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# A SIMPLE GREEN STRATEGY TO PRODUCE A NANO-COMPOSITE WITH CONSOLIDATION AND HYDROPHOBIC ABILITY TO CALCAREOUS SUBSTRATES

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## ABSTRACT

Materials that dispose hydrophobic and super-hydrophobic properties have been increasing interest in the last decades, as they could remove water and develop consolidation properties on substrates. This strategy involves an effective process to protect building materials from damage, caused both by weathering and environmental air pollution, especially in the ongoing climate change. This research study presents the synthesis of a transparent, hydrophobic and superhydrophobic coating (under specific cases), named STP-Gns, that is implemented using the sol-gel method. Ingredients of STP-Gns include tetraethoxysilane (TEOS), completely hydrolyzed by oxalic acid, incorporating a hydrophobic molecule, the hydroxyl-terminated polydimethylsiloxane (PDMS). Hydrophobicity is enhanced in the coatings by embedding silica ($SiO_2$) nanoparticles into the polymer solution, at an appropriate concentration. STP-Gns was applied on Alfas stones as well as Pentelic and Carrara marbles to evaluate the hydrophobic properties. Treated specimens were evaluated by FT-IR spectroscopy, SEM/TEM microscopy, Dino-lite, colorimeter and static contact angle measurement. The innovation of this synthesis lies in the application of a super-hydrophobic and consolidant nanocomposite that gives high contact angles degrees. The produced crack-free coating is non-toxic, eco-friendly, and compatible with various substrates, while requiring a simple and non-energy-intensive production process.

**KEYWORDS:** TEOS-SiO2-PDMS nanocomposite, superhydrophobicity, coating, cultural heritage, STP-Gns, Silica nanoparticles, FT-IR, SEM and TEM microscopy, contact angle

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## 1. INTRODUCTION

From the beginning of human civilization until now, extensive parts of architectural design and expression were defined by the building materials that have been used. However, physical, chemical and biological parameters relative to weather conditions of each period cause decay of the structure's materials and consequently significant alteration of monumental and modern structures.

An important development in the field of materials is the control of decay and their protection with innovative technological materials. Into this framework, nanomaterials could exploit the physical and chemical properties of nanoparticles. In addition, they mimic the processes of nature to produce materials with enhanced properties. Indicatively, the synthesis of bioinspired nanomaterials with enhanced properties is achieved displaying increase of strength, durability, self-cleaning and protection (Maravelaki et al., 2018).

In recent years, climate change and air pollution have accelerated the decay of the construction materials of ancient monuments and modern buildings. In particular, water is one of the main damage factors to building materials, promoting dissolution process and accelerating chemical reactions over time. Consequently, it becomes imperative the need for intervention targeting to their protection against environmental loading. The development of innovative materials for the maintenance and protection of surfaces from corrosive agents places particular attention as a strategy to mitigate adverse climatic events. Great interest has attracted the last decades in the design of new innovative coatings, that will enhance the durability of building materials and will keep their cost of repair low. The use of nanoparticles is a common strategy for achieving surface waterproofing and moisture resistance. These coatings will be used for the restoration of monuments and buildings construction (Maravelaki et al., 2014).

It is essential for coatings to allow trapped moisture vapor to escape. In order to avoid further decay, coatings offering the capability of breathing, without trapping the moisture inside are required **Σφάλμα! Το αρχείο προέλευσης της αναφοράς δεν βρέθηκε.**. After the nanomaterial application, any color deterioration or aesthetical change are undesirable effects on the treated surface. A significant feature of the protective materials includes their easy and deeper penetration to the building material.

Materials exhibiting the aforementioned properties could be prepared by the sol-gel method; a process used to produce hydrophobic and super-hydrophobic films, suitable for the waterproofing of various surfaces. Organosilicon compounds, such as tetraethoxysilane (TEOS), are extensively applied in the field of restoration and consolidation of heritage monuments and modern constructions. Coating products allow the easy polymerization of TEOS inside the pore network of the stone substrates, initiated by the influence of atmospheric humidity. This process leads to the formation of amorphous silica. Additional advantages of TEOS modified materials are the high penetration of stone building materials. It is facilitated by the low viscosity, as well as the easy gelation and formation of Si-O-Si network (Verganelaki et al., 2015).

