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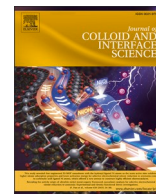
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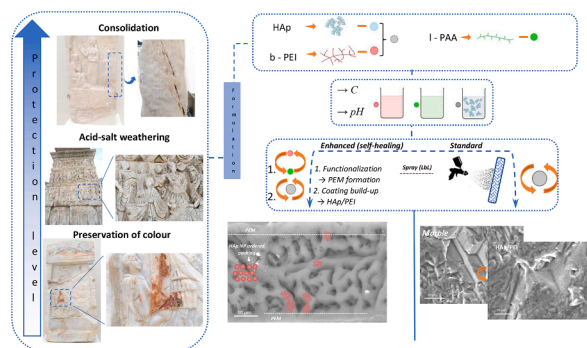


## Regular Article

## Bioinspired nanostructured hydroxyapatite-polyelectrolyte multilayers for stone conservation

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## GRAPHICAL ABSTRACT



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## ABSTRACT

Stone-built cultural heritage faces threats from natural forces and anthropogenic pollutants, including local climate, acid rain, and outdoor conditions like temperature fluctuations and wind exposure, all of which impact their structural integrity and lead to their degradation. The development of a water-based, environmentally-friendly protective coatings that meet a combination of requirements posed by the diversity of the substrates, different environmental conditions, and structures with complex geometries remains a formidable challenge, given the numerous obstacles faced by current conservation strategies. Here we report the structural, electrical, and mechanical characterization, along with performance testing, of a nanostructured hydrophilic and self-healing hybrid coating based on hydroxyapatite (HAp) nanocrystals and polyelectrolyte multilayers (PEM), formed in-situ on Greek marble through a simple spray layer-by-layer surface functionalization technique. The polyelectrolyte-hydroxyapatite multilayer (PHM) structure resembled the design of naturally forming trabecular bone, attained at a short procedural time. It exhibited chemical affinity, aesthetical compatibility and resistance to weathering while offering reversibility. The proposed method is able to generate micron-sized coatings with controlled properties, such as adhesion and self-healing, leading to less weathered surfaces. Our results show that the PHM is a highly effective protective material that can be applied for stone protection and other similar applications.

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## 1. Introduction

Factors like local climate, anthropogenic air pollutants, and outdoor conditions affect the structural integrity of stone-built cultural heritage sites and artefacts in our modern times [1–3]. Given the urgency and multifaceted nature of this problem, numerous protection methods have been developed in order to accommodate specific needs. Selection of the most appropriate protection method requires considering factors such as historical significance, architectural or geometrical characteristics (e.g., location, size and shape, accessibility), ethical considerations, available materials, local regulations, and practitioner expertise. Available protection materials include polymers, silanes, and nanocomposites that act mainly as water repellents, salt inhibitors, and biocides [4,5]. Most of these products and methods are either generic (e.g., alkoxysilanes) or are designed to have highly-specialized and target-specific properties (e.g., hydrophobicity), thus potentially limiting their applicability [5–7]. Coatings based on mineral salts including hydroxyapatite (HAp,  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ) have been proposed recently as an alternative route for stone protection [8,9]. However, these methods have some inherent limitations, such as long treatment times, and difficult applicability since the coatings are formed in-situ on the substrates surface after the application of a protective solution (e.g., DAP/diammonium hydrogen phosphate), usually through brushing-soaking and wrapping, or immersing [8–12].

Polyelectrolytes (PEs) play a crucial role in surface functionalization by providing a versatile platform for modifying the chemical and physical properties of surfaces such as their wettability, adhesion, and biocompatibility [13–15]. Thus, they are used extensively in the preparation of layer-by-layer (LbL) multilayer films with tunable properties [16]. The combination of polyethyleneimine (PEI) and polyacrylic acid (PAA) as agents for PEM formation has recently drawn attention for applications such as smart self-healing materials, amongst others [17]. Similarly, HAp nanocrystals have been studied as components for LbL assemblies and as coating materials in orthopaedics to enhance the substrates (e.g. metallic, and ceramic) mechanical strength and biocompatibility [18–20]. HAp is a multifunctional material with advantageous properties (e.g., thermal stability, ion-exchange capability) with numerous environmental applications ranging from catalysis to environmental remediation [21]. When combined with other substances (forming composite materials), it is able to adhere more effectively on surfaces [22] while in its nanocrystalline form it is able to produce transparent aggregates [23]. Such properties constitute HAp as a promising material for cultural heritage applications. Considering these beneficial properties and environmentally friendly impact of all method components (i.e., PEM, and HAp), we have combined them to develop a hybrid polyelectrolyte-hydroxyapatite multilayer (PHM) coating with adjustable properties.

Expanding on our previous work [24], here we report the formation mechanism, properties, and method validation of PHM as an effective stone-protecting material. We employ spraying, instead of other conventional methods, due to its efficiency and ability to control coating properties like thickness [25,26]. This method relies on readily available water-soluble PEI, PAA, and HAp nanocrystals, synthesized by a straightforward cost-effective method [24]. As many different protection scenarios and cases are available, the uniqueness of our method lies in its ability to generate coatings with diverse properties and performance characteristics through simple compositional modifications, thereby offering multifunctionality. The stones are covered through a LbL process that ensures use of minimum amounts (through solution nebulization) and results in coatings with variable thicknesses, attained at a short procedural time. The sequence (and number) of layer deposition yields coatings with different properties and performance, thus providing versatility. Coatings with enhanced multifunctional properties are attained through surface functionalization by a polyelectrolyte multilayer (PEM), through an alternate deposition of positively charged PEI and negatively charged PAA, followed by the sequential deposition

of HAp/PEI nanoparticles (colloid solution). Similarly, stone protection can also be attained by omitting the functionalization step, and by depositing only the HAp/PEI nanoparticles.

## 2. Materials and methods

### 2.1. Marble substrates

Two types of white Greek marble with different crystal sizes and composition were selected as test substrates. A dolomitic medium grained (0.5–1.3 mm) marble originating from the island of Thassos (T1) and a calcitic fine grained (0.01–0.5 mm) marble originating from Penteli (T2) (Fig. S1A, and S1B). Test samples were extracted from commercially sold rectangular slabs (thickness of 2 cm) and prepared according the type of experiment (Table S1).

### 2.2. Reagents

All prepared coating solutions were of analytical grade. Calcium chloride and dipotassium hydrogen phosphate stock solutions were prepared from crystalline reagent grade chemicals (Merck, Emsure®). Polyelectrolytes, namely polyacrylic acid (PAA; 25 % aqueous solution, molecular weight of 345,000) and branched polyethylenimine (PEI; 33 % aqueous solution, molecular weight of 750,000), were obtained from Polysciences© and used without any further purification. Solution pH adjustments were performed with the addition of small amounts of dilute HCl and NaOH solutions (1 N). All solutions were dissolved in ultrapure water and filtered (Millipore, 0.45  $\mu\text{m}$ ) prior use.

### 2.3. Coating solutions

Polyelectrolyte solutions were freshly prepared before each deposition. For preparation of the PEM we used a PEI solution with a concentration of 40 mM (per monomer unit) and a pH value of 9.5, and a PAA solution with a concentration of 80 mM and at a pH value of 4.5. The HAp/PEI hydrogel was obtained by mixing at room temperature equal volumes, 100 ml each, of equimolar calcium chloride and dipotassium phosphate solutions ( $[\text{Ca}^{2+}] = [\text{P}_i] = 20 \text{ mM}$ ), at pH = 9 in the presence of polyethylenimine (300 mg/L) [24]. In brief, after completion of the reaction, the precipitate (hydrogel) was collected on membrane filters through filtration (Millipore, 0.45  $\mu\text{m}$ ) and washed with ultrapure water. Subsequently, the HAp/PEI spraying colloid solutions were prepared by re-suspending the HAp/PEI hydrogel, through stirring and sonication, in a PEI solution (40 mM, pH of 6.2) and in two selected HAp mass to solvent ratios (10 % and 20 %), denoted as HAp(10 %) and HAp(20 %).

A number of coating combinations were tested. In the initial scenario, the functionalization step was omitted, and the test samples were solely sprayed with the HAp/PEI colloid solutions, labeled as BlankHAp. In the remaining two cases, samples underwent functionalization by deposition of either one or three PEI/PAA multilayers. Each multilayer comprised five consecutive depositions of PEI (5PEI) succeeded by five consecutive depositions of PAA (5PAA). Specifically, PEM1 refers to the application of one 5PEI/5PAA multilayer, PEM3 refers to the application of three 5PEI/5PAA multilayers, and PEM3HAp denotes the final application layer containing the HAp suspension. With successive spraying, this layer eventually forms the polyelectrolyte-hydroxyapatite multilayer (PHM).

### 2.4. Surface preparation

The surface of the marbles, after cutting and prior to any spraying sequence or test, was grinded with silicon carbide sandpaper up to a grit size of P240 (unless stated otherwise), sonicated for 15 min in ultrapure water (18.2 M $\Omega\cdot\text{cm}$ ), washed and dried at 45 °C for 48 h.

## 2.5. Spraying procedure

Samples were coated by a mini spray gun (Walmec Asturo, nozzle 0.3 mm) and at two operating pressures (1.5 and 2.0 bar). In all occasions, the nozzle of the spray gun was kept at a distance of about 30 cm from the target. According to the relevant test or analysis, we followed different spraying procedures (Table S1).

Two main modes of spray-gun operation were employed, burst (B) and continuous (C). In the first case, a one-layer deposition was considered the release of a quick burst of solution from the spray gun to the surface of the substrate (burst operation), while for the latter (marble) the side-to-side (and back) pass of the spray gun over the substrates surface or a full rotation for the three-dimensional cylindrical samples, in front of the spray gun while keeping it at a steady position (continuous operation) (Fig. S1C, and S1D). For both cases, the layer was forced-dried with air (from the spray gun) after each deposition and before the application of the next layer.

Despite the variability of physical characteristics of the the tests substrates (e.g., size, and shape) (Table S1), they did not affect the spraying procedure since coated samples exhibited similar surface coverage and texture for the same coating (Fig. S1C, D, and E, Fig. S10A). Each layer deposition lasted from seconds, during the early coating stages, to a few minutes as the layers increased. With increasing the number of deposited layers (especially for the functionalized samples), the force-drying stage required more time as a result of their high hydration levels. Overall, the procedure was effortless but required maintaining a steady, continuous motion while spray coating in order to ensure even and smooth application of each layer; a practice commonly followed in spray paint applications. It is safe to assume that this process is scalable and thus can also be applied for larger structures [27,28].

