vapor permeability (WVP) analyses of bare and coated samples were evaluated by means of the methodology described in the standard protocol UNI 15803 [12].

C. Outdoor exposure

In order to assess the efficacy of the synthesized polymeric coating in preventing marbles deterioration, both bare and coated stones were exposed in a typical urban environment [13-15] placed at the top of Monza Cathedral (see Figure 2b).

The chosen site was at open air without any washout protection. The exposure test was carried out for 493 days (22nd March 2019 to 28th July 2020). The wetting properties of the bare and coated samples, together with the materials permeability and their surface color variation were investigated after the outdoor exposure.

Moreover, Ion Chromatography (IC) was employed for the quantification of the main inorganic constituents of the

deposits. About 2 mg of polymer powder, collected according to our previous works [8,16], was placed in a test tube and treated with 10 mL of Milli-Q water. The solutions were put in an ultrasonic bath for 1 h, then centrifuged for 30 min and injected for IC analyses. Measurements of anionic (NO₃⁻ and SO₄²⁻) species were carried out by using an ICS-1000 HPLC system equipped with a conductivity system detector. The analysis was carried out with an IonPac AS14A column (Dionex S.p.a., San Donato Milanese, Italy) using 8 mM Na₂CO₃/1 mM NaHCO₃, flow rate of 1 cm³ min⁻¹, using a conductivity system detector working with an anion self-regenerating suppressor ULTRA (ASRS-ULTRA) (Dionex S.p.a., San Donato Milanese, Italy).

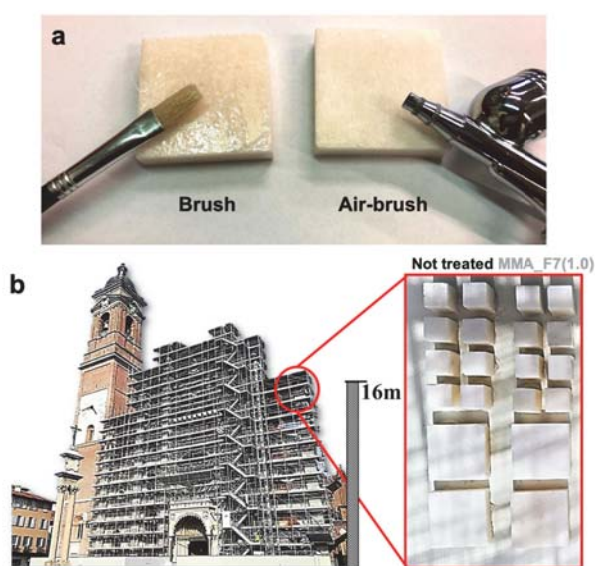


Fig. 2. (a) Photographs of deposition method with a comparison between brushed and air-brushed coated samples. (b) Schematics of the exposure site indicating the location (Monza Cathedral) and the collected samples.

A blank sample consisting of a marble specimen, both not treated and not exposed, was also analyzed (namely absolute white). Anions concentrations determined in the blank sample were subtracted from values obtained from the exposed ones, either bare or treated.

III. RESULTS AND DISCUSSION

The effective synthesis accomplishment together with the macromolecular features of the prepared polymer (MMA_F7(1.0)) were obtained by ¹H-NMR, FTIR and DSC analyses. Figure 1b exhibits the relative spectrum from which the co-monomer amount was calculated (equal to 0.8% mol/mol) revealing fully in accordance with the theoretical one (*i.e.* 1.0%). Peak 2 (clearly highlighted in the inset of Fig. 1b) underlines the actual occurrence of the reaction since the fluorinated co-monomer became part of the polymer chain. FTIR spectrum evidenced the presence

of absorption peaks (a) in the ca. 3100-2800 cm^{-1} range relative to the bending of C-H aliphatic bonds; (b) the stretching of the carbonyl ester groups between ca. 1750-1700 cm^{-1} and (c) the absorption band for the symmetric stretching vibration of C-O conjugated to carbonyl ester groups in the range ca. 1350-1100 cm^{-1} . Moreover, the glass transition temperature (T_g) of about 94 °C allows its potential use in the Cultural Heritage preservation.

Concerning the WCA values on polymeric substrate, the wetting difference between the air and the PTFE sides of the polymeric foils can be ascribable to the reorganization of the fluorinated groups of the polymer chains during the evaporation of the solvent and to the high affinity with the apolar mold surface. Indeed, during the solvent evaporation process, the apolar groups in contact with the PTFE hydrophobic surface are oriented towards it due to the poor affinity with the solvent itself. Thanks to this selective orientation, the PTFE side is characterized by higher WCAs (ca. 95°) than the ones measured at the air side of the films (ca. 74°, see Table 1).

Table 1. Average molecular weight by size exclusion chromatography (SEC), water contact angles (WCAs) of MMA_F7(1.0) polymer before and after the UV aging test.

| Sample | \overline{Mn} (Da) | | WCA (°) air side | | WCA (°) PTFE side | |
|-------------|----------------------|-------|------------------|--------|-------------------|--------|
| | Pre | Post | Pre | Post | Pre | Post |
| MMA_F7(1.0) | 28500 | 27000 | 74 ± 2 | 73 ± 2 | 95 ± 5 | 93 ± 5 |

Besides, UV accelerated aging tests were performed to investigate the long-term properties of the polymeric resin. Table 1 shows a comparison of the average molecular weight and the water contact angles before and after the UV test. No significant differences were observed regarding either the macromolecular or the wettability features.