However, TEOS-based coatings were associated with some specific drawbacks. In particular, the development of cracking is observed in the gel network, due to the induced capillary pressure during the solvent evaporation from the substrate. Furthermore, silica has inefficient chemical bonding to non-silicate substrates, causing failure and possibly rejection of the treatment material. Another drawback includes the temporary hydrophobicity of these materials. As a result, water ingress is observed and consequently building decay. Additionally, biological growth is responsible for the degradation of coatings and their development on building substrates (Maravelaki et al., 2006).

The purpose of the current research work was to synthesize and evaluate a green simple nanocomposite, which provides crack free surfaces with superhydrophobic properties. Some of the features of this nanocomposite accomplish the following requirements: a) It is eco-friendly, including low energy footprint, both during preparation as well as in their composition. b) It is simple and cost-effective, c) it disposes acceptable gelation time and no cracking during drying. The performance of the produced nanocomposite STP-Gns, as well as its effectiveness in different applications has been examined in detail. Finally, STP-Gns were applied in a series of substrates. Subsequently, the applications were characterized and evaluated using macroscopic, microscopic analytical techniques and chemical analysis.

## 2. METHODS AND INSTRUMENTATION

### *2.1. Synthesis of STP-Gns coating*

Tetraethylorthosilicate (TEOS), hydroxyl-terminated polydimethylsiloxane (PDMS), 2-propanol (ISP) and oxalic acid dihydrate (Ox) were obtained from Sigma-Aldrich. The preparation of the coating product, designated as STP-Gns is displayed in Figure 1. Initially, Ox is dissolved and stirred in water and ISP (solution A), then PDMS was dissolved to solution A (solution B); the final step involves the addition of TEOS. Acid hydrolysis of TEOS is achieved

through the addition of Ox, which assumes the role of acid catalyst. This efficient synthesis yielded a low viscosity fluid (3.1 mPa·s) and the corresponding xerogel without cracking. The molar ratio of the final reactants and solvents Ox/H2O/ISP/PDMS/TEOS was equal to 0.02/4.81/2.31/0.34/1.

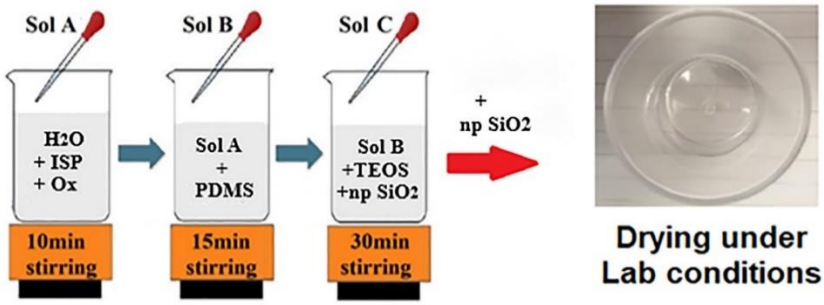


**Figure. 1. One-Pot synthesis of STP-Gns.**

The next step, for the preparation of the super-hydrophobic coating, named STP-Gns, is the addition of silica nanoparticles ($SiO_2$) with an average diameter of 7 nm (Sigma-Aldrich, St. Louis, MO, USA), to the previously prepared hydrophobic coating. The concentration of silica nanoparticles in the initial solution is critical and it ranges from 1 to 5% w/w since super-hydrophobicity of surfaces can be achieved within this concentration range. The first step involves the addition of $SiO_2$ in a concentration range of 1-5% w/w in STP-Gns. The mixture was left under vigorous stirring for 30 minutes.

## 2.2. *Test methods*

The produced xerogel was characterized by numerous analytical techniques. The viscosity of STP-Gns was measured using a rotational viscometer (Brookfield DV-II + Pro spindle: S18). The weight loss of the xerogel was determined as a percentage, compared to the initial volume and mass respectively of the sol cast in the mold [EN 15802:20090]. The digital microscope Dino-Lite (AM4515T5 Edge, equipped with a color CMOS sensor) was used for the microscopic assessment of STP-Gns xerogel [Maravelaki et al., 2006].

