Stearyl methacrylate co-polymers: towards new polymer coatings for mortars protection

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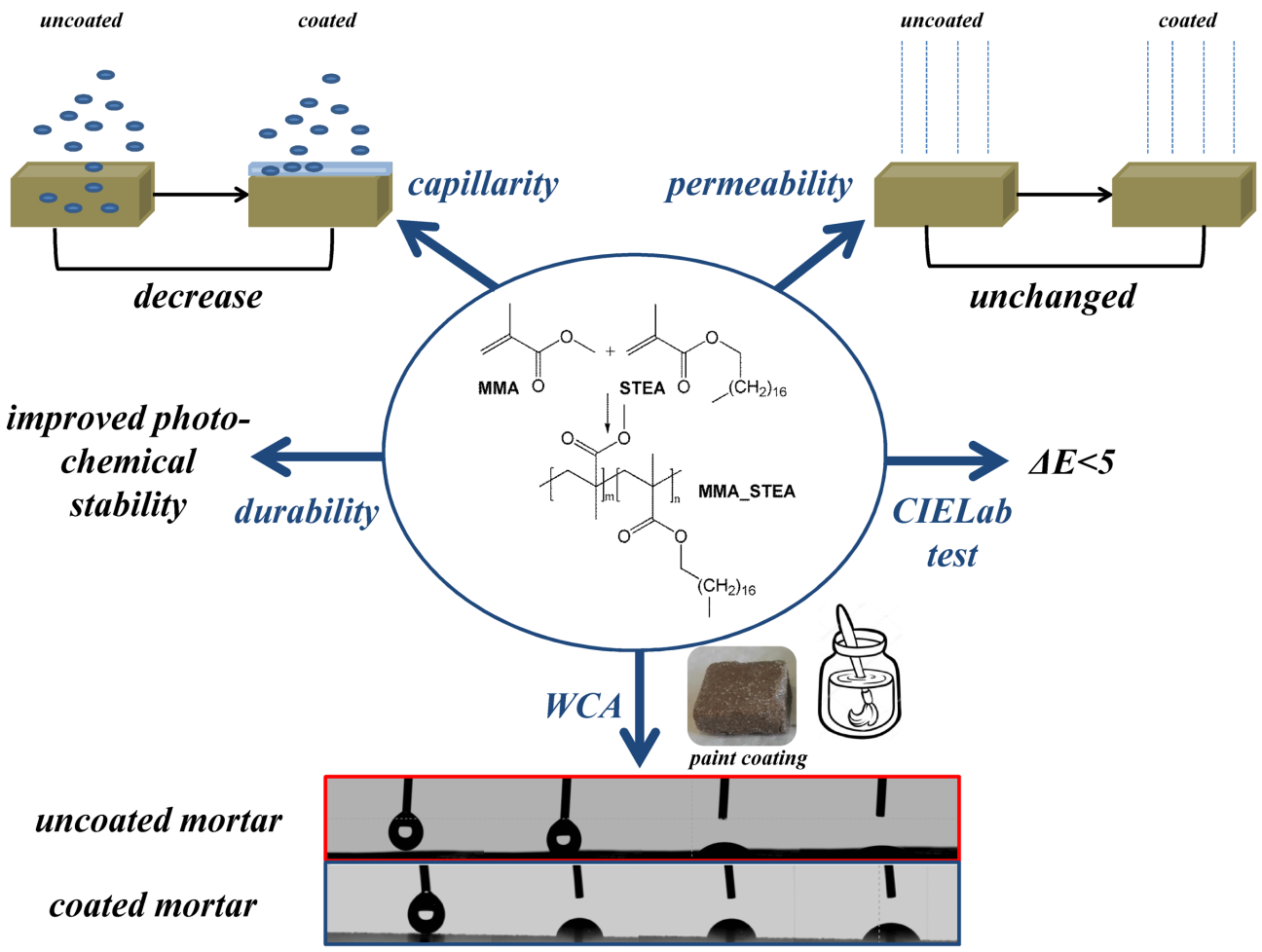

ABSTRACT

In the present work, a novel polymeric coating for mortars protection was prepared via free radical polymerization between methyl methacrylate (MMA) and stearyl methacrylate (STEA) to overcome the well-known technical problems related to the use of commercial Polyacrylic protectives. The physico-chemical properties of MMA_STEA and the effect of different STEA amounts (1.0-2.5-5.0% mol/mol respect to MMA) on MMA_STEA features were determined via ^{1}H NMR and FT-IR spectroscopy, Gel Permeation Chromatography (GPC) and Differential Scanning Calorimetry (DSC). Furthermore, the long-term behavior of these polymeric protective agents was evaluated by means of accelerated aging tests exploiting UV radiations. MMA_STEA coatings were applied to air-hardening calcic lime mortars and their performances were studied using different surface techniques: static water contact angles (WCAs), CIELab colorimetric tests, water absorption by capillarity and water vapor permeability (WVP). All measurements were also performed after an UV aging test to study the durability of the coatings applied on mortar. This work demonstrates that a polymer coating prepared starting from methyl and stearyl methacrylates-based comonomers is an efficient way to obtain mortar protectives with satisfactory water repellent behavior, transparency and durability.

Keywords: cultural heritage, mortar, polymeric coating, free radical polymerization, surface modification.

1. INTRODUCTION

The protection of building materials, such as mortars, stones and marbles, is one of the most critical and important steps for the conservation of cultural heritages and modern architectures.

The main causes of building materials deterioration exposed to outdoor conditions are water permeation into the material [1], corrosion by chemical pollutants [2], freezing/thawing cycles [2] and crystallization/precipitation of salts solutions absorbed from the environment [3].

Thus, the use of protective and consolidating coatings to construction materials is an efficient way to hinder and protect cultural heritages and buildings from the natural decay, avoiding or limiting the water penetration into the substrates [4,5].

A protective coating for a building material should satisfy several requirements: *i*) water repellency reducing the capillarity rise, *ii*) minimum alteration of the natural water vapor permeability of the material, *iii*) no significant variation of the aesthetical appearance, *iv*) durability against external conditions and *v*) easiness of application and removal [6].

