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Waterborne Silane/Polysiloxane Hydrophobic Coating for Stone-Built Cultural Heritage Conservation

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Abstract: Stone-built cultural heritage is historical evidence that represents past human events and activities. Therefore, it must be preserved for later generations since its deterioration would hardly be recovered to be the original. One of the effective ways to protect the stone-built cultural heritage from damaging factors is by applying a protective coating on the stone surface. This work aimed to prepare a waterborne protective coating with hydrophobic and self-cleaning properties. Tetraethoxysilane (TEOS) and hydroxy-terminated polydimethyl siloxane (PDMS-OH) were used to produce a protective coating due to their ability to form siloxane (Si-O-Si) bonds with inorganic substrates and to enhance a water-repellent property. The optimum weight ratio of TEOS:PDMS-OH at 80:20 was used to formulate this coating. The effect of TEOS/PDMS-OH mixture concentrations in a water medium on the properties of coated limestone substrates was studied by using coatings with different concentrations at 5, 10, 15, and 20 wt%. The TEOS/PDMS-OH coating with 5% and 10% concentrations showed good stability with no viscosity change for at least 2 months. The performance of the coated limestone was evaluated by water contact angle measurement, tape peel test, capillary water absorption, and dirt pick-up resistance test. The optimum TEOS/PDMS-OH concentration found was 10 wt% which showed significant improvement in hydrophobicity as evidenced by an increment of average water contact angle from 0° in the uncoated surface to 96° in the coated surface. The color difference (ΔE^*) was 1.21 and the gloss values slightly increased from 2.23 to 2.63 GU. Furthermore, the area after the peel test still maintained good hydrophobicity. The dirt pick-up resistance test revealed that the coating could protect the surface from dirt, while the uncoated surface was still covered with dirt. The results confirmed that the waterborne coating with 10 wt% TEOS/PDMS-OH is appropriate for limestone substrate protection.

Keywords: Stone-built cultural heritage, Water-based coating, Hydrophobicity, Tetraethoxysilane, Polydimethylsiloxane

1. Introduction

Archaeological sites are non-renewable resources that represent historical events and activities. They require academically proper conservation for existence in future generations. One of the materials widely used for historical objects and buildings is a natural stone, e.g., limestone, sandstone, and marble, due to its durability and high strength.

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However, these stone-built cultural heritages are generally located outdoor and continuously deteriorated from environmental factors, e.g., acid rain, moisture, and pollutants. The deterioration of stones over time significantly decreases the durability and stability of constructions.

In order to minimize the deterioration of these stone-built cultural heritages, they should be protected from the damaging factors. One of the effective ways is the application of protective coatings on the stone surface. The desirable properties of protective coatings are hydrophobicity, good adhesion, high weathering resistance, no cause of damage to the applied surface, and maintaining the original appearance of the stone [1]. The protective coatings can be divided into two main groups, organic and inorganic coatings. The organic coatings, such as acrylate and vinyl polymers, can increase hydrophobicity and do not chemically react with stone substrates. However, they are likely to turn yellow after long-time exposure to ultraviolet (UV) radiation. The inorganic coatings have good compatibility with stone in terms of chemical and physical characteristics. Nevertheless, their drawbacks are low penetration and poor elasticity which lead to film cracking [2].

Alkoxysilanes are widely used as a stone consolidant due to their viscosity