Fourier Transform Infrared Spectroscopy (FTIR) was utilized to determine the chemical composition and structure of STP-Gns xerogel. The absorption spectra were recorded with a Perkin-Elmer 1000 spectrometer, in the spectral range from 4,000 to 400 $cm^{-1}$.

The differential thermal and thermogravimetric analyses (DTA-TGA) of the developed xerogel was recorded by a Setaram LabSys Evo 1600. During the measurement, the sample heated up to 1000 $^{o}$C with a heating rate of 10 °C/min, under nitrogen atmosphere.

High-resolution TEM images of STP-Gns xerogel were obtained on a JEOL JEM-2100 Transmission Electron Microscope, operated at 80 and 200 kV, respectively. TEM sample preparation includes the evaporation of sample suspension after drop-casting on Formvar/Carbon coated TEM grids (Analytical Instruments S.A.).

SEM images were recorded according to standard procedure. STP-Gns nanoparticles were sprinkled on a two-sided carbon tape, coated with 100 Å gold utilizing a BAL-TEC SCD 050 Sputter Coater. Samples were examined by using a JEOL JSM-6390LV Scanning Electron Microscope at 20 kV electron voltage.

## 2.3. *Application and characterization of the coating on Alfas stone, Pentelic and Carrara marbles*

STP-Gns was applied on the surface of a local limestone called Alfas, Pentelic and Carrara marbles by brushing. The specimens used in this study are cubic ones with dimensions of 5 × 5 × 5 cm. These specimens are lustrous and prepared before the application of the produced coatings. The preparation process includes washing with deionized water, overnight drying at 50 $^{o}$C, measuring of the specimen's initial weight, and storing in desiccators before treatment. The applied layers of STP-Gns ranged between three and five. After the application process, all the specimens are kept at room temperature. After 48 hours, the specimens are ready to be tested in the lab, where various macroscopic, microscopic, physical and chemical measurements are taken in order to draw conclusions on the effectiveness of the applied coatings.

The surfaces previously were sprayed with ISP to open substrate pores. Initially, the specimens were left at room temperature in order for the solvent evaporation to be achieved and then, the properties of their surface were analyzed. The stone protection efficiency was assessed by using analytical techniques, such as FTIR spectroscopy, color differences with a

portable spectrophotometer, determination of contact angle, etc. Both treated and untreated specimens were analyzed. Contact angle studies were carried out to determine the wettability of STP-Gns on the above substrates [Berry et al., 2015]. The sessile drop method was used to display the effectiveness of the produced coating [Kapridaki et al., 2013]. The procedure involves the deposition of methylene blue solution drops on the coating substrate and the performance with the portable microscope Dino-lite, in a horizontal position supported by a mounting bracket. Three droplets of methylene blue solution were applied on the specimen's surface, using a needle, and the image of the droplet was recorded immediately (0 seconds) and after 20 seconds, in order to measure the static contact angles and the standard deviation. For a detailed microscopic observation of the treated specimen surfaces and the xerogel, a portable microscope named Dino-Lite Edge Digital Microscope model AM4515T5 was used.

For the estimation of color changes on treated specimens, a colorimeter (Micromatch Plus, Sheen Instruments Ltd.) was used to measure the chromatic parameters. The gloss and color of the coatings were monitored during the time. Color differentiation (ΔE) was determined according to equation:

$$\Delta E^* = \sqrt{(L_t - L_0)^2 + (a_t - a_0)^2 + (b_t - b_0)^2}$$

where, ($L_t$, $\alpha_t$, $b_t$) describe a differentiation in brightness, red and yellow, respectively and ($L_0$, $\alpha_0$, $b_0$) is the initial color of the coating [Maravelaki et al., 2006].

## 3. RESULTS & DISCUSSION

An efficient and optimized synthesis that was developed yielded a coating product (STP-GTns), displaying hydrophobic properties with low viscosity (3.1 mPa·s) and crack free xerogel. The produced xerogel presents a homogenous and compact appearance without any cracking. During the drying process, about 70% of the coating mass was lost, due to the solvent's evaporation. FTIR spectroscopy was utilized to reveal the chemical composition of STP-Gns.