For all the samples tested (i.e., for adhesion, acid dissolution, water absorption, and salt-weathering), the spraying procedure involved larger volumes of solution and included intermediate time intervals for curing at room temperature (for the final HAp/PEI coating). The total amount of the final solution was 40 ml per sample (10 ml per 24 h over a period of four days).

For the thin sectioned marble samples used for the deposition, short-term acid exposure, and self-healing experiments, the whole spraying sequence was performed within a day without any curing intervals and the samples after treatment were left to dry at 40 °C overnight prior to testing.

## 2.6. Surface analysis

The morphology and electrical properties (work function) of different coating layers were studied by atomic force microscopy (AFM; Park NX10) and scanning electron microscopy coupled with energy dispersive spectrometry (SEM/EDS; Carl Zeiss EVO/Oxford Aztec). For AFM, surface morphology was acquired in non-contact mode on marble samples after the deposition of each major layer (PEM1, PEM3, PEM3-HAp), applied using the same spraying protocol as method testing samples (continuous operation), while surface charge properties (and topography) were examined in more detail (all LbL layers) through frequency modulated Kelvin probe force microscopy (FM-KPFM or sideband KPFM) [29,30] on highly orientated pyrolytic graphite (HOPG). HOPG was selected to perform electrical measurements due to its high conductivity, flatness and since it has a well-documented work function [31–34] which allowed us to calibrate the tips work function by assuming that HOPG had a work function value of  $\phi^{HOPG} = 4.6$  eV [35,36]. All measurements were carried out with a two-pass method (lift mode), using an elevation height of 30 nm and with a tip bias and sample bias of 2 V. The coatings electrical connectivity to sample holder was ensured by applying conductive adhesive tape and silver paste between the substrate and the sample holder. In all cases, to ensure that obtained AFM images were representative, scanning was performed to five or more different locations of each sample and work function values were

calculated from  $20 \times 20$   $\mu\text{m}$  scan areas (except in the case of PEI which were calculated from specific scan areas).

Surface morphology of the final overall coatings were examined also with a series of other microscopy techniques such as stereoscopy (Leica S APO), and digital microscopy (Hirox-KH8700).

For the AFM analysis of the marbles, small rectangular cut samples were embedded in epoxy resin (one exposed surface); grinded up to a grit size of P240, washed thoroughly with deionized water, sonicated and dried at room temperature. After the deposition process, a thin section ( $\approx 1.0$  mm) was cut (IsoMet Low Speed Precision Cutter), fragmented to smaller marble pieces ( $\approx 5.0 \times 5.0$  mm) and mounted to the holders that were then analysed.

## 2.7. Coating cross-sectional analysis

A cross-section of the PHM coating was obtained by performing the spraying sequence on a clean laboratory glass-slide (Thermo, Menzel Glazer), instead on the marble (Table S1). Prior to spraying, the glass-slide was cleaned with deionized water and ethanol, dried and finally sprayed. Subsequently, the glass-slide was cut to two-halves, with a diamond-cutter, and joined together with the coating layers facing each other, after being hydrated with a one drop of deionized water. The sample was then allowed to dry at room temperature, embedded in epoxy resin, cured, grinded (up to P1200), and polished (up to  $2 \mu\text{m}$  of polishing suspension). Finally, a thin section ( $\approx 1.0$  mm) was cut (IsoMet Low Speed Precision Cutter) and mounted on specific holders for further AFM and SEM analysis.

## 2.8. Method testing

### 2.8.1. Scratch – Dissolution experiments

Marble disk cross-sections ( $\approx 5$  mm), obtained from cut T1 marble cylindrical cores ( $d = 2$  cm,  $h = 2$  cm), were sprayed in similar conditions as the ones applied for method testing samples (Table S1). In the case of non-functionalized samples, the PEM deposition was omitted and the surface was sprayed with one hundred layers of the HAp/PEI colloid solution (e.g. BlankHAp100). On the other hand, T1 marble was functionalized by the deposition of three polyelectrolyte multilayers (PEM3), followed by the application of one hundred spraying layers of the same HAp/PEI colloid solution (e.g. PEM3HAp100) and dried at 40 °C for 24 h. Subsequently, the coated surface was scratched causing fracture deformation with a surgical scalpel blade (Swan Morton #23). Two levels of penetration into the coating-surface were achieved by hand-pressing the blade onto the marbles surface at different loads and dragging it on a straight line by keeping the load constant. The first load level was low with the blade leaving a groove on the coatings surface while the other was higher with the blade penetrating the coating and reaching the marbles surface. Finally, the samples were submerged half-way through in 10 ml of a combined acids aqueous solution ( $\text{H}_2\text{SO}_4/5 \times 10^{-6}\text{M}$ ,  $\text{HNO}_3/10^{-5}\text{M}$ ) at room temperature ( $24 \pm 3.0$  °C) and pH 5.00 ( $\pm 0.10$ ) for three days. After completion, the samples were removed, rinsed thoroughly with deionized water and dried at room temperature.

### 2.8.2. Adhesion testing

The bonding efficacy of different coatings was evaluated by adhesion pull-off tests (Elcometer 510) on marble samples ( $d = 5$  cm,  $h = 2$  cm), according to a modified ASTM D4541 standard (Fig. S1E) [37]. For epoxy glue coatings, the marbles surface was grinded up with a rough sandpaper (P80), washed thoroughly with distilled water, sonicated and dried at 40 °C for 24 h. For PHM and HAp/PEI coatings, no surface preparation was performed. In both cases, epoxy glue (Araldite) was applied to the underside of an aluminum dolly ( $d = 20$  mm), positioned carefully over the tested surfaces with the application of a light load, and left to cure at room temperature for 24 h. All tests were carried out in triplicate and at a pull-off rate of 0.2 MPa/sec.



### 2.8.3. Acid resistance, water uptake and water capillary absorption

The acid resistance of coatings was evaluated by fully submerging (all surfaces exposed) marble cylinder test samples ( $d = 2$  cm,  $h = 2$  cm) in 100 ml of acidic solution ( $\text{H}_2\text{SO}_4/5 \times 10^{-6}\text{M}$ ,  $\text{HNO}_3/10^{-5}\text{M}$ ) at room temperature ( $24 \pm 3.0$  °C), pH 5.00 ( $\pm 0.10$ ), and in active immersion (with agitation) for a period of 44 days. SEM/EDS and fourier transformation infrared spectroscopy (FTIR; Agilent/Exoscan 4100) analyses of the coated surfaces were performed at different time intervals to monitor the dissolution of coatings. The samples were placed in closed polypropylene containers by laying them on top of plastic holders at the bottom of the container, in a shaking water bath. The holders prevented the samples from moving excessively and kept them protected from any excess friction. The experiments consisted of two steps: one immersion (for 2 days) and one drying cycle (1 day at 50 °C). After each cycle, the solutions were replaced with fresh ones. At the end of each cycle, the samples were washed with deionized water and dried. The weight of the dried samples was measured by an analytical balance (Kern ABT 100–5 M,  $d = 0.01$  mg). The weight percent variation of the samples was calculated with respect to their initial weight at the end of each cycle by the following equation:

$$\text{Weight loss (\%)} = \left( \frac{m^i - m^f}{m^i} \right) \times 100 \quad (1)$$

where  $m^i$  and  $m^f$  are the initial and final sample weight. The dissolution rate, on the other hand, was calculated by the slope of the weight loss versus time diagram (R,  $\text{d}^{-1}$ ). SEM/EDS analysis was performed at the end of the experiments, whereas FTIR measurements were carried out at various time intervals (6 days, 22 days, 44 days).

For water uptake, the cylindrical core marble samples were immersed in ultrapure water (pH =  $5.90 \pm 0.05$ ) for 24 h, dried with residue free cloth (KIMTECH tissue wipes) and weighed at various time intervals [38].

For the acid resistance, water absorption, porosity and salt crystallization experiments, cylindrical core samples with a height and diameter of 2 cm were also cut from the same slabs (Milwaukee Diamond Max Hole Saw/22 mm) and prepared following the procedure described above.

### 2.8.4. Color measurements

All samples, after their preparation and prior to any coating procedure, were marked with a permanent blue marker to serve as an indicator for monitoring color changes during the acid dissolution experiments. Variation of color (according to CIELAB color system) was assessed by measuring the samples lightness ( $L^*$ ) and the other two chromatic axes of this three-dimensional model ( $a^*$ , green from  $-a^*$  to red  $+a^*$ ;  $b^*$ , blue from  $-b^*$  to yellow  $+b^*$ ), with a spectrophotometer (Stihl Ruby) consisting of a tungsten halogen lamp with a spectral range of 400–800 nm (CIE1964, D65 illuminant, 126 Hz). Calibration was performed against a white standard and a light trap (black calibration). The working distance from the surface was set at 80 mm with a  $10^\circ$  beam angle and a spot size of 2 mm. Color differences ( $\Delta E^*$ ) were calculated as follows:

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

where  $\Delta L$  represents the lightness difference between the sample and the standard,  $\Delta a^*$  represents the difference in redness or greyness between the sample and the standard, and finally the  $\Delta b^*$  denotes blueness–yellowness differences between the sample and the standard.

### 2.8.5. Artificial weathering and porosity

For the salt crystallization tests, cylindrical core marble samples were positioned vertically on their uncoated base at the bottom of a petri dish. Subsequently, 15 ml of a 14 %  $\text{Na}_2\text{SO}_4$  solution (Sigma Aldrich,  $\geq 99.0$  % anhydrous) was carefully poured into the dish until the sample

was partially immersed up to a height of around 5 mm, and partially covered with their lid to avoid excessive evaporation. The samples at the initial stages of the experiments were placed in an environmental chamber (temperature, moisture, light), followed by outdoors exposure during the time period July–September 2023 (Table S5). The objective of these tests was to evaluate the susceptibility of marble to salt degradation caused by capillary action, comparing treated and untreated samples since the potential accumulation of salts behind the treated surface with this method is favored [7].

The procedure consisted of three main phases: immersion, desalination/cleaning, and drying. Immersion lasted from two to five days of exposure (salt weathering cycles/swc). In a few occasions and due to excessive heat, the  $\text{Na}_2\text{SO}_4$  solution was evaporated, thus the samples were either removed for further processing, or the solution was replenished for further exposure. After removal, the samples were thoroughly washed with deionized water to remove any salt efflorescence from the surface. In almost all occasions, and especially in the initial stages of the experiments, salts were easily removed either by softly rubbing the samples or by water, while for the latter stages this was significantly more difficult because the salts were more strongly attached to the surface, having higher amounts of water to be removed. Additionally, at the final stages of the experiments the T2 marbles started showing signs of sugaring which also marked the end of the experiments (8 swc). Finally, the samples were dried in an oven for 24 h at 45 °C, and weighed.