Up to now, two main categories of protectives for building materials are commercially available, *i.e.* pure organic resins (such as polysiloxanes [7] and polyacrylates [8]), or hybrid coatings (TiO_2 or SiO_2 together with polymers) [4]. Referring to organic products, polymer coatings prepared starting from acrylic monomers are typically employed as protective agents of building materials for cultural heritages and modern architectures [9]. During the last decades, the most satisfactory commercial acrylic resin, (obtainable via free radical polymerization technique starting from a mixture of acrylic and methacrylic monomers, ethyl methacrylate, EMA and methyl acrylate, MA), was Paraloid B72®, due to its good water repellence and optically clear appearance [10]. Despite the common use of photo-stabilizing agents with Paraloid B72® [11], the presence in the acrylic monomer of a hydrogen atom in alpha position to carbonyl group, that is capable to start photo-chemical degradation reactions leads to severe durability issues [12].

To overcome the above-mentioned limits, in our previous works [13,14] we have exploited the use of innovative polymer coatings as protectives of precious marbles showing satisfactory water repellent properties and improved durability, combining the use of fluorinated and methacrylic monomers and without the addition of any photo stabilizer agent.

Thus, the development of new polymer coatings able to overcome the technical problems previously reported not only for precious stones but also for commercial marbles and mortars is still a challenge. Despite fluorine-based coatings are considered the most promising candidates [15], there are needs to work out the large-scale low-cost fabrication routes.

Hence, in order to overcome the above-mentioned limits of polyacrylic and polymethylmethacrylate resins, the aim of the present work was to synthesize a new polymer coating combining the use of methyl and stearyl methacrylates comonomers, without the addition of any fluorinated comonomer. The effects in terms of water repellency of long alkyl chains on the surface properties of the resulting coating have been deeply studied.

Specifically, a new type of polymer protective was prepared via free radical polymerization between methyl methacrylate -MMA- and stearyl methacrylate -STEA- (MMA_STEA), changing the loading of STEA comonomer (1.0-2.5-5.0% mol/mol respect to MMA). In order to determine the long-term properties of MMA_STEA resins, accelerated exposure tests under UV radiations were performed. The macromolecular structure, molecular weights and thermal features of MMA_STEA resins, were investigated before and after the UV exposure simulation test via ^1H NMR and Fourier Transform-Infrared (FT-IR) spectroscopies, Gel Permeation Chromatography (GPC) and Differential Scanning Calorimetry (DSC) measurements.

Finally, the synthesized resins were applied on typical air-hardening calcic lime mortars and their performances as protective agents were studied using different surface techniques such as water

contact angle measurements (WCA), CIELaB colorimetric analyses, water absorption by capillarity and water vapor permeability (WVP). Furthermore, WCA, colorimetric, permeability and WVP data were measured and compared before and after the accelerated ageing test.

2. EXPERIMENTAL

2.1. Materials

Methyl methacrylate (MMA, 99%), stearyl methacrylate (STEA, mixture of stearyl and cetyl methacrylates), α,α'-Azoisobutyronitrile (AIBN, 99%), toluene (99.8% anhydrous), methanol (99.8% anhydrous), tetrahydrofuran (THF, 99.8% anhydrous), dichloromethane (DCM, 99.8% anhydrous), distilled water Chromasolv® (≥99.9%) and chloroform-d ($CDCl_3$, 99.96 atom % D) were supplied by Sigma Aldrich and used without purification. For the mortars preparation, white cement (Portland cement, TECNOCEM, Italcementi S.p.A.), hydrated lime NHL 3.5 (from Soc. Calce Raffinata, Savignano sul Panaro), pure quartz sand (0.1 – 0.3 mm, from C.T.S., Altavilla Vicentina), GEO coarse pumice, fine pumice (Hess Pumice Idaho USA, 0.3 mm), thinner (Sika® ViscoCrete® 5380, polystearic esters) and aerating agent (ARMIX, aqueous solution of sulfonated polymers) were adopted.

2.2 Synthesis of MMA_STEA copolymers

Three MMA_STEA copolymers with increasing nominal amount of STEA -1.0_2.5_5.0% mol/mol- respect to MMA comonomer were synthesized.

In a typical polymerization procedure, a 100 cm^3 one-necked round bottom flask was equipped with a nitrogen inlet adapter, a reflux condenser and an overhead magnetic stirrer. The flask was flushed with nitrogen, charged with 40 cm^3 of toluene, MMA, STEA and AIBN, the latter used as free radical initiator at 1% mol/mol respect to MMA and STEA comonomers. The solution was put in an oil bath, heated for 24 h at 80°C and then gradually cooled down to room temperature. The solution obtained was precipitated into a large excess of methanol under stirring and a white solid precipitate was obtained. The solid was recovered via filtration and washed at room temperature with distilled water for several days under stirring to assure the complete removal of unreacted methacrylic monomers from MMA_STEA samples. After washing, the polymers were dried in a vacuum oven (about 4 mbar) at 40°C for 48 h and then the absence of residual solvents was checked via isothermal thermogravimetric analysis (TGA), performed for 2 h at 70°C under nitrogen flow. Figure 1 shows the representative procedure for the synthesis of MMA_STEA co-polymers.

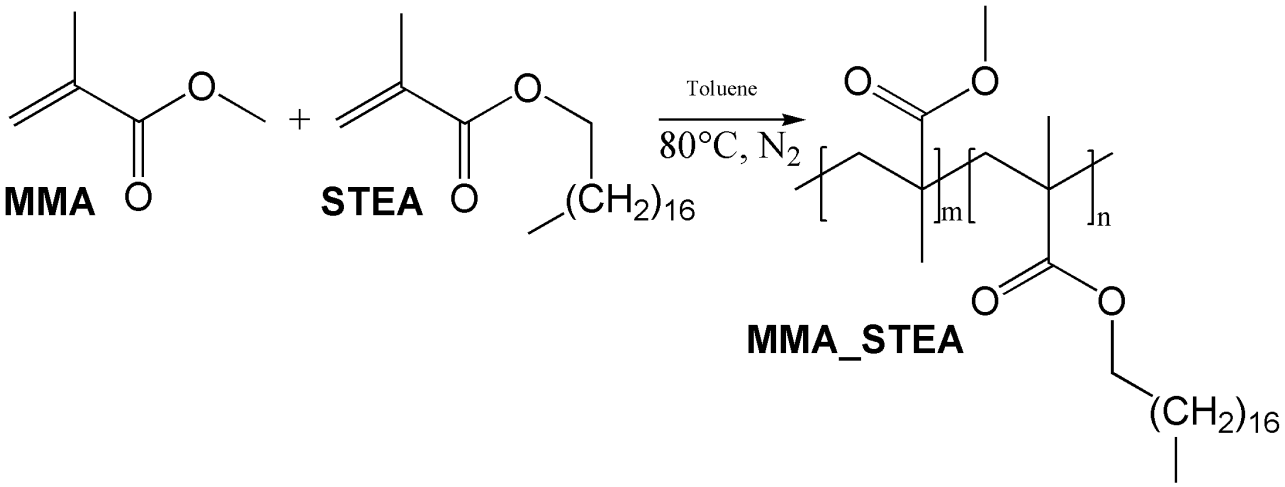

Figure 1. Synthetic route MMA_STEA copolymers.