Once investigated the polymer itself, it was air-brushed onto Candoglia marble. The hydrophobicity was evaluated by measuring both the water contact angles (WCA) and the reduction of the amount of water absorbed by capillarity. Concerning the former analysis, an increase of almost 40% was achieved by depositing MMA_F7(1.0) onto the natural stone, as clearly visible in Figures 3a,b. The promising hydrophobic behavior was further corroborated by water capillary rise that evidenced an optimal reduction of the absorbed water higher than 50%. Finally, by adopting the air-brushing deposition technique, we observed a negligible surface color variation ($\Delta E^* < 5$ [17]) which is not attainable by using a simple brush as shown in Figure 2a.

Furthermore, the synthesized protective coating guaranteed a good water vapor permeability since the computed reduction of vapor permeability (RVP) value is

within the threshold limit of 50% [18].

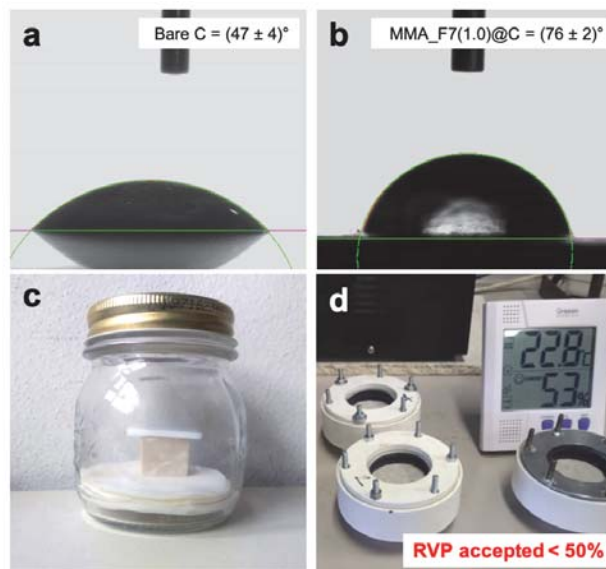


Fig. 3. Water contact angles (WCAs) of (a) bare and (b) coated marble specimens. Experimental set-ups of (c) water capillary and (d) water vapor permeability tests.

In order to assess the effective polymer protective features, exposure in a real polluted environment was carried out. In particular, the adopted site was at the top of Monza Cathedral (near Milan, see Fig. 2b), avoiding any washout protection. Once more, wettability features together with water vapor permeability and color variation were studied. Furthermore, the interaction among atmospheric gases and aerosol with stone surfaces was determined by ion chromatography, since one of the main environmental degradation processes that occur on the surfaces of monuments and historical buildings, is subsequent to atmospheric pollution.

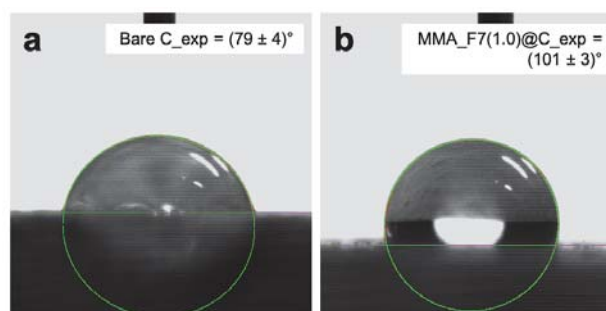


Fig. 4. Water contact angles (WCAs) of (a) bare and (b) coated marble specimens after outdoor exposure.

The hydrophobicity and permeability preservation were confirmed even after the one-year exposure, and no evident yellowing effect was noticed. By measuring WCAs, we noticed a significant decrease of surface wettability for both bare and MMA_F7(1.0)-coated

specimens. In particular, the average contact angle value for the former increased from ca. 47 to $(79 \pm 4)^\circ$, whereas in the presence of the polymeric coating it reached around 100° (as shown in Figure 4). This rise is probably due to impurities and carbonaceous dirt related to the outdoor environment. However, notwithstanding this aspect, the adopted polymer has not been ruined and degraded by the atmospheric agents.

Furthermore, sulphates and nitrates have been investigated as the main products of the interaction between atmospheric gaseous species and stones surfaces. Indeed, the former are the products of carbonatic stones degradation (due to SO_2 oxidation and subsequent interaction with the stone itself), whereas nitrates are mainly caused by atmospheric deposition [8,16,19]. The relative studies are still going on but, from preliminary results, it seems the adopted resin limits the eventual stone dissolution caused by the atmospheric agents.

IV. CONCLUSIONS

This work demonstrated that a polymeric protective prepared from a co-monomer bearing a medium-length (seven fluorine atoms) fluorinated pendant chain is characterized by satisfactory hydrophobic and durability features. Moreover, such polymer does satisfy many of the parameters required for an optimal protection of stone materials: *i*) the side-chain fluorination improves the coating water repellency without affecting its durability; *ii*) the stability both after UV accelerated aging tests and even after a one-year exposure in a polluted environment indicate its suitability in the Cultural Heritage conservation field.

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