Changes in porosity of cylindrical samples subjected to salt weathering were measured by  $\text{N}_2$  adsorption through the static volumetric method (3P sync), by placing the sample(s) in a special measuring cell (Fig. S1G). Adsorption isotherms were obtained and basic adsorption parameters (e.g., surface area, average pore size) were calculated.

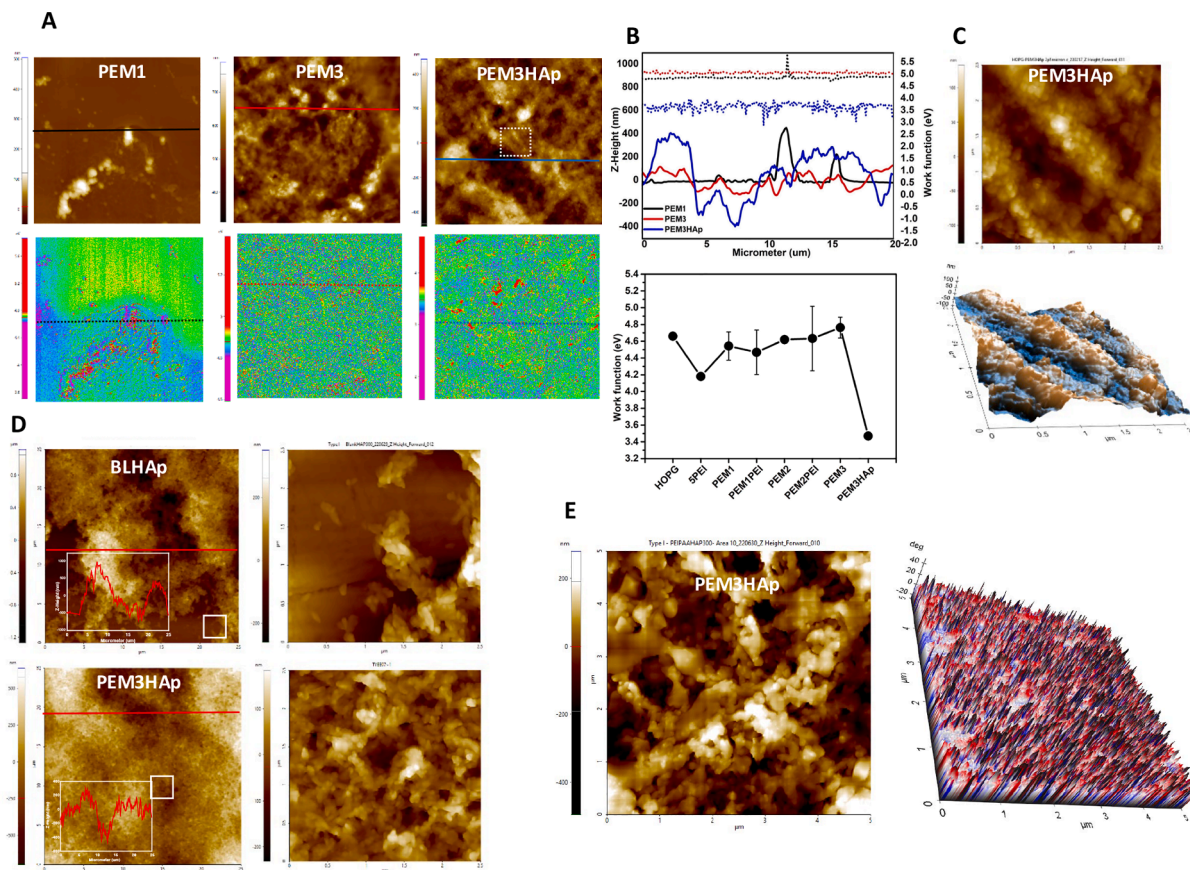
## 3. Results and discussion

### 3.1. Surface reactivity and morphology of coatings

The reactivity of each layer comprising the overall LbL coating was assessed through frequency-modulated Kelvin probe force microscopy (FM-KPFM) measurements. Traditionally, material surface charges in wet conditions are measured using streaming potential [39] or other electrical techniques [40], while KPFM has emerged as a novel method for studying surface properties [41] with electron work function measurements providing information for material properties such as corrosion, amongst others [42]. Due to the sensitivity of KPFM, specific criteria were required for our experiments, including a suitable substrate (HOPG) and precise control of the spraying process, involving minimal deposited amounts, spraying time, and spray-gun pressure (Table S1).

The structural and electrical data for major layers comprising the complete PHM coating are provided in Fig. 1. Following application of the initial positively charged polyelectrolyte (5PEI), the substrate surface exhibited partial coverage by an amorphous glassy phase, appearing either as isolated droplets or as a continuous layer, with heights up to 500 and 100 nm, respectively (Fig. S2A, and S2B). This surface heterogeneity was observed both within the same scanned areas and across different regions. Across all covered areas, the work function of HOPG ( $\phi^{\text{HOPG}} = 4.66 \pm 0.036$  eV) decreased, exhibiting a correlation with the amount of material deposited. In areas with incomplete coverage, we observed a noticeable fluctuation in the work function value. Consequently, for this particular layer, the work function value was selectively determined and calculated from specific scanned regions exhibiting stable work function values. The measured work function for the first deposited layer was determined to be  $\phi^{5\text{PEI}} = 4.18 \pm 0.026$  eV, which is considerably lower than that of HOPG, indicating that the covered areas are more reactive than HOPG.

The surface morphology of the first PEM, following the deposition of the negatively charged polyacrylic acid (5PEI + 5PAA=PEM1), also displayed non-uniform characteristics, accompanied by a significant



**Fig. 1.** A) 2D- KPFM height (top) and work function images (bottom) of major LbL coatings deposited on HOPG (scan size:  $20 \times 20 \mu\text{m}$ ). B) Superimposed height and work function FM-KPFM line signals of major coating layers depicted in (A) (top), and the fluctuation of measured surface work function of all coating layers (bottom) ( $n = 5-10$ ). C) FM-KPFM 2D (top) and 3D (bottom) height images of the final PEM3HAP coating layer highlighted in (A) (scan size:  $2.5 \times 2.5 \mu\text{m}$ ). D) Non-contact 2D-AFM height images, with inserted line height diagram, after the deposition of the final HAP/PEI colloid solution (10 % HAp) over non-functionalized (top) and functionalized (bottom) marble surfaces. Highlighted areas on the left images are presented on the right (scan size:  $25 \times 25 \mu\text{m}$ ;  $2.5 \times 2.5 \mu\text{m}$ ). E) Non-contact 2D-AFM height (left) and 3D-phase (right) images after the deposition of the final HAP/PEI colloid solution (10 % HAp) over the functionalized (PEM3) marble surface, showing its two-phase composition (scan size:  $5.0 \times 5.0 \mu\text{m}$ ).

increase in work function values ( $\phi^{\text{PEM1}} = 4.54 \pm 0.17 \text{ eV}$ ) (Fig. 1A, and 1B). In this case, the surface of HOPG was entirely covered by two layers, predominantly comprising an underlying amorphous smooth glassy phase, and areas covered by round-shaped nanoparticles (Fig. S3A1, and S3A2). The nanoparticles had sizes in the range of 100 nm or less, and were either isolated and dispersed across the surface or aggregated into larger formations several hundred nanometers in size (Fig. 1B and Fig. S3A2). Certain regions showed signs of a developing network of interconnected nanoparticles (Fig. S3B). These morphological differences can be attributed to the uneven and partial coverage of the HOPG surface with PEI, potentially leading to uneven mixing of the two polyelectrolytes, yielding areas with distinct characteristics. Overall, the initial multilayer application (PEM1) produced a predominantly heterogeneous surface, with amorphous areas showing higher reactivity than those with specific morphological characteristics.

As the number of coating layers increased from PEM1 to PEM3, the presence of amorphous-phase covered areas diminished, yielding fully formed bead-like nanostructures (Fig. 1A, Fig. S4), which are the result of electrostatic interactions between the oppositely charged polyelectrolytes [43]. Surface reactivity also decreased, as observed by the gradual increase in work function values (reaching  $\phi^{\text{PEM3}} = 4.76 \pm 0.12 \text{ eV}$ , Fig. 1B), while the observed number of larger nanoparticles also increased (Fig. S4D). This is attributed to the reduction of electrostatic repulsions between primary polyelectrolyte complexes favoring the formation of secondary larger particles through aggregation [44,45]. However, while the surface morphology appeared similar with

increasing PEM layers, there was a notable variation in the work function values, particularly evident in the PEM1PEI and PEM2PEI layers ( $\phi^{\text{PEM1PEI}} = 4.47 \pm 0.26 \text{ eV}/\phi^{\text{PEM2PEI}} = 4.63 \pm 0.38 \text{ eV}$ ). Differences in localized nanostructure density seemed to produce regions with varying reactivity gradients, impacting the overall work-function measurements.

Specifically, for the PEM1PEI layer, measurements taken at different spots indicated that the presence of a well-formed underlying nanostructured layer decreased the overall background surface reactivity, as evidenced by the increased work function baseline signal (Fig. S4A). In contrast, for the PEM2PEI layer, while the surface morphology exhibited greater uniformity, measurements of the work function displayed notable fluctuations both across different spots and within the same scanned area (Fig. S4B, and S4C). From these observations, it appears that the addition of PEI has a stronger impact on surface reactivity compared to PAA, likely due to its higher molecular weight and branched structure, resulting in localized variations in PEI concentration that contribute to the observed fluctuations in work function. Overall, the application of polyelectrolyte multilayers (without HAp) resulted in the formation of a well-defined bead-like nanostructure, with surface reactivity decreasing as the number of multilayers increased.

Application of the final HAP/PEI layer (PEM3HAp) resulted in a more reactive surface, as evidenced by the lower work function values (Fig. 1B,  $\phi^{\text{PEM3HAp}} = 3.47 \pm 0.04 \text{ eV}$ ), indicating significant alterations in surface properties due to the presence of HAp nanocrystals over the polyelectrolyte matrix. Uniform surface morphology was observed

across all scanned areas, with HAp nanocrystals covering the previously formed nanostructure in the form of agglomerates having sizes smaller than 100 nm (Fig. 1C). Although the work function measurements were consistent among different spots (with small deviations from each other), significant fluctuations were observed within the same scan area, exhibiting values of 0.7 eV (Fig. 1B/blue lines), with work function signal minima concentrated at areas where HAp agglomerates are present (Fig. 1A/purple regions). This suggests that the resulting two-phase coating renders the surface more reactive than before. As a result, the presence of the PEM can be advantageous, as the polymeric nanostructure tends to increase the work function of the surface, thereby imparting chemical inertness to the overall coating.