2.3 Characterization of polymers

2.3.1 Nuclear magnetic resonance: ^{1}H NMR

^{1}H NMR spectra were collected at 25°C with a BRUKER 400 MHz spectrometer. Samples for the analyses were prepared dissolving 10-15 mg of MMA_STEA samples in 1 cm^3 of $CDCl_3$.

2.3.2 UV exposure simulation test

To evaluate the stability of the polymers under UV radiations, an accelerated aging test was performed according to UNI 10925:2001 standard method [16]. The test was conducted for 100 h (T = 25°C and p = 1 atm), with Ultra Vitalux lamp characterized by a wavelength of 315-400 nm for UVA rays and 280-315 nm for UVB ones.

2.3.3 Fourier Transform- Infrared (FT-IR)

FT-IR spectra of MMA_STEA polymers were obtained on a Spectrum 100 spectrophotometer (Perkin Elmer) 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}. A single-bounce diamond crystal was used with an incidence angle of 45°. FT-IR spectra were collected before and after the UV aging test.

2.3.4 Differential Scanning Calorimetry (DSC)

DSC analyses were conducted using a Mettler Toledo DSC1; the samples were prepared weighting from 5 to 10 mg each in a standard 40 µL aluminium pan, with an empty 40 µL aluminium pan as reference and using the following thermal program: *i*) 25-150°C at 10°C/min; *ii*) 5 min at 150°C; *iii*) 150-25°C at 10°C/min; *iv*) 5 min at 25°C and *v*) 25-170°C at 10°C/min. The thermal behaviour of the samples obtained after the UV exposure simulation test was studied with the same thermal program.

2.3.5 Gel Permeation Chromatography (GPC)

The effect of UV exposure on the molecular weight of the polymeric samples was evaluated using a GPC system having Waters 1515 Isocratic HPLC pump and a four Phenomenex Phenogel (5×10^{-3}Å-5×10^{-4}Å-5×10^{-5}Å-5×500Å) columns set with a RI detector Waters 2487 using a flow rate of 1 cm^3/min and 40 µl as injection volume. Samples were prepared dissolving 40 mg of polymer in 1 cm^3 of THF; before the analysis, the solution was filtered with 0.45 µm filters. Molecular weight data were expressed in polystyrene (PS) equivalents. The calibration was built using monodispersed PS standards having the following nominal peak molecular weight (Mp) and molecular weight distribution (D): Mp = 1600000 Da (D≤1.13), Mp = 1150000 Da (D≤1.09), Mp = 900000 Da (D≤1.06), Mp = 400000 Da (D≤1.06), Mp = 200000 Da (D≤1.05), Mp =90000 Da (D≤1.04), Mp =50400 Da (D=1.03), Mp= 30000 Da (D=1.06), Mp = 17800 Da (D=1.03), Mp = 9730 Da (D=1.03), Mp = 5460 Da (D=1.03), Mp = 2032 Da (D=1.06), Mp = 1241 Da (D=1.07), Mp = 906 Da (D=1.12), Mp = 478 Da (D=1.22); Ethyl benzene (molecular weight = 106 g/mol). For all analyses, 1,2-dichlorobenzene was used as internal reference. The molecular weights of the samples obtained after the UV exposure test were also determined.

2.4 Mortar preparation and characterization

2.4.1 Mortar formulation

Four mortar tiles of 5×5×1 cm and four of 2×2×1 cm were prepared as following: white cement (134.1 g, 26.8% w/w), lime (45.0 g, 9.0% w/w), sand (45.0 g, 9.0% w/w), coarse pumice (44.7 g, 8.9% w/w), fine pumice (143.7 g, 28.7% w/w), deionized water (84.3 g, 16.9% w/w), thinner (2.7 g, 0.5% w/w) and aerating agent (0.3 g, 0.1% w/w) were thoroughly mixed in a 500 cm^3 plastic container. Then, the viscous paste was put in epoxy molds and dried for 4 weeks in air at room temperature in order to favour the carbonation process.

2.4.2 Scanning Electron Microscopy – Energy Dispersive X-ray Spectroscopy (SEM - EDX)

Mortar tiles morphology and elementary composition were determined by SEM Hitachi TM-1000 equipped with an energy dispersive X-ray spectroscopy EDX Hitachi ED3000. The investigations were performed with an acceleration voltage of 15 kV and 50 pA of current probe.

2.5 Application of polymer coatings on mortars surface and their characterization

2.5.1 MMA_STEA application on mortars surface

Polymers were dissolved in DCM using 20% w/w concentration. The application of coatings on mortars surface was carried out using a brush with bristles made with Polyamide 6 in order to obtain a homogeneous and thin polymer layer of 200 mg (determined by weighing) onto the mortar surface. The coated mortar tiles were dried at 40°C for 1 h and then used for water contact angles analyses (WCA), CIELab colorimetric measurements, water absorption by capillarity and water vapour permeability (WVP) tests. To evaluate the polymer stability under UV radiations, an

accelerated aging test was performed as reported in paragraph 2.3.2 and WCA, CIELab, capillarity and WVP analyses were also repeated on aged coated mortars.

2.5.2 Water Contact Angle (WCA) analyses

Surface wetting properties of the both pristine and coated mortar tiles were assessed by contact angle measurements using a Krüss Easydrop Instrument. The contact angle values were obtained by depositing a drop (5 μL) of distilled water. At least fifteen measurements were taken on each sample to get reliable values, averaging the obtained results. The wetting properties of the coated samples, obtained after the UV exposure, were also determined.