The FTIR spectrum of STP-Gns is illustrated in Figure 2. Two distinct bands are observed at 1075 and 806 $cm^{-1}$, which are assigned to the antisymmetric and symmetric stretching bonds of the developed Si–O–Si network, respectively. These bands confirm the successful hydrolysis and polymerization of TEOS, as well as the creation of a Si-O-Si network. The characteristic band of PDMS is observed at 1269 $cm^{-1}$. This band corresponds to the symmetric C-H deformation of the CH3 groups in Si -($CH_3$) 0. In addition, the band at 934 $cm^{-1}$ is attributed to asymmetric Si-OH vibrations groups of hydrolysed TEOS. The peak observed at 848 $cm^{-1}$ is attributed to the copolymerization of PDMS and TEOS, corresponding to Si-C vibration 0. The band at 2962 $cm^{-1}$ is assigned to the C−H stretching mode of the $CH_3$ groups in Si -($CH_3$).

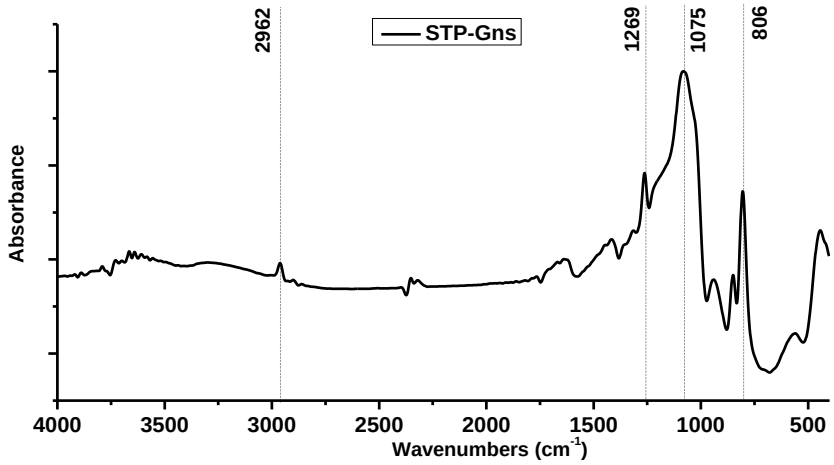


*Figure. 2. FTIR spectrum of STP-Gns nanocomposite.*

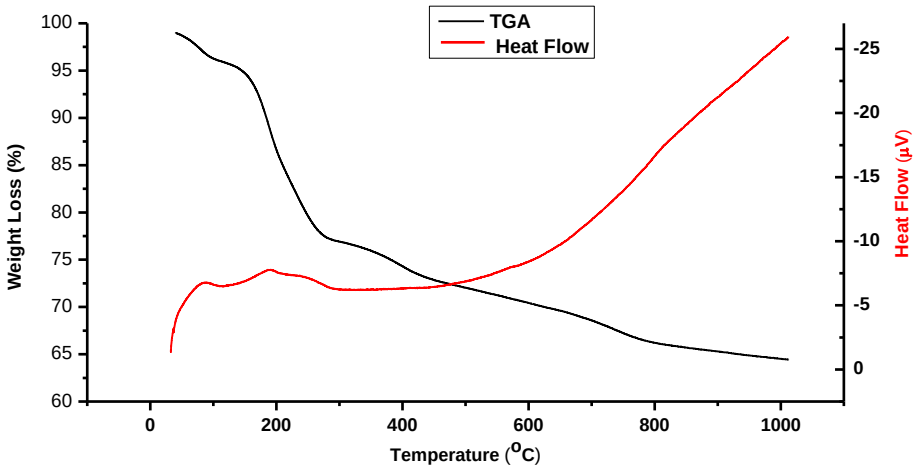


*Figure 3. TGA analysis of STP-Gns.*

Figure 3 displays TGA analysis of STP-Gns, showing the DTA (red line) and TG curves (black line) of the STP-Gns xerogel. During the thermal decomposition of the STP-Gns, three stages of weight loss were displaying at 190, 380 and 730 °C, exhibiting three domains. In the first domain, weight loss occurred in the temperature range of 30-300 °C. About 25% of the STP-Gns weight was lost due to physically adsorbed water and organic molecules. This weight loss is accompanied by two endothermic peaks at 84 and 189 °C, due to the evaporation of water, as well as the thermal decomposition and volatilization of the remaining organic solvents. In the second temperature range between 300 and 600 °C, a weight loss of 10% is observed, which is assigned to the decomposition of the remaining organic components. At temperature higher than 600 °C the STP-Gns exhibited an additional weight loss due to the dehydroxylation of silanol Si-O-H groups, which is accompanied by weight losses of 5% for STP-Gns [Kapridaki et al., 2013 & 2014; Manoudis et al., 2014].