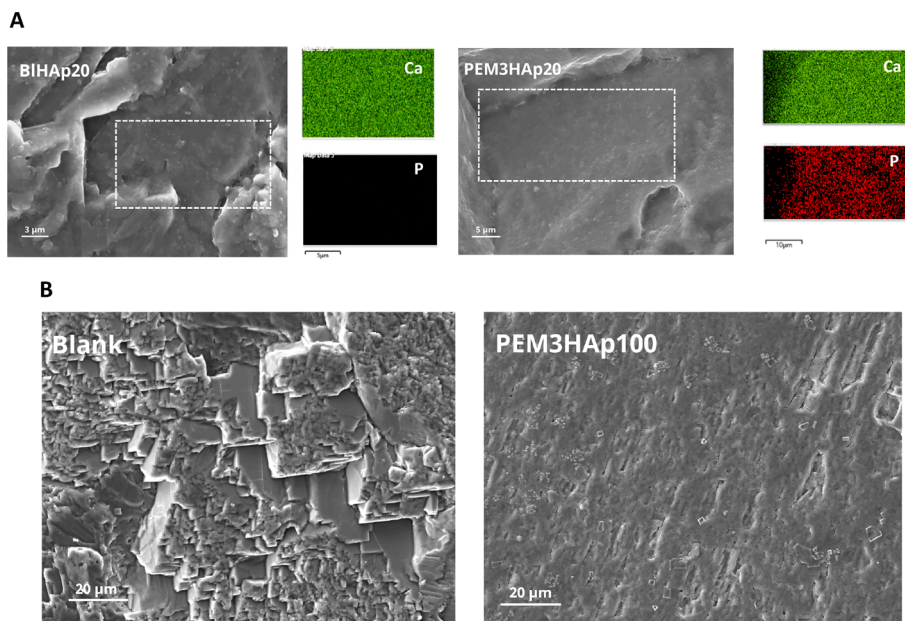
In the case of marble substrates, surface functionalization (PEM3) effectively facilitated the uniform dispersion of HAp nanocrystals over the marble substrate, as evident from the AFM images following the application of the initial HAp/PEI layer. A clearly defined crystal layer, free from large height variations or aggregates, was prominently observed (Fig. 1D/bottom and Fig. S5A/bottom). The dual-phase nature of the surface was shown by the AFM phase imaging, with characteristic phase line signal spikes from the presence on exposed HAp nanocrystals being clearly visible (Fig. 1E). On the other hand, HAp deposition over non-functionalized samples (without PEMs) was non-uniform, forming small and large crystal aggregates over the marbles surface (Fig. 1D/top, and Fig. S5A/top). In this case, the deposition of nanoparticles seemed to follow a “coffee ring” evaporation-drying pattern by showing signs of preferential evaporation occurring at the edges of the three-phase contact line (Fig. S5B). Through this mechanism, any evaporated material is replenished from the droplet center to the edges through capillary flow that transports and deposits particles towards the droplet edges, forming the characteristic ring pattern [46]. For the PHM coating, however, this drying pattern and deposition of nanoparticles was not observed, likely for two reasons. First, the particle–surface interactions increase through surface functionalization that attracts particles to the surface, and second by the reduction of particle–particle interactions through the addition of high MW PEI to the HAp colloid suspension, which acts as a particle aggregation inhibitor [47].

SEM/EDS analyses of the surfaces showed that as additional HAp/PEI layers were applied (coating build-up), surface coverage steadily increased, leading to the progressive coverage of surface irregularities

(e.g., crystal terraces and edges), with both marble types exhibiting the same surface coverage for the same number of spraying layers. Functionalized samples showed faster coating build-up than non-functionalized ones, with differences in surface morphology and elemental composition appearing at an earlier spraying stage. SEM/EDS analysis of samples carried out during the early stages of the spraying procedure showed a significant difference in the amounts of deposited HAp over the surface, with functionalized samples having significantly higher amounts for the same number of spraying passes than non-functionalized ones, as evidenced by the increased detection of phosphorus (Fig. 2A). Seemingly, the presence of the PEM acts as a barrier by inhibiting the transportation of HAp nanoparticles deep into the pores of the substrate and retaining them on the surface. When the PEM is absent, the nanoparticles are allowed to diffuse freely and penetrate deep into the crystal grain boundaries, making them hard to detect especially early on during the spraying process. Recent studies have shown the effectiveness of LbL-prepared PEMs onto various substrates, as water-permeable nanometer-sized separation membranes by showing their efficiency in solute retention [48]. In all cases, complete (or almost complete) coverage of marble crystals was obtained after application of roughly 100 layers of the HAp/PEI solution (Fig. 2 B, and Fig. S6A).

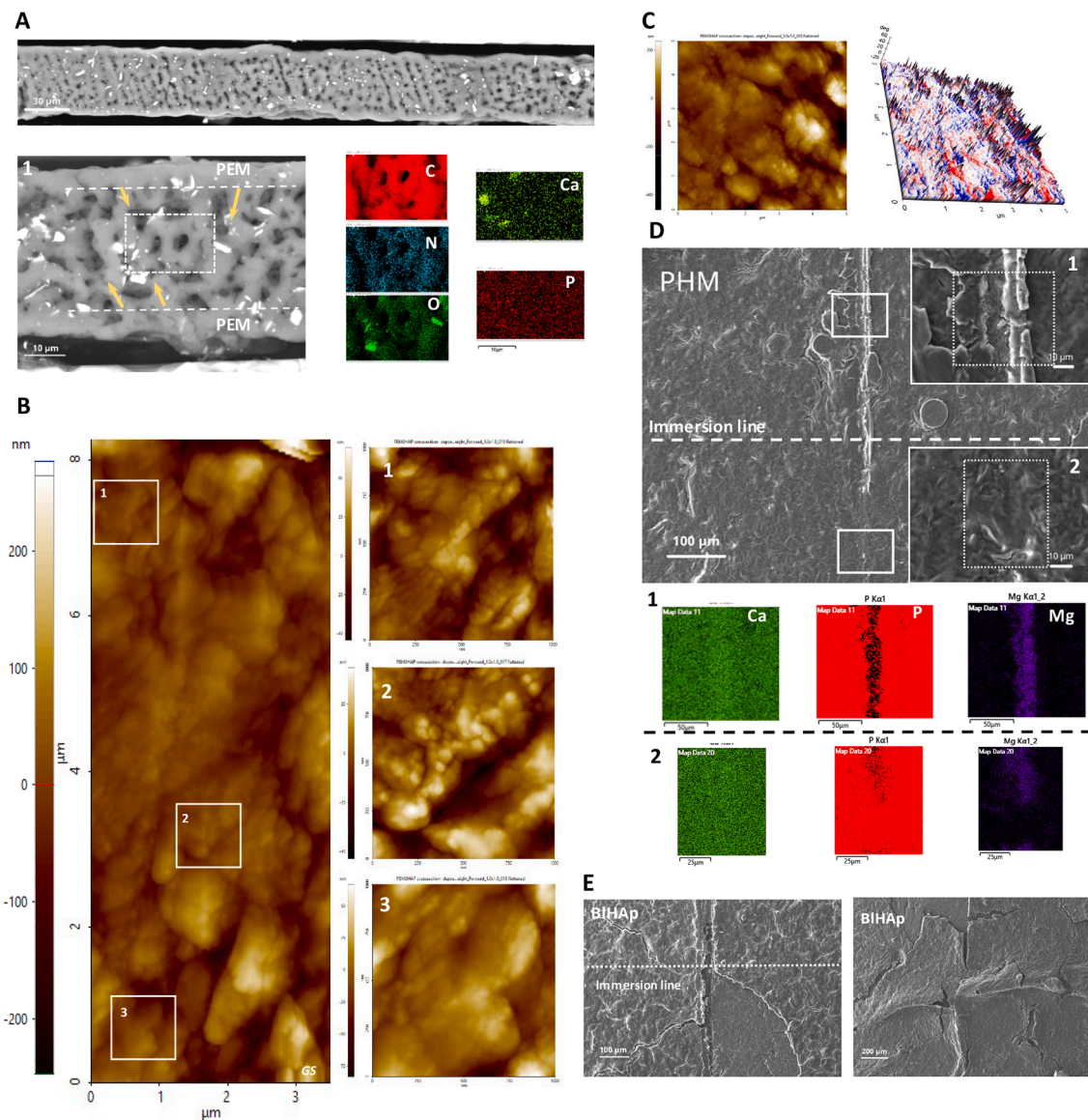
### 3.2. Polyelectrolyte-hydroxyapatite multilayer (PHM) micro/nanostructure and self-healing

The PHMs microstructure exhibited trabecular-like characteristics throughout the cross-section, resembling the morphology of a naturally forming bone (Fig. 3A) [49]. Such structures are considered ideal for load bearing applications, and its general functional role in bones is to transfer external load away from the joint, caused by movement, muscle motion or body weight, and dissipate it towards the denser cortical bone, thus dampening excessive stresses that can cause damage [49,50]. Two distinctive morphological regions were apparent. The first region appeared denser and was positioned right above the surface of the substrates (PEM), while the other appeared porous and extended to the interior obtaining a trabeculae form (Fig. 3A1, Fig. S7A). AFM imaging in different regions of the PHMs cross-section revealed that HAp nanocrystals were closely packed together with an ordered orientated nanostructure, appearing similar to the one of natural bone (Fig. 3B;



**Fig. 2.** A) SEM/EDS analysis of non-functionalized (left) and functionalized (right) T1 marble, after the application of twenty spraying layers of the final HAp/PEI colloid solution (20% HAp), showing increased amounts of detected HAp nanocrystals over the latter. B) SEM images of the surface of T2 marble before (left) and after (right) one hundred spraying layers (HAp100) of the HAp/PEI colloid solution (20% HAp).





**Fig. 3.** A) Backscatter SEM/EDS analysis of the PHMs cross-section, deposited on a glass slide (GS). B) Non-contact AFM 2D-height images of the PHMs cross-section (left), with highlighted areas presented on the right (scan size 3.5 × 8.2 μm; 1.0 × 1.0 μm). C) Non-contact 2D-AFM height (left) and 3D-phase (right) images of the PHMs cross-section, showing a predominantly single-phase composition (scan size: 5.0 × 5.0 μm). D) SEM image of PHM coated T1 marble at the immersion surface, with inserted highlighted areas 1 (above the immersion line) and 2 (below the immersion line), with their respective SEM/EDS analysis (bottom). E) SEM surface analyses from scratched non-functionalized T1 marble at the immersion interface, showing coating detachment (left) and folding (right).