2.5.3 CIELab colorimetric measurements

Colorimetric measurements were performed to verify the colour modification of the protective films after the UV aging test. The chromatic coordinates were calculated according to the Commission Internationale d'Eclairage (CIELab method) [17], starting from diffusive reflectance spectra acquired in the UV-Vis spectral range from 800 to 200 nm with a UV-Vis SHIMADZU spectrophotometer model UV 2600 instrument. According to the literature, no significant variation occurs when $\Delta E^* < 5$ [18].

2.5.4 Water absorption by capillarity

Capillary water absorption measurements were performed on bare and coated materials by the gravimetric sorption technique, as described in the standard protocol UNI EN 15801 [19]. Total amount of water absorbed by a material (Q_f), capillary absorption (CA) and relative capillarity index (CI_{rel}, which give information about the resistance to capillary rise when prolonged contact with water occurs) were determined, accordingly.

2.5.5 Water vapour permeability (WVP)

WVP analyses of bare and coated mortars were evaluated by means of the methodology described in the standard protocol UNI 15803 [20]. Reduction in Water Vapour Permeability (RVP) was calculated; according to the standard protocol, a polymer material cannot be used as protective for mineral substrate if RVP>50%. WVP analyses were repeated on aged materials.

3. RESULTS and DISCUSSION

3.1 Synthesis, characterization and aging study of MMA_STEA copolymers

Novel protective polymers (MMA_STEA) were through the free radical polymerization between MMA and STEA, varying the molar percentage of STEA with respect to MMA co-monomer (1.0-2.5-5.0% mol/mol). Their actual chemical structures were determined via ^{1}H NMR spectroscopy (Figure 2): by comparing the spectra of MMA_STEA samples (Figure 3) with different STEA loadings, the increase of the integral area of the peak relative to STEA (**a**) is clearly appreciable.

Furthermore, the real amount of STEA in MMA_STEA copolymers can be quantitatively determined by ^{1}H NMR spectra using Equation 1 where *"I_{STEA}"* is the integral area of peak **[a]**, *"I_{MMA}"* is the integral area of peak **[b]**, *"2"* corresponds to the number of STEA protons related to the integral area of peak **[a]** and *"3"* is the number of MMA protons for the integral area of peak **[b].**

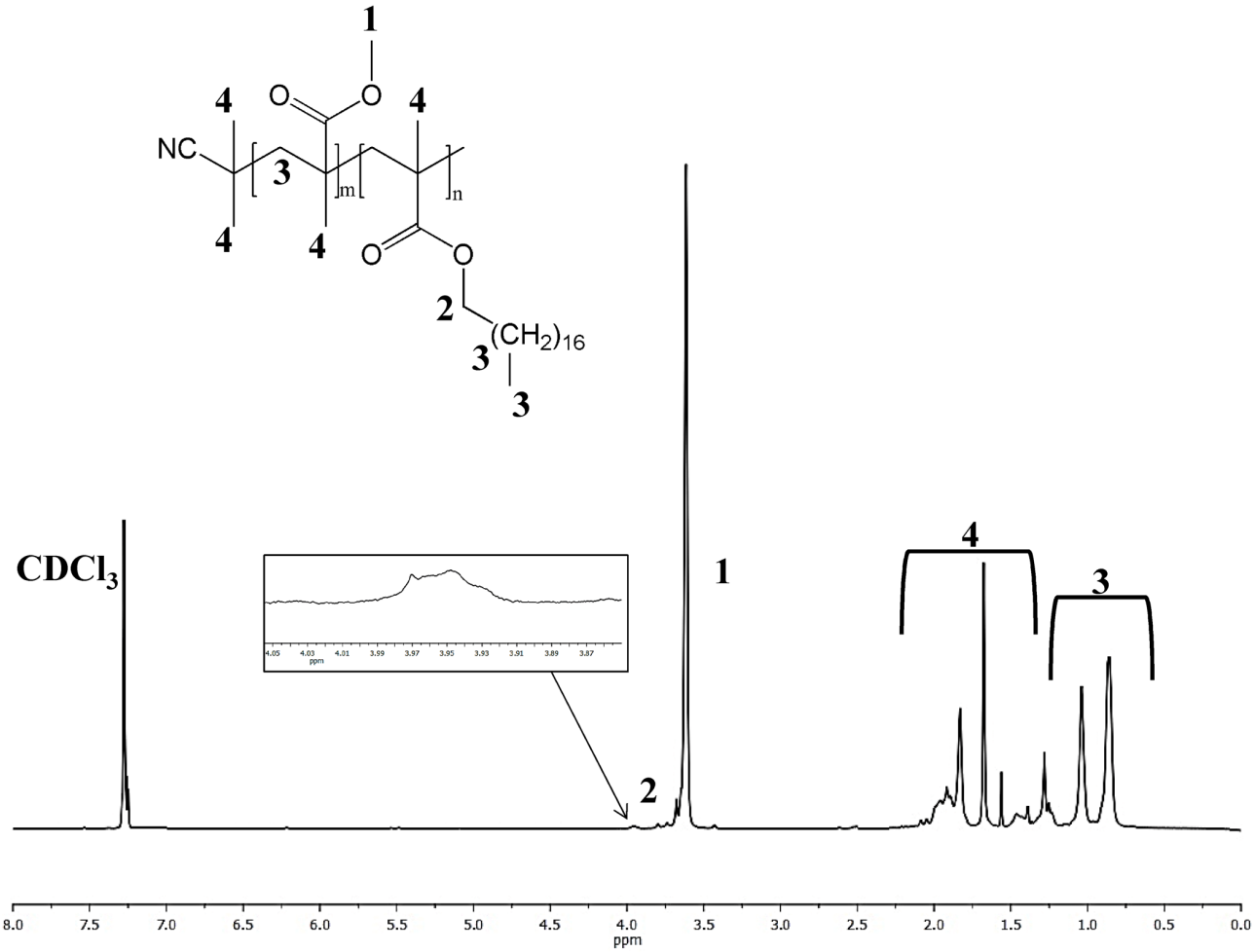

Figure 2. ^{1}H NMR spectrum of MMA_STEA_1.0.