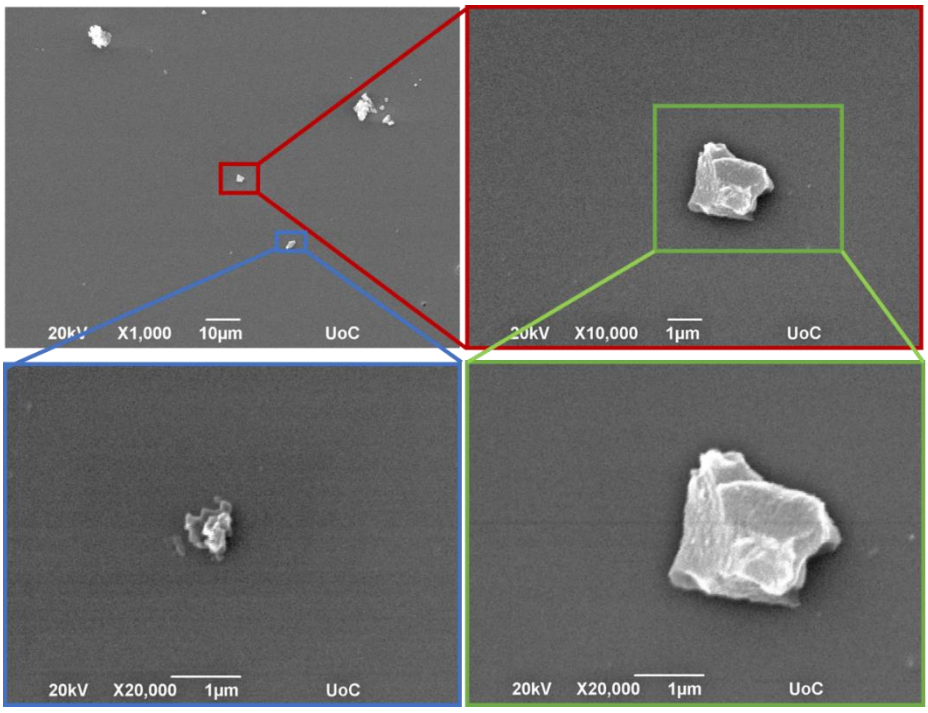


*Figure 4. SEM images of STP-Gns.*

Figure 4 shows the SEM images of STP-Gns xerogel. SEM images of the STP-Gns appear to be homogeneous and crack-free xerogel. The surface of xerogel is displayed completely flat. The absence of cracking and micro-cracking is remarkable. Several micro-

crystals are observed on the surface of xerogel, due to the existence of unreacted $SiO_2$ nanoparticles. The images registered at higher magnification to appreciate the surface morphology. The surface appeared to be considerably homogeneously uniform, due to the favoured copolymerization process of TEOS and PDMS.

The morphology of STP-Gns coating was exhibited by TEM microscopy. According to TEM images (Figure 5), an amorphous polymer film is observed, owing to the copolymerization of TEOS and PDMS. The existence of darker and lighter areas indicates a multilayer polymer coating. In addition, the morphological profile of STP-Gns exhibits several aggregates dissolved in the silicon polymer. These aggregates probably consisted of $SiO_2$ nanoparticles.