Fig. S7B, and S7C) [51,52]. The shape of nanoparticles was noticeably different when compared with HAp nanocrystals from surface analysis samples, by appearing rounder and not rod-like (Fig. 3B1 to 3B3; Fig. S5A). Finally, the PHMs cross-section was single-phase, denoting homogeneity, as can be seen by its respective phase image where no phase separation is visible, unlike the one observed in surface analysis samples (Fig. 3C, Fig. 1E) [53]. This indicates that during the coating build-up (wet-dry cycles), HAp nanoparticles are able to move more freely through hydration and diffusion and embed uniformly into the polyelectrolyte matrix [54].

Self-healing properties of scratched functionalized (PHM) and non-functionalized (sprayed only with the HAp/PEI solution) marble samples (BIHAp) were assessed by immersing them in a dilute acidic solution for three days at room temperature. Results showed that in the first case, the scratches track (of a width of 15 – 20 μm) was covered with a new coating demonstrating the PHMs self-healing properties (Fig. 3D). SEM/EDS analysis of the PHM coating along the scratch track showed substantial coating regeneration, as evidenced by the forming material

connecting the edges of the scratch, covering the previously exposed marble surface, which was further confirmed by the high amount of detected phosphorus (Fig. 3D2, and Fig. S7D). On the other hand, for non-functionalized samples (BIHAp), a significant amount was removed from the HAp/PEI coating at the contact point of water level and scratch track, whilst showing signs of further detachment and folding below its surface (Fig. 3E, and Fig. S7E). The underlying repair mechanisms for self-healable materials involve mainly physical or chemical processes, or a combination of both, occurring at the molecular level [55]. In our case, processes such as wetting, surface re-arrangement, diffusion, and ionic interactions may have contributed to the self-healing ability of PHM [56]. With no spontaneous self-healing mechanism in place, wetting acts as an external stimulus that triggers surface re-arrangement, both within the coating and at its interface with the substrate. PEMs are known for their swelling properties and self-healing abilities upon solvation, and HAp for their absorptive properties [16,57]. Moreover, since the damaged surface and coating are both hydrophilic, the fluid may run easily over both sides of the scratch track upon wetting, bringing both

sides closer and forming a new interface. Finally, when both sides come close enough, ionic interactions become important, creating new bonds and thus forming bridges across the interface, that impart the self-healing process [58].

### 3.3. Adhesion of coatings

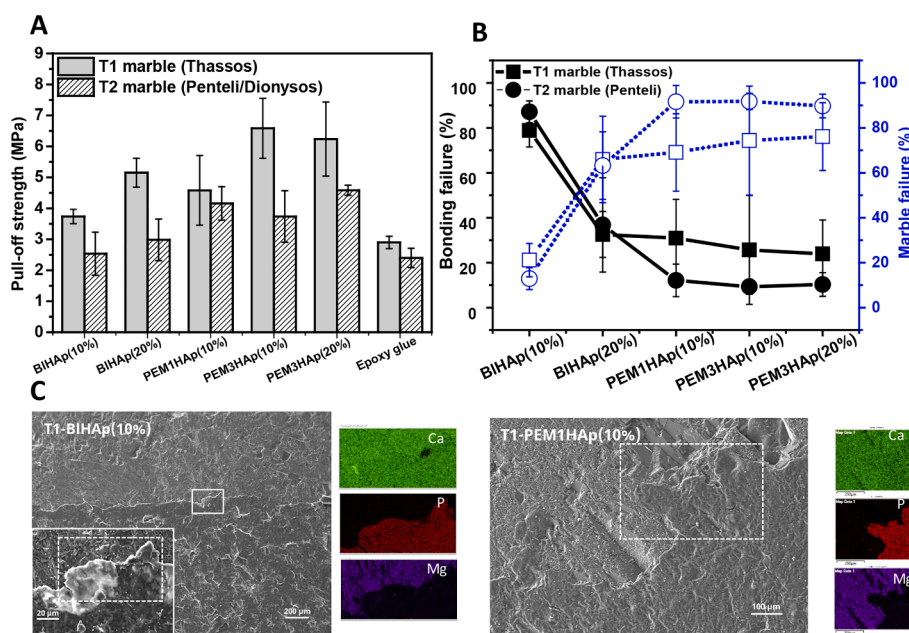
To assess the adhesion of different LbL coating combinations, we conducted pull-off tests by varying their functionalization level (PEM1 or PEM3) and HAp/PEI content (10 or 20 % HAp) (Fig. S1E). These tests do not only determine the overall coating pull-off strength, but also differentiate between various failure modes, providing valuable insights for failure analysis [59]. Additionally, we tested epoxy coatings on the marbles to compare and identify any discrepancies in adhesion strength and failure mode.

Results from adhesion pull-off tests on spray-coated marble disks are depicted in Fig. 4. Coating thickness ranged from 5.0  $\mu\text{m}$  for the 10 % HAp content, to 10  $\mu\text{m}$  for the 20 % HAp content (Fig. S8A). Non-functionalized samples with 10 % HAp content exhibited the lowest adhesion strength, with T1 and T2 marbles showing values of  $3.73 \pm 0.23$  MPa and  $2.53 \pm 0.69$  MPa, respectively. In contrast, maximum strengths were observed for functionalized (PHM) samples, with values of  $6.58 \pm 0.97$  MPa for T1-PEM3HAp(10 %), and  $4.58 \pm 0.16$  MPa for T2-PEM3HAp(20 %) (Fig. 4A).

The T1 samples showed greater adhesion strength compared to the T2 for identical coatings, suggesting a relationship between substrate mechanical strength and adhesion with two types of failure occurring: i. e., bonding and marble failure (Fig. 4B) [59]. The presence of marble failure in all cases suggests strong adhesion, as it indicates that the bonding between the surface and the coating exceeds the cohesion strength of the marble grains (Fig. S8C). These findings highlight the ability to customize the performance of the coatings through simple compositional adjustments, offering a wide array of potential applications with diverse requirements (Fig. S8C). The increase in HAp content (from 10 to 20 %), which led to an increase in coating thickness, resulted in better adhesion, as indicated by the increased pull-off strengths for T1 (3.73–5.15 MPa; a 38 % increase) and T2 (2.53–2.98 MPa; an 18 %

increase) marbles (Fig. 4A). Furthermore, the observed increase in substrate failure (from 10–20 to 65–70 %) for both marbles highlights this strong adhesion (Fig. 4B). These observations indicate that the load transfer to the substrate, which led to its failure, was significant. In cases of strong adhesion, the increase in coating thickness results in the lowering of stress concentrations located at the interface between the coating and substrate, as the former can support more load (if we assume that the marbles surface is harder than the deposited HAp crystals) [60]. Previous studies have indicated that increasing coating thickness can either have no impact [61] or improve adhesion [60,62,63]. Their observations highlighted the importance of the specific thickness range and the presence of cracks, which often develop in sol-gel systems during drying [64]. In our case, the presence of surface cracks on the HAp(20 %) coatings had no significant impact on adhesion.

Surface functionalization with a polyelectrolyte multilayer further improved the bonding of HAp nanoparticles to the marble surface by serving as an intermediate layer that develops strong interactions with both materials. Effective supramolecular polymeric adhesives emphasize the importance of optimizing the balance between adhesive and cohesive properties. High levels of supramolecular cross-linking can enhance intermolecular cohesion, which in turn reduce the number of exposed functional groups at the interface, significantly decreasing interfacial adhesion [65]. In our case, the physical cross-linking of PEI and PAA resulted in increased adhesion, indicating that the balance between these two properties was maintained. The adhesion strength of coatings on T1 marble with a 10 % HAp content (BIHAp(10 %), PEM1HAp(10 %), and PEM3HAp(10 %)) gradually increased by 76 %, from 3.73 MPa to 6.58 MPa. For T2 marble, the adhesion strength increased by 47 %, from 2.53 MPa to 3.73 MPa (Fig. 4A). While increase in HAp content had no significant effect on the observed failure mode amongst T1 and T2, functionalization had a more profound effect on T2 by showing higher levels of marble failure (Fig. 4B). It seems that T2's smaller grain size and larger grain boundary surface area facilitated the anchoring of the polymeric matrix to the marble surface more effectively, thereby promoting its failure. Recent studies on similar PEI/PAA systems have indicated that effective physical cross-linking between PEI's amino groups ( $-\text{NH}_2$ ) and PAA's carboxylic groups ( $-\text{COOH}$ ) can



**Fig. 4.** A) Adhesion pull-off strength (MPa) of different coatings on T1 and T2 marble samples (dolly diameter: 2.0 cm; rate: 0.2 MPa/sec;  $n = 2-3$ ). B) Effect of marble surface functionalization (PEM1, PEM3) and HAp concentration (10 or 20 %) on the observed pull-off failure mode. C) SEM/EDS surface analysis performed at the test pull-off boundary area from the non-functionalized (left) and PHM (right) coated T1 marble, showing bonding failure for the former and a combination of bonding and marble failure for the latter.



be achieved through electrostatic interactions and hydrogen bonding, rather than covalent bonds, resulting in materials with strong adhesion [66,67].

SEM/EDS analysis in areas where bonding failure occurred, showed that the absence of HAP nanocrystals on the surface was notable as the coating detached uniformly, leaving the surface unchanged from its pre-coating state (Fig. 4C/left). Distinct variations in surface morphology were evident in regions where bonding and marble failure occurred, revealing previously concealed dolomitic crystals or crystal planes that were beneath the smooth surface (Fig. 4C/right).