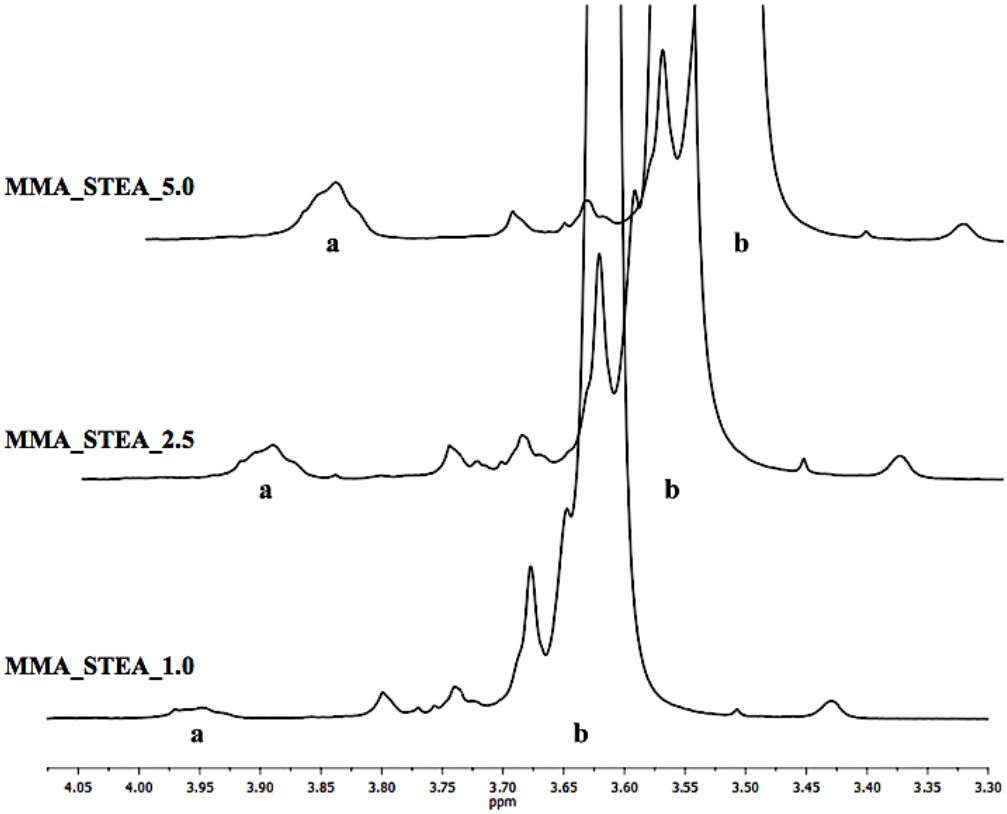

Figure 3. Magnification of MMA_STEAs ^{1}H NMR spectra.

$$\text{STEA \% mol/mol} = \frac{(I_{STEA}/2)}{(I_{MMA}/3)} \quad (1)$$

The results are reported in Table 1, highlighting that the theoretical and the experimental values are fully in accordance, confirm that MMA_STEA copolymers were successfully synthesized.

Sample	theoretical STEA % (mol/mol)	real STEA % (mol/mol)
MMA_STEA_1.0	1.0	1.0
MMA_STEA_2.5	2.5	2.1
MMA_STEA_5.0	5.0	5.3

Table 1. STEA molar percentage in MMA_STEAs determined via ^{1}H NMR spectroscopy.

To determine the long-term stability of the new tailored MMA_STEA resins, a UV accelerated exposure test was performed. Figure 4 shows a comparison between FT-IR spectra of different MMA_STEAs, collected before and after the aging test. The peak (a) in the ~3100–2800 cm^{-1} range is related to the bending of C-H aliphatic bonds [21]; the stretching of carbonyl ester groups (C=O) (b) lies in the range between ~1750 and 1600 cm^{-1} [21].