The application of the synthesized coatings on the selected lithotypes were first evaluated by macroscopic and microscopic observations. Any color change or alteration on the treated surfaces were not noticed. However, microscopic observations through the portable Dino-Lite microscope showed in some areas a concentration of material on the surface of the specimens and some minor cracks that have been created after the application of the coatings. In an effort to reduce the small cracks and keep the remaining ingredient's portions constant, the PDMS content was increased, thus creating a sol with higher nanoparticle density, that offers super-hydrophobicity to the treated surfaces. By changing both the ingredient's ratio and the sol's preparation, it was noticed that the micro-cracks have decreased or even disappeared. The solution with the fewest small cracks includes 2% $SiO_2$ w/w nanoparticles and gives contact angles on Alfas greater than 150 degrees, so it can be characterized as a superhydrophobic.

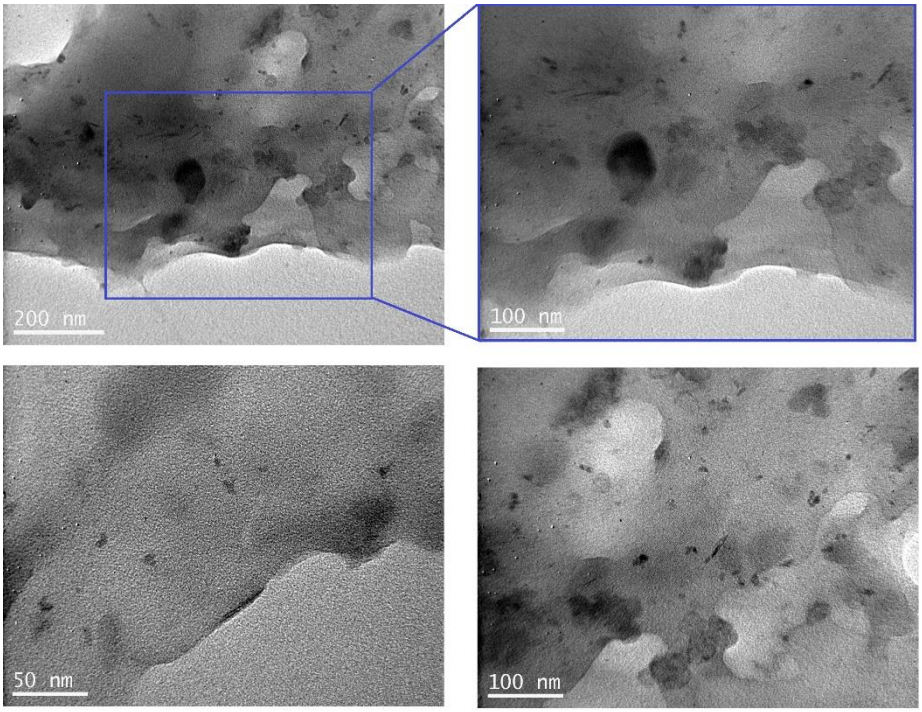


***Figure 5. TEM images of STP-Gns.***

Physical analysis of the specimens was performed before and after treatment, by using colorimeter and contact angle measurements. The surfaces of the specimens were tested to detect any staining or discoloration after treatment. Colorimeter testing revealed that the value $\Delta E^*$ was less than 3, which means that the color changes in the treated sample are not visible to the naked eye and are acceptable. Finally, contact angle measurements, before treatment, showed the Alfas stone surface is hydrophilic and absorbs almost immediately the water. Specifically, at 0 seconds the contact angle does not exceed 25 degrees, while at 20 seconds the contact angle is equal to 0 degrees, because of the totally absorbed water. After the application of STP-Gns, the contact angle of the Alfas stone surface exceeds 150 degrees, and the surface becomes super-hydrophobic (See Figure 6). The contact angles of Carrara and Pentelic marbles are notably decreased, with their values not exceeding 135 and 130 degrees, respectively. These results indicate that STP-Gns induces hydrophobic properties to surface of marbles [Chelazzi et al., 2018].

The specimens used in the various experimental compositions were exposed to environmental conditions and re-analyzed 5 to 6 months later to determine

the material's durability. It was observed that both at the macroscopic and microscopic level the materials yielded the same results. Specifically, the contact angles remained the same, whereas no cracks on the surface were observed.