### 3.4. Acid resistance and color change of coatings

Non-coated marble samples (blank), exposed for forty-four days in acid solution, exhibited significant signs of chemical weathering, evident from the alterations in surface morphology. Both marble types displayed surface voids, indicating significant crystal detachment (Fig. S9A). Mass change measurements revealed that T2 experienced a total weight loss of up to 0.45 %, corresponding to a dissolution rate of  $10.9 \times 10^{-3} \text{ d}^{-1}$ , whereas T1 exhibited a weight loss of 0.30 % and a dissolution rate of  $7.6 \times 10^{-3} \text{ d}^{-1}$ , respectively (Fig. 5A). For both types of marble, the coatings with the highest surface reactivity, as expressed by their increased weight loss and dissolution rate, were the non-functionalized samples (BIHAp(20 %)), whereas the PHMs were the ones with the lowest reactivity, corroborating with the findings from surface work function measurements. The dissolution rate for both types followed the order  $R^{\text{BIHAp(20\%)}} > R^{\text{Bl}} > R^{\text{PEM3HAp(20\%)}}$  (Fig. 5A, table). Surface morphology analysis showed that all coatings protected the marble by either slowing down the dissolution process (non-functionalized samples), with the coating being gradually removed acting as a sacrificial layer, or by totally preventing it (functionalized samples). For the former, although most of the coating had been removed from the surface for both marble types, the surface was less weathered compared to untreated samples, with fewer signs of crystal detachment (Fig. 5B). Conversely, for the latter PHMs, the surface of the marble was nearly fully covered by the coating (Fig. 5B1, and Fig. S9A). FTIR measurements performed at various time intervals on the marbles surface showed that for the non-functionalized samples, the characteristic stretching vibrations of the mineral's phosphate group ( $\nu_1$ -954  $\text{cm}^{-1}$ ,  $\nu_3$ -1010, 1105  $\text{cm}^{-1}$ ), gradually disappeared after 22 days of exposure, whereas for the PHMs, those peaks were still present after 44 days of exposure, indicating still the presence of a calcium phosphate polymorph(s) (Fig. S9B) [68]. Clearly, the underlying polyelectrolyte nanostructure is able to bind the initially deposited HAP nanocrystals effectively within its matrix, thus protecting them from dissolution.

For both marble types, the overall visual appearance of the samples remained largely unchanged to the naked eye after applying both coatings (i.e., after 0 days exposure) (Fig. S10A). After the coating process, the recorded color changes ( $\Delta E^*$ ) in white areas for non-functionalized and functionalized coatings and T1 marble were  $\Delta E^{\text{T1-BIHAp(20\%)}/\text{white}} = 8.00$  and  $\Delta E^{\text{T1-PEM3HAp(20\%)}/\text{white}} = 13.69$ , while for blue painted regions, they were  $\Delta E^{\text{T1-BIHAp(20\%)}/\text{blue}} = 11.15$  and  $\Delta E^{\text{T1-PEM3HAp(20\%)}/\text{blue}} = 9.92$ , respectively. For T2 and white areas, these values were  $\Delta E^{\text{T2-BIHAp(20\%)}/\text{white}} = 1.06$  and  $\Delta E^{\text{T2-PEM3HAp(20\%)}/\text{white}} = 3.44$ , while for blue regions,  $\Delta E^{\text{T2-BIHAp(20\%)}/\text{blue}} = 12.12$  and  $\Delta E^{\text{T2-PEM3HAp(20\%)}/\text{blue}} = 9.64$ , respectively (Tables S2 and S3).

At the end of the experiments and for uncoated samples (i.e., after 46 days exposure), the color differences for white areas of T2 and blue painted regions were  $\Delta E^{\text{T2-Blank}/\text{white}} = 18.69$  and  $\Delta E^{\text{T2-Blank}/\text{blue}} = 38.98$ , respectively (Table S3). The noticeable color change in white is attributed to the marbles obtaining a darker hue, marked by the decrease in lightness ( $L^*$ ) (53.67–39.39), and in blue by the removal of the blue paint from its surface, marked by an increase in  $b^*$  values (–22.75 to –9.74) (Fig. 6A, and Table S4). Similarly, the color difference of white areas and blue regions of T1 was  $\Delta E^{\text{T1-Blank}/\text{white}} = 19.25$  and  $\Delta E^{\text{T1-Blank}/\text{blue}} = 31.14$ , respectively, with notable decrease in lightness

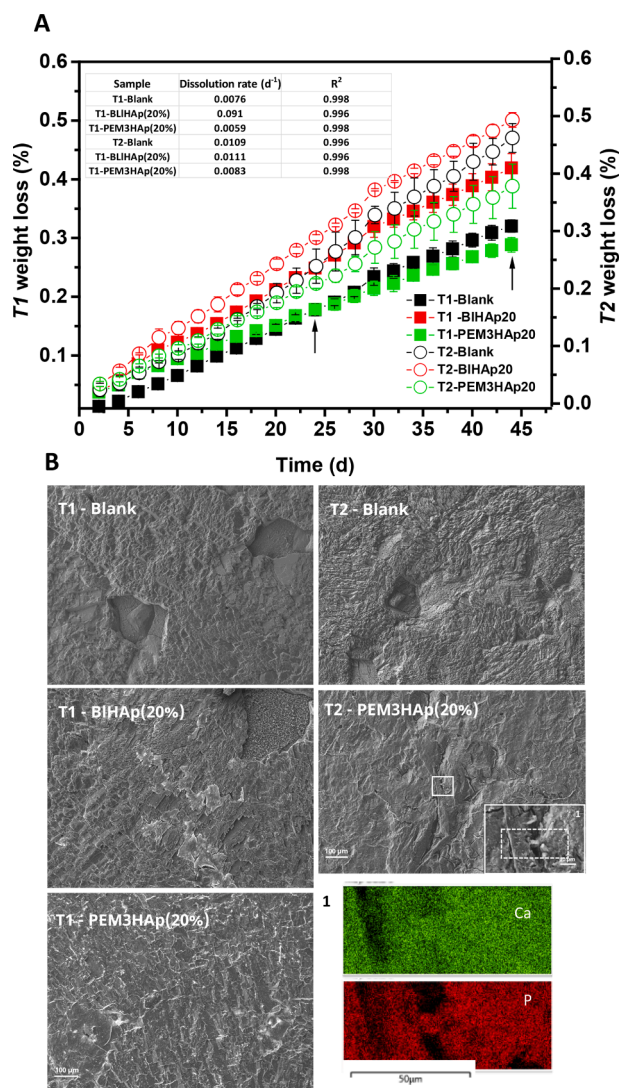
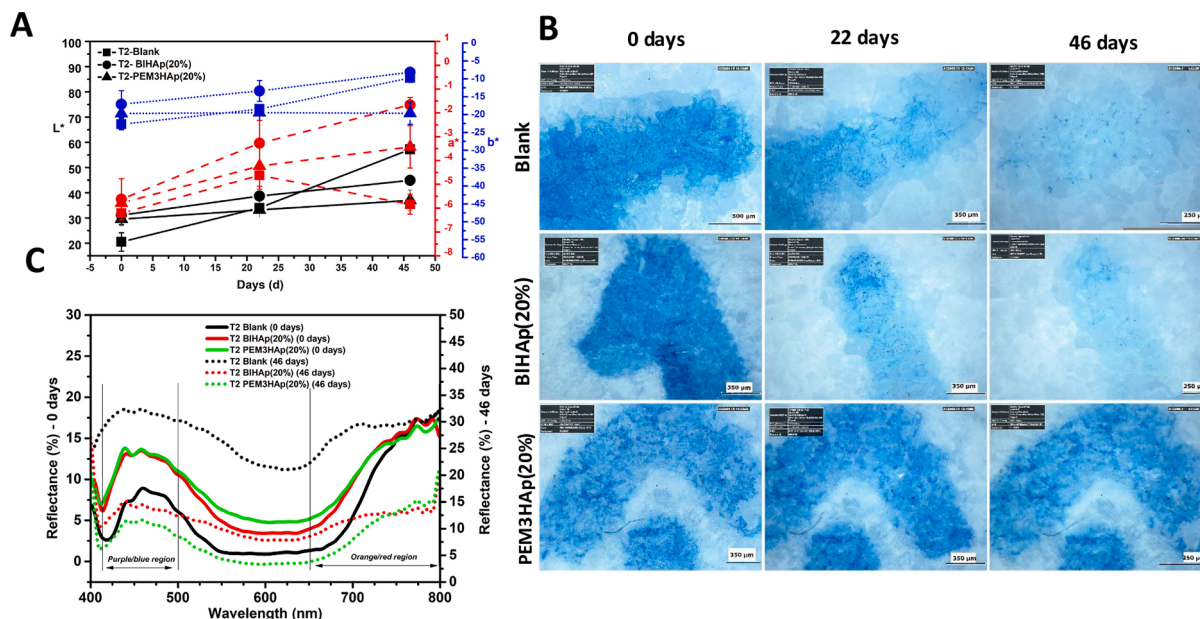


Fig. 5. A) Weight loss (%) with time (days) of non-coated and coated T1 and T2 marble samples from the long-term acid exposure experiments (44 days), with inserted dissolution rate ( $\text{d}^{-1}$ ) table. B) SEM images from the surface of coated and non-coated T1 (left) and T2 (right) marble samples after 44 days of acid exposure, with SEM/EDS analysis from selected area highlighted in 1.

and increase in  $b^*$  values as well (Fig. S10B, and Tables S2 and S4). The decrease in lightness is commonly observed in marble surfaces at acidic environments and is attributed to surface oxidation [69].

In contrast, coated samples exhibited less profound color changes. For non-functionalized T2 marble, the color differences in the white areas and blue regions were  $\Delta E^{\text{T2-BIHAp(20\%)}/\text{white}} = 16.95$  and  $\Delta E^{\text{T2-BIHAp(20\%)}/\text{blue}} = 28.94$ , respectively. These changes were even less significant with the functionalized samples, with values of  $\Delta E^{\text{T2-PEM3HAp(20\%)}/\text{white}} = 14.12$  for white and  $\Delta E^{\text{T2-PEM3HAp(20\%)}/\text{blue}} = 17.16$  for blue regions. The dissolution resistance of the PHM coating was evidenced by the stability and limited change in  $b^*$  and lightness values (Fig. 6A). Similar observations were made for coated T1 marbles. With the BIHAp(20 %) coating, color changes in white areas and blue regions exhibited values of  $\Delta E^{\text{T1-BIHAp(20\%)}/\text{white}} = 14.61$  and  $\Delta E^{\text{T1-BIHAp(20\%)}/\text{blue}} = 15.90$ , respectively, while with the PEM3HAp(20 %) coating, these values were  $\Delta E^{\text{T1-PEM3HAp(20\%)}/\text{white}} = 13.79$  for white and  $\Delta E^{\text{T1-PEM3HAp(20\%)}/\text{blue}} = 7.14$  for blue regions (Table S2). Similar trends were observed in lightness and  $b^*$  values (Fig. S10B). Macroscopic observations at the end of the dissolution experiments for both marble types, revealed that for the non-functionalized samples coating traces of blue paint were still