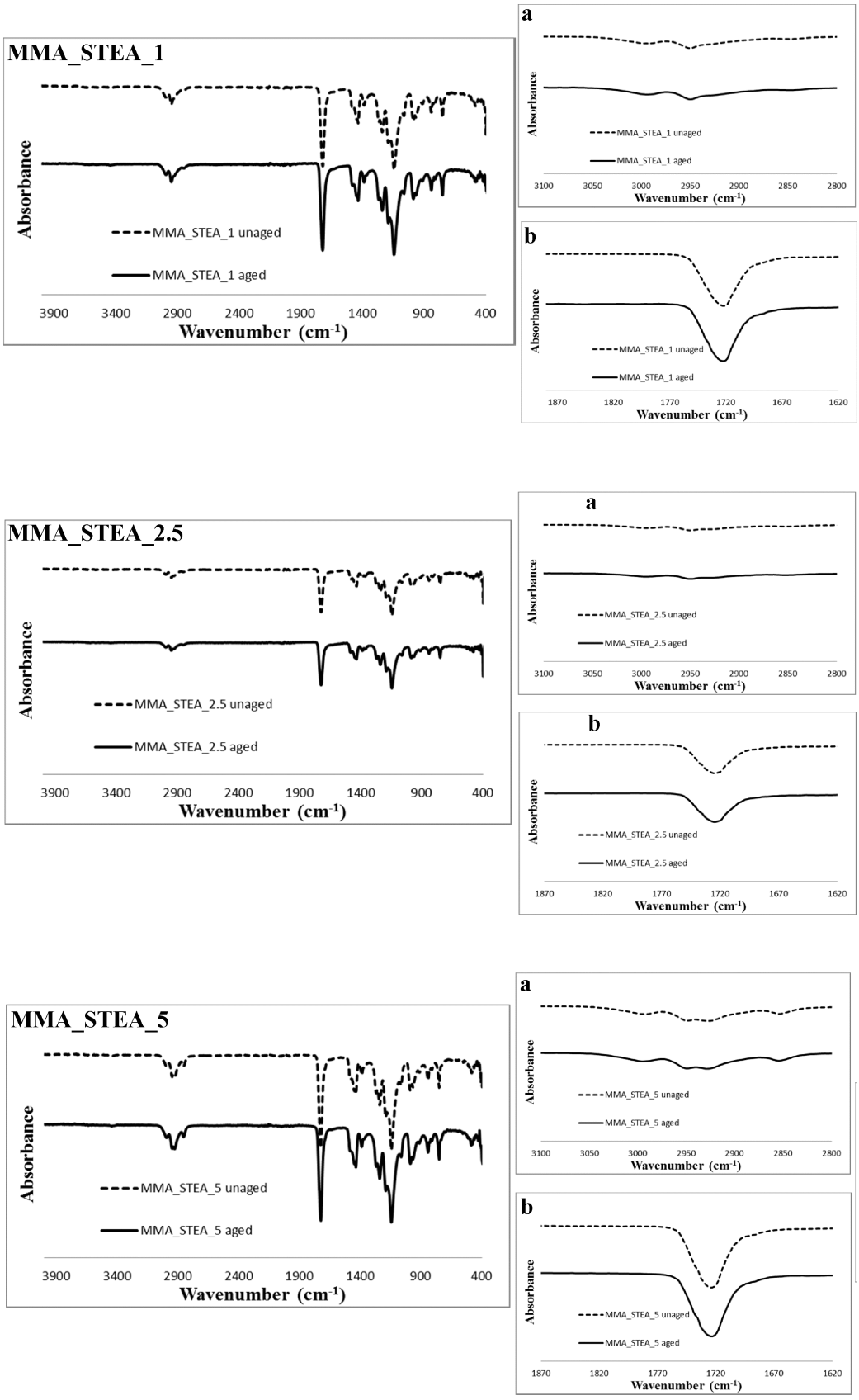

Figure 4. FT-IR spectra of MMA_STEAs collected before and after the aging test, and magnification of a) bending C-H area and b) stretching C=O area.

In the case of polyacrylates, the shape of (a) and (b) absorption peaks changes dramatically after the UV aging test, showing a significant variation of the bands related to C-H aliphatic bonds and the same carbonyl groups, due to degradation phenomena of polymeric bonds (breaking of macromolecular chains where aliphatic and carbonyl groups are present) [12]. This behaviour is probably due to the presence in polymer structures of hydrogen atoms, deriving from acrylic monomers, in alpha position to carbonyl groups that are able to start the photo-chemical degradation of the polymers themselves [22]. Here, no significant variations are detectable among the MMA_STEA FT-IR spectra (Figure 4) collected before and after the aging test, suggesting the high photochemical stability of the new synthesized resins. Furthermore, the effect of UV exposure can be highlighted by the evaluation of the number average molecular weight ($\overline{Mn}$), the weight average molecular weight ($\overline{Mw}$), the peak molecular weight (Mp) and the molecular weight distribution (D) by GPC analyses (Table 2). MMA_STEA_1.0/2.5/5.0 polymers remain soluble in DCM after the aging test, suggesting the absence of radicals that allow the formation of a partially reticulated polymer via cross-linking reactions [12]. Furthermore, the variation of the molecular weights and their relative distribution (Table 2) before and after the aging test is negligible, clearly evidencing the photo-stability of the tailored resins [23].

Sample	$\overline{Mn}$ (Da)	$\overline{Mw}$ (Da)	Mp (Da)	D	T_g (°C)
MMA_STEA_1.0 unaged	4500	12000	10000	3.4	95.3
MMA_STEA_1.0 aged	4400	11900	9800	3.3	97.2
MMA_STEA_2.5 unaged	3800	11000	9300	2.9	75.7
MMA_STEA_2.5 aged	3700	10800	9300	2.8	75.3
MMA_STEA_5.0 unaged	3700	17800	9900	4.8	69.0
MMA_STEA_5.0 aged	3600	17700	9800	4.9	66.2

Table 2. GPC data and glass transition temperatures of MMA_STEA samples before and after the aging test.

MMA_STEAs thermal properties were also assessed and compared with the ones obtained after the UV aging test (Table 3). The glass transition temperatures (T_g) of MMA_STEA_1.0/2.5/5.0 samples are respectively 95.3, 75.7 and 69.0°C. Thus, by increasing the STEA amount, *i.e.* aliphatic pendant chains in the final polymer, the T_g tends to decrease. After the aging test, MMA_STEAs T_g remains almost the same, in according with FT-IR and GPC analyses. The comparison of FT-IR, GPC and DSC data measured before and after the aging test demonstrates that a polymer resin prepared starting from MMA and STEA is an efficient way to obtain a protective with enhanced photo

chemical durability. Within this context, the use of MMA_STEA based resins can be a way to obtain a satisfactory protective for mortar substrates.

3.2 Deposition of MMA_STEA copolymers onto home-made mortars and relative protective features

Both the morphology and the elementary composition of the mortar sample were preventively characterized by SEM-EDX analyses (Figure S1), in order to investigate the efficiency of mortar tiles formation in terms of surface homogeneity and quality of carbonation process. In according to the data reported in literature [24], the mortar appears as a homogeneous surface, without cracks and holes, characterized by an EDX peak related to calcium element having high intensity, confirming the successful carbonation process. Indeed, the pumice presence is reported not only to give mortars excellent binding and durability features, improving both their strength and abrasion resistance, but also to reduce the flow/workability of fresh mortars [24].

MMA_STEA_1.0/2.5/5.0 resins were applied via paint-coating onto a mortar substrate prepared as reported in Materials and Methods section, and their wetting properties, CIELab colorimetric features, water absorption by capillarity capability and WVP properties were assessed. Furthermore, all of these analyses were repeated after an UV accelerated aging test. The bare mortar surface shows a high-water wettability, not measurable by contact angle instrument due to the immediate absorption of water onto mortar tile (Figure 5a). When MMA_STEA resins were applied, at first the coatings limit the water absorption onto mortar surface (Figure 5b) allowing the contact angle measurements: actually, WCA values (Table 3, 2nd column) increase at increasing of the STEA loading, passing from 75° in the case of MMA_STEA_1.0 to 83° for MMA_STEA_5.0, almost reaching the hydrophobicity threshold (Figure 5b). The WCAs of coated mortars were re-measured after an UV accelerated aging test and, in according to the data previously presented and discussed, it is possible to observe from Table 3 that the wetting features remain similar.