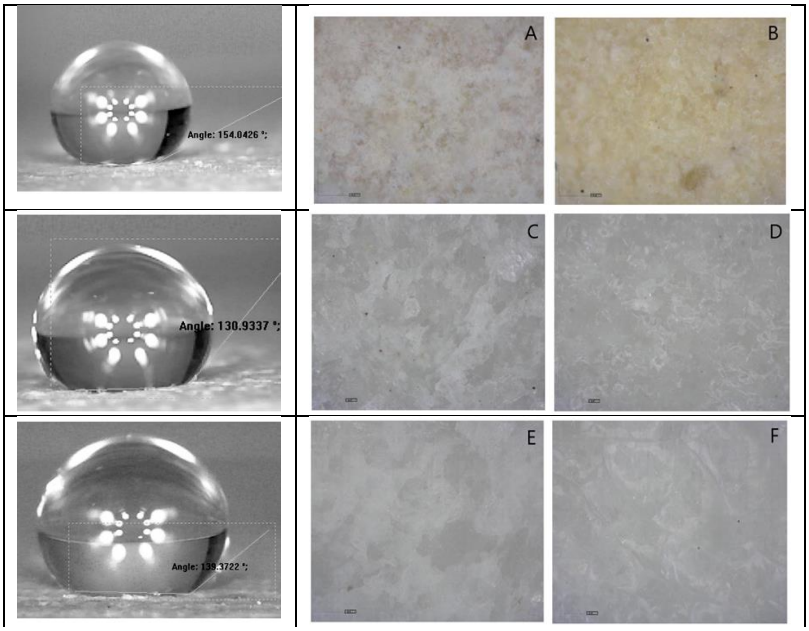


*Figure 6. Static contact angles of treated Alfas (B), Pentelic marble (D) and Carrara marble (F) and Optical Microscope images captured before and after treatment with STP-Gns of Alfas (A, B), Carrara marble (C, D) and Pentelic marble (E, F), respectively.*

The optical microscopy images of treated and untreated samples with STP-Gns are displayed in Figure 6. The treated samples do not reveal alterations or cracking onto their surfaces. Indeed, there are remarkably similarities between treated and untreated substrates. The magnified images appear no cracking at the treated surfaces that is probably attributed to the optimal copolymerization of TEOS with PDMS and nanoparticles SiO2. The particular synthetic route of STP-Gns favor the low surface energy of the system and as a result the consequent prevention of coating cracking.

## 4. CONCLUSIONS

In this study, an innovative nanohybrid hydrophobic coating product is prepared for the protection and restoration of stone monuments and buildings construction. It was successfully synthesized through a simple sol-gel process and meets the requirements set by the international standards for stone protection materials. The synthesis of this nanomaterial is simple, cost -effective, eco-friendly, and compatible with different substrates, while requiring a simple and non-energy-intensive production process. For its synthesis, TEOS was polymerized through acid catalysis of oxalic acid. The copolymerization of TEOS with PDMS introduces hydrophobicity and lack of cracking to the nanomaterial. Addition of silica $SiO_2$ nanoparticles in a concentration of 5% w/w allows a further increase of hydrophobicity. The incorporation of nanoparticles $SiO_2$ within the silica matrix contributes to the protection of coatings from cracking. The hydrolysis of TEOS as well as its copolymerization with PDMS within the silica network were demonstrated by the FTIR analysis. The SEM and Dino light analysis revealed a crack-free coating. Contact angle measurements reveal the enhancement of coatings' hydrophobicity. Finally, the variation of the water vapor permeability and color parameters ranged within acceptable limits. The aforementioned results of the analyses as well as the applications on alfas and marbles substrates, indicate that the newly designed coatings can be effectively used to protect building surfaces made out of stone. Finally, a suggestion for future exploration would be to use STP-Gns in other types of substrates, such as concrete and their optimization for these different types of building material.

**Author Contributions**:

Conceptualization, D.S., I.K. and P.M.; methodology, D.S. and P.M.; software, D.S.; validation, A.K., S.L. and D.S.; formal analysis, P.M. and I.K..; investigation, A.K., S.L. and D.S.; resources, P.M.; data curation, A.K. and D.S.; writing—original draft preparation, A.K., D.S and P.M.; writing—review and editing, P.M; visualization,

D.S. and P.M.; supervision, P.M.; project administration, P.M.; funding acquisition, P.M. All authors have read and agreed to the published version of the manuscript."

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