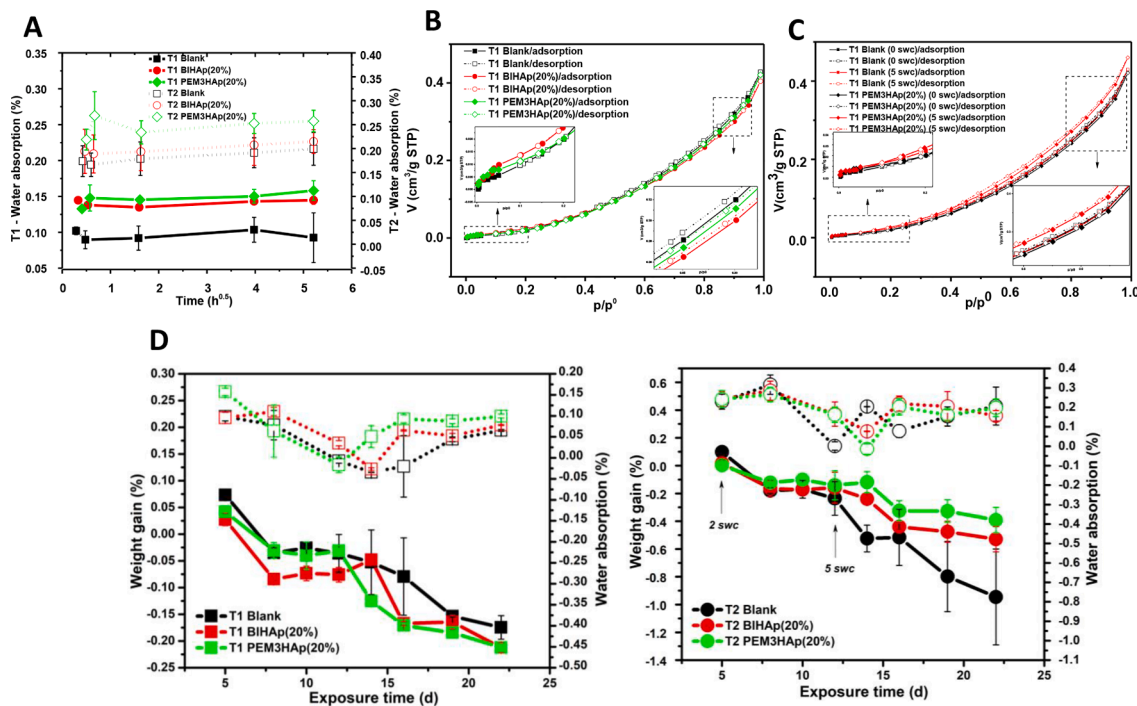


**Fig. 6.** A and B) Colour space (CIELAB,  $L^*a^*b^*$ ) measurements ( $n = 3$ ) (A), and optical micrographs (B) from the blue paint in non-coated and coated T2 samples, at three different time intervals of acid exposure (0, 22, 46 days). C) Fiber optics reflectance spectra of non-coated and coated T2 samples, before (left, solid lines), and after (right, dashed lines) the acid exposure experiments. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

present on the samples surface while for the functionalized ones it remained almost unaltered (Fig. 6B and Fig. S10C).

The reflectance spectra of the blue paint before and after coating, as well as following the dissolution experiments, are depicted in Fig. 6C. Within the visible light range (400–800 nm), the spectra exhibit typical blue colour characteristics, with a notable minimum ranging from 550 nm to 800 nm, indicating absorption of wavelengths associated with

green/yellow hues. In contrast, in the ranges of 400–500 nm and of 700–800 nm, the spectra reflected wavelengths corresponding to blue/cyan and orange/red colours, respectively. The spectra of blue paint before and after coating shared a similar shape, displaying all the characteristic peaks of the blue colour appearing at the same wavelengths, as it can be seen by the first derivative curves of the spectra (Fig. 6C, and Fig. S10D) [70]. However, they differed in reflectivity,



**Fig. 7.** A) Water absorption (%) with time ( $h^{0.5}$ ) for non-coated and coated T1 (solid lines) and T2 (dotted lines) marble samples ( $n = 3$ ). B) Adsorption/desorption isotherms of  $N_2$  at 77 K for non-coated and coated T1 marble samples. C) Adsorption/desorption isotherms of  $N_2$  at 77 K for non-coated and PHM-coated T1 marble samples, before (0 swc) and after five salt weathering cycles (5 swc). D) Mass change (%) (solid lines) and water adsorption measurements (%) (dotted lines) of non-coated and coated T1 (left) and T2 (right) marble samples, with salt weathering exposure time (d).

with the coated samples showing higher levels. After dissolution the spectra of coated samples resembled the spectra of blue colour at the pre-coating state but with slightly less intensity. The spectrum of the uncoated sample was significantly different with its reflectivity being higher, indicating the removal of blue paint and signal acquisition originating from the support (marble) [71].

### 3.5. Physical properties and salt weathering

The wetting properties of the T2 marble were found to exceed those of T1, as indicated by its significantly higher water absorption ( $0.19 \pm 0.03$  % compared to  $0.09 \pm 0.03$  % for T1) (Fig. 7A). Water absorption is influenced by factors such as surface area, pore size distribution and surface chemistry. Since both marbles have nearly identical chemical compositions, the difference in water absorption is attributed to the effects of the smaller grain size and increased number of grain boundaries of T2, which may facilitate capillary action, thus enhancing water absorption. Despite that T2 exhibited a lower surface area than T1 ( $0.041 \text{ m}^2/\text{g}$  compared to  $0.056 \text{ m}^2/\text{g}$  for T1), its average pore size was higher (56.11 nm compared to 47.48 nm for T1), potentially facilitating easier water penetration into the pores of the stone (Table 1).

Given the close connection between wetting properties and salt weathering, protective coatings, are typically formulated to repel water as mentioned above. However, in this case, all coated marbles exhibited increased water absorption when compared with their uncoated counterparts, with the PHM coating (PEM3HAp(20 %)) having the highest absorbed amount (Fig. 7A). In this case, due to surface chemistry differences, the water absorptive behaviour is mainly influenced by other phenomena such as hydration (for the non-functionalized samples) and swelling (for the PHM samples). Common strategy for adhesion on wet surfaces relies on a diffusion-based mechanism, with interfacial water posing a challenge for the formation of fast and robust adhesion between wet surfaces [72]. Here, the swelling effect of the PEM and the repeating wet-dry cycles, enhanced the separation effect of the interfacial water most likely through a combination of a diffusion-based and dry-crosslinking adhesion [72]. Hydroxyapatite, due to its chemical composition and structure, is hydrophilic since the hydroxyl (–OH–) groups located on its surface are able to form hydrogen bonds with water molecules, thus enhancing its hydration capacity [21]. For the PHM on the other hand, swelling occurs due to electrostatic interactions between the charged polymer chains and water molecules, leading to its hydration [73,74]. For T1 marble, both the BIHAp(20 %) and PEM3HAp(20 %) coatings exhibited a 60 % and 78 % rise in water absorption, reaching  $0.144 \pm 0.006$  % for the former and  $0.16 \pm 0.01$  % for the latter. In contrast, for T2, there was a 10 % and 36 % increase, leading to levels of  $0.21 \pm 0.02$  % for the former and  $0.26 \pm 0.02$  % for the latter, respectively (Fig. 7A). From our previous work [24], marble samples coated with five polyelectrolyte multilayers exhibited reduced water uptake in comparison to their non-coated counterparts, whereas here, non-functionalized and functionalized samples exhibited both higher uptakes. In the case of the PHMs, the merging of PEMs and HAp/PEI nanoparticles seemingly led to a hybrid material with different wetting properties.

Porosity measurements on all samples, through  $\text{N}_2$  gas adsorption, showed that all surfaces exhibited mesopore characteristics as indicated by the obtained isotherm shape (Type IV/H3, IUPAC classification), indicating the presence of slit-shaped/grooved pores (Fig. 7B, and Fig. S11) [75,76]. At the relative pressure range utilized for BET analysis ( $p/p^0 = 0.05 - 0.1$ ), the BIHAp(20 %) coating and for both types of marble exhibited a noticeable increase in surface area, in contrast to the PEM3HAp(20 %) coating, where minor differences were observed. The BET surface area of the BIHAp(20 %) and PEM3HAp(20 %) coatings on T1 and T2 marbles respectively were measured at  $0.074 \text{ m}^2/\text{g}$  (32 % increase) and  $0.051 \text{ m}^2/\text{g}$  (9 % decrease) for the former, and  $0.055 \text{ m}^2/\text{g}$  (34 % increase) and  $0.042 \text{ m}^2/\text{g}$  (2 % increase) for the latter (Table 1). In the case of BIHAp(20 %) coating, this increase is attributed to the

**Table 1**  
Surface area and porosity measurements ( $\text{N}_2$  at 77 K) for T1 (Thassos) and T2 (Penteli) marble during the salt weathering experiments.\*

| Sample       | Salt weathering cycle number (0 or 5 swc) | Single point surface area at $p/p^0 = 0.2 \text{ (m}^2/\text{g)}$ | BET surface area† ( $\text{m}^2/\text{g}$ )/Corr. Coeff. | Average pore diameter (4 V/A) (nm) | BJH adsorption cumulative surface area ( $\text{m}^2/\text{g}$ ) | BJH desorption cumulative surface area ( $\text{m}^2/\text{g}$ ) |
|--------------|-------------------------------------------|-------------------------------------------------------------------|----------------------------------------------------------|------------------------------------|------------------------------------------------------------------|------------------------------------------------------------------|
| T1-Blank     | 0                                         | 0.069                                                             | 0.056/0.92                                               | 47.48                              | 0.516                                                            | 0.529                                                            |
|              | 5                                         | 0.084                                                             | 0.062/0.94                                               | 42.85                              | 0.506                                                            | 0.424                                                            |
| T1-BIHAp20   | 0                                         | 0.085                                                             | 0.074/0.96                                               | 33.88                              | 0.472                                                            | 0.477                                                            |
|              | 5                                         | 0.067                                                             | 0.055/0.93                                               | 46.71                              | 0.479                                                            | 0.446                                                            |
| T1-PEM3HAp20 | 0                                         | 0.070                                                             | 0.051/0.99                                               | 50.80                              | 0.488                                                            | 0.496                                                            |
|              | 5                                         | 0.094                                                             | 0.060/0.93                                               | 47.60                              | 0.552                                                            | 0.518                                                            |
| T2-Blank     | 0                                         | 0.062                                                             | 0.041/0.91                                               | 56.11                              | 0.460                                                            | 0.469                                                            |
|              | 5                                         | 0.074                                                             | 0.050/0.92                                               | 46.84                              | 0.480                                                            | 0.443                                                            |
| T2-BIHAp20   | 0                                         | 0.078                                                             | 0.055/0.99                                               | 42.69                              | 0.457                                                            | 0.465                                                            |
|              | 5                                         | 0.070                                                             | 0.049/0.91                                               | 48.97                              | 0.503                                                            | 0.457                                                            |
| T2-PEM3HAp20 | 0                                         | 0.070                                                             | 0.042/0.92                                               | 56.66                              | 0.485                                                            | 0.490                                                            |
|              | 5                                         | 0.088                                                             | 0.063/0.97                                               | 41.03                              | 0.525                                                            | 0.495                                                            |

\* Measurements were performed in a special designed BET cell able to contain two cylindrical marble samples.