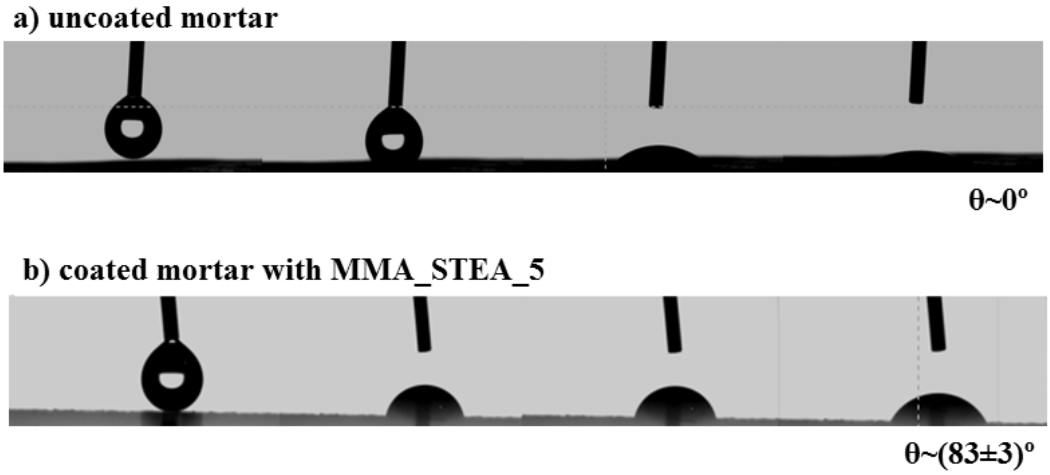

Figure 5. WCA frames of a) uncoated mortar and b) coated mortar with MMA_STEA_5.0.

Sample	θ (°)	ΔE
MMA_STEA_1.0 unaged	75±4	3.1
MMA_STEA_1.0 aged	68±5	
MMA_STEA_2.5 unaged	79±3	2.4
MMA_STEA_2.5 aged	73±3	
MMA_STEA_5.0 unaged	88±3	0.9
MMA_STEA_5.0 aged	75±5	

Table 3. WCA data of MMA_STEA-based mortars before and after the aging test and colorimetric variations between unaged and aged coated mortars.

To corroborate the optical durability of the as prepared polymers, the CIELab color space [25] was determined. It provides a standard and approximately uniform scale that can be used to compare the color modification of an object over the time or after a critical event, such as solar and/or thermal aging tests [26]. In this work, the colorimetric measurements were carried out on the MMA_STEA-based mortars treated before and after the UV aging test to determine if chromatic alterations occur after the prolonged exposition to an ultraviolet radiation. According to the literature [18], a chromatic difference, expressed by the ΔE parameter, less than or equal to 5 ($\Delta E \leq 5$) is not considered significant. ΔE values for MMA_STEAs, shown in Table 3 (3rd column), were calculated from DRS analyses. For all the samples, the undesired threshold was not achieved, thus the chromatic alteration can be considered negligible. The unchanged optical properties of the novel resins confirm the durability results obtained via FT-IR, GPC and DSC analyses; MMA_STEAs seem to be promising as mortar protective coatings.

Then, the water absorption test by capillarity is one of the most effective methods to evaluate the penetration and the relative capillarity rise of water within a mineral substrate such mortars, and to estimate the effectiveness of a water-repellent treatment. In this work, the measures of water

absorption by capillarity on bare and coated mortars were conducted in accordance with UNI 10859 standard method. Furthermore, the total amount of water absorbed by the material (Q_f), the capillary absorption (CA), the relative capillarity index (CI_{rel}) were determined, accordingly. Figure 5 shows the results of bare and MMA_STEA-based mortars, both before (Figure 6a) and after the UV aging test (Figure 6b).

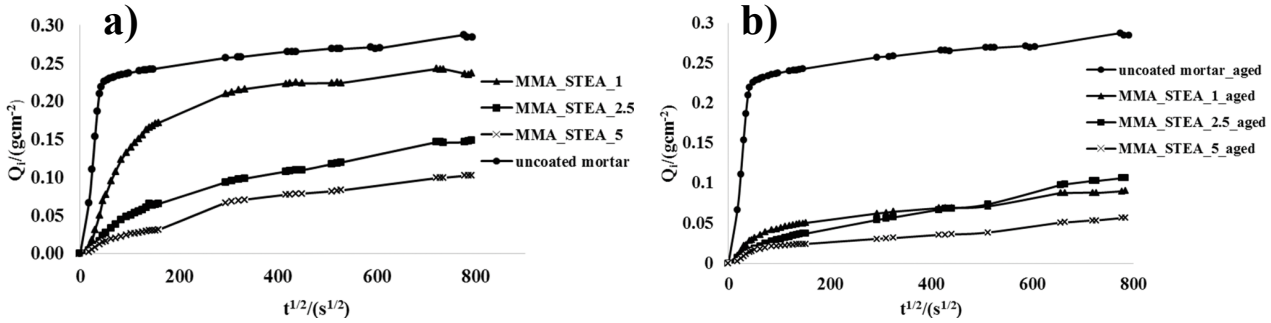

Figure 6. Capillarity data for bare mortar and mortars coated with MMA_STEA samples measured a) before and b) after the aging test.

A different trend between the water absorption curves of the uncoated and coated mortars can be clearly observed. The capillarity curve of the untreated mortar is characterized by a very steep linear step followed by a plateau region. This behavior corresponds to the saturation of the material occurred after a fast absorption of water (saturation time: 3 hours). On the contrary, MMA_STEA-based samples do not reach saturation and there is a gradual increase of the water absorbed as a function of time. Indeed, the mortar water absorption is reduced by the presence of the protective coatings, which waterproof the mortars surface, preventing the rising of water. Furthermore, the waterproofing behavior of MMA_STEA resins increases as the amount of STEA gets higher. As reported in Table 4, the total amount of water absorbed by the material (Q_f parameter) decreases as the loading of STEA in MMA-based copolymers increases, as well as CA and CI_{rel} parameters.

Sample	Q_f ($g \times cm^{-2}$)	$CA \times 10^3$ ($g \times cm^{-2} \times t^{-1/2}$)	IC_{rel}	RVP (%)
bare mortar-unaged	0.28	5.50	-	-
bare mortar-aged	0.28	5.47	-	-
MMA_STEA_1.0-unaged	0.24	1.70	0.72	41
MMA_STEA_1.0-aged	0.09	0.67	0.23	5
MMA_STEA_2.5-unaged	0.60	0.60	0.36	34
MMA_STEA_2.5-aged	0.11	0.04	0.23	32

MMA_STEA_5.0-unaged	0.40	0.40	0.24	63
MMA_STEA_5.0-aged	0.06	0.05	0.13	41

Table 4. Capillarity and permeability parameters for bare mortar and MMA_STEA-based mortars.

The capillarity tests repeated on the aged samples (Figure 6b) show that there is an increase of the waterproofing behavior of the synthesized resins and consequently, a decrease of Q_f, CA and IC_{rel} parameters, in accordance with the high photochemical stability of MMA_STEA coatings (Table 4). The improvement of capillarity performances for aged MMA_STEAs mortars in comparison to unaged samples, is probably due to the complete evaporation of the paint-coating solvent traces [27,28].

Ideally, a protective coating for a mortar should prevent the capillary absorption of water, but at the same time, it should allow the permeation of water vapour through the material pores. Indeed, a hard reduction of WVP can damage the mortar, since a long permanence of water and aqueous solutions inside the porous matrix of the mineral can favour the formation of salt aggregates able to determine mechanical stress such as cracks, promoting the detachment of the protective coating from the mortars surface [29,30]. Indeed, the parameter related to the reduction of water vapour permeability (RVP) was determined for either the unaged or aged coated mortars. According to the standard protocol, a polymer material cannot be used as protective for mortar substrate if RVP > 50%. Figure 7a and b show the WVP curves of unaged and aged MMA_STEA-based mortars, respectively. Comparing WVP data, in the case of unaged samples (Figure 7a and Table 4, 6th column), it is possible to observe a reduction of permeability for all the STEA-clad mortars. Specifically, MMA_STEA_5.0 reaches an RVP value of 63%, out of the permitted threshold.

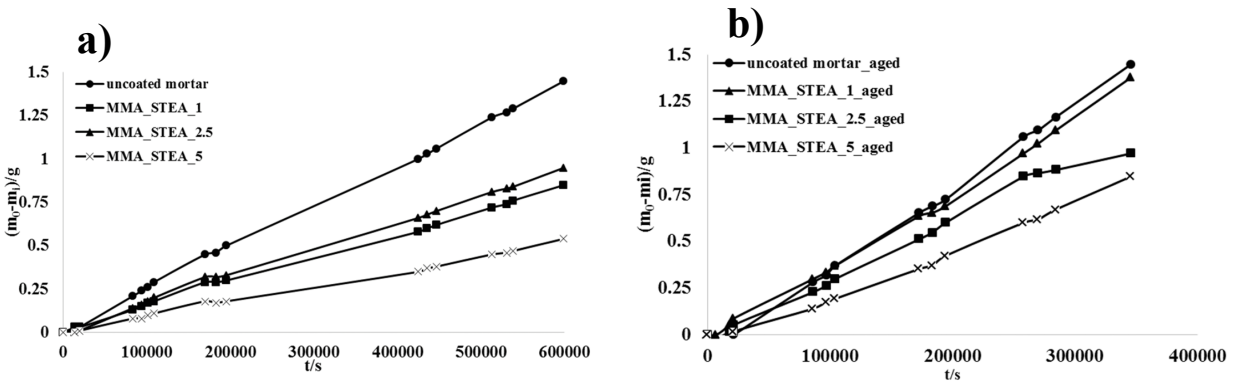

Figure 7. Permeability data for bare mortar and mortars coated with MMA_STEA samples measured a) before and b) after the aging test.

In the case of aged samples (Figure 7b), there is an improved permeability for all the coated mortars, *i.e.* all the coated-samples with RVP data always <50%. Furthermore, as for unaged samples, the permeability gets higher as STEA amount increases. As stated for capillarity tests, the increase of permeability performances for aged MMA_STEAs mortars in comparison to unaged ones is probably due to the complete evaporation during the aging test of the paint-coating solvent traces that could have remained inside the polymer coatings. In the future, best conditions of coating application and drying, in terms of resin deposition technique and the nature of the solvent, will be studied. Moreover, by correlating MMA_STEAs chemical data obtained before and after the aging test, the novel polymer coatings prepared in this work could be, in a future, used as innovative waterproofing and durable protective also for several types of mortar.

4. CONCLUSIONS

The development of new polymer coatings characterized by hydrophobic properties and high photo-chemical stability is the key of success in the field of building materials protection for cultural heritage and modern architecture. Within this context, the use of polymer resins bearing methacrylic and stearyl monomers along the polymeric chain can be a way to create tailor-made waterproofing materials with enhanced UV durability.

A new kind of polymer protective was prepared via free radical polymerization between methyl methacrylate (MMA) and stearyl methacrylate (STEA) comonomers, varying the molar percentage of STEA with respect to MMA (1.0-2.5-5.0% mol/mol). In order to determine the long-term properties of MMA_STEA resins, an accelerated UV exposure test was performed. The macromolecular structure, molecular weights and thermal features of MMA_STEAs were investigated before and after an UV test via ^{1}H NMR and Fourier Transform-Infrared (FT-IR) spectroscopies, Gel Permeation Chromatography (GPC) and Differential Scanning Calorimetry (DSC) studies.

Combining the data measured before and after the aging test, it was possible to conclude that a polymer protective prepared starting from methyl and stearyl methacrylates monomers is an efficient way to obtain a resin with satisfactory photo-chemical stability.

Furthermore, MMA_STEA resins were successfully applied onto air-hardening calcic lime mortar tiles and their wetting properties, CIELab colorimetric features, capillarity and permeability were assessed and compared before and after the UV aging test. It was found that all the new resins synthesized maintain unchanged their features in terms of waterproofing resins with high durability and capability to favor the water vapor transpiration and to avoid the water absorption inside the mineral substrate over the time.

To the authors' best knowledge, the present results, *i.e.* the development of durable waterproofing resins-based on MMA_STEA polymers, have never been reported in previous scientific works.
The work will be continued with an emphasis placed on the study of the influence of different processing conditions, such as the loading of STEA monomer, on the properties of MMA_STEA resin. Water repellent behavior, chemical and biological durability will be investigated further on.

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Supporting Information

Figure S1: SEM-EDX analyses data relative to bare mortars.

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