† BET surface area relative pressure calculation range  $p/p^0 = 0.05-0.1$ .

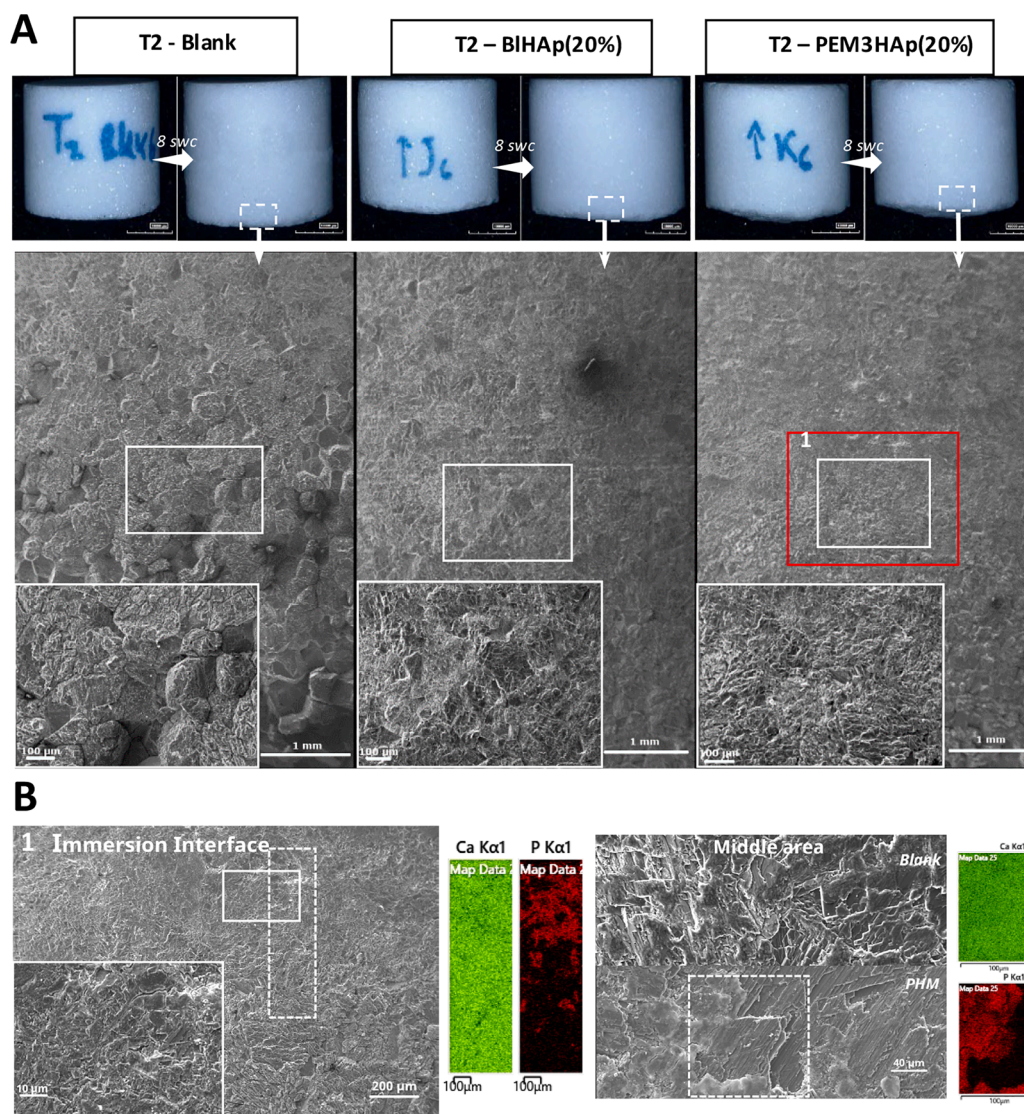


presence of deposited HAp nanoparticles over the surface of the marbles, which due to their high surface-to-volume ratio introduces additional surface area to the stone [77]. However, in the case of the PHM coating, the embedment of HAp nanocrystals into the polyelectrolyte matrix resulted to a surface with characteristics similar to the pore size and surface area of the substrate (Fig. 7B; Fig. S11A, and Table 1).

After five salt weathering cycles (5 swc) and for non-coated samples, the surface area increased whereas the average pore size diameter decreased. Since salt weathering typically involves processes such as material dissolution and the deposition and crystallization of salts within the pores of a material, we can assume that these processes increased the number of smaller pores while maintaining or decreasing the number of larger pores, resulting to an increased surface area. For non-functionalized samples (BI(HAp(20 %)) and for both types of marble, the opposite trend was observed (decrease in surface areas and increase in average pore size diameter) where as for functionalized samples (PEM3HAp(20 %)) the trend was similar as the one encountered for their non-coated counterparts. Considering the nearly identical  $N_2$  adsorption isotherms for the non-coated and BIHAp(20 %) coatings at 0 and 5 swc, and the noticeable difference for the PHM coatings, we can assume that for the former most of the coating had been removed from

the surface, while for the latter significant amounts may still have been present (Fig. 7C; Fig.S12B, and S12C). This is further supported by the similarity of BET surface area and pore size values for the T1/T2-Blank samples at 0 swc and T1/T2-BI(HAp(20 %) at 5 swc, whose values are nearly identical, indicating surfaces with similar characteristics (Table 1).

The mass change measurements for both types of marble followed a similar pattern, characterized by two distinct regions. In the first region, there was a sharp mass loss in the samples, which is attributed to the transitioning of samples from an environmental chamber to outdoor exposure, followed by a steady loss around the fifth salt weathering cycle (5 swc) (Fig. 7D). In the second region, the weight loss was more pronounced and with an increasing rate, particularly noticeable in the case of T2 marble. In the case of non-coated samples, after the fifth cycle, signs of sugaring appeared in the marbles, leading to significant errors in mass measurements due to substantial crystal detachment. This phenomenon was not observed in the coated samples, providing further indirect evidence of their protective properties. Notably, this effect was more evident in T2 marble, which exhibited inferior mechanical properties compared to T1 marble. Additionally, water absorption for all samples displayed a slight decreasing trend with increasing salt



**Fig. 8.** A) Micrographs of T2 marble test samples prior and following the salt weathering experiments (top), and SEM images of surface regions located at their base (immersion interface) (bottom). B) SEM/EDS surface analyses of the PHM (PEM3HAp(20 %)) coated marble from highlighted region 1 depicted in (A) (left), and from non-coated (top right) and PHM coated (bottom right) T2 marble from regions located midway from its longitudinal axis.

weathering cycles, although no significant differences were observed among the samples.

SEM/EDS analyses of the weathered samples indicated severe weathering for non-coated samples, contrasting with the less weathered appearance for the coated ones, particularly evident in the case of PHMs (Fig. 8A). An extensive previous study on artificial salt weathering of commercially available acrylic and silicone-based polymers has shown that, while these products are protective, they are prone to chemical alterations. Both types of polymers underwent structural changes, leading to their irreversible attachment to the substrate [78,79]. Silicone-based polymers formed cross-linked structures, while photo-oxidation in acrylic polymers resulted in strongly cross-linked structures, thus limiting their removability from treated surfaces. In our case however, all coatings exhibited reversibility since in areas of extreme exposure (below the immersion line), they were either completely removed from the surface (Fig. 8A/left) or still present in areas above. For the latter, exposed areas substantial amounts of coating were still present throughout their surface, reaching all the way to the sample's middle and top areas. The surface of non-coated samples exhibited irregular morphology with amorphous areas and exposed crystal planes, whereas for the PHM coated ones, the exposed crystals maintained their initial morphology (smooth and flat) (Fig. 8B/right, and Fig. S12B). Specifically, in areas below the immersion line, surface weathering was more pronounced in the case of non-coated samples, exhibiting crystal detachment and a rougher surface compared to their coated counterparts, where such characteristics were less prevalent (Fig. 8A, and Fig. S12A). SEM/EDS analysis of coated samples revealed that substantial amounts of coating were still present in areas above and at the immersion interface, specifically in the case of PHMs (Fig. 8B/left). Given the above observations, it is evident that both coatings proved to be beneficial for both marble types since they were able to withstand (PHM) or delay (BIHAp(20 %)) the effects of salt weathering.

#### 4. Conclusions

We have developed an alternative method to preserve stone materials by employing a bioinspired protective coating based on hydroxyapatite nanocrystals and polyelectrolytes, and demonstrated its efficacy on marble. The components used in our method are water-soluble and readily-accessible/easily-produced, and require minimal parametric adjustments to achieve the desired outcome in a timely manner. By altering the deposition sequence, we were able to generate coatings with micron-sized thickness and tuneable properties such as adhesion, self-healing, and resistance to weathering. Considering the wide variety of available polyelectrolytes and nanoparticles, with different properties and structures, we can assume that the methodology proposed here can produce a wide range of coatings for other applications (e.g., in biotechnology). However, while some formulations improved certain characteristics, like adhesion, they had adverse effects on others, such as weathering. Therefore, careful selection of the methodology parameters is essential, in order to meet the desired requirements for each specific case. Although tested coatings showed their protective capabilities, there is still room for improvement since the optimal conditions regarding hydroxyapatite concentration and number of multilayers were not completely determined. Overall, our results indicate that similar or even better outcomes can be achieved with lower concentrations of HAp and levels of functionalization, paving the way for environmentally friendly coatings inspired by nature, utilizing readily available and easy-to-produce components, suitable for application on both indoor and outdoor structures with complex geometries. That said, and considering that the coatings were tested in small-scale weathering experiments on marble here, further experimental investigations on a larger scale and with other commonly used substrates, such as limestone and sandstone, are required.

#### CRediT authorship contribution statement

**Iosif T. Hafez:** Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **George Biskos:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Funding acquisition.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jcis.2024.06.191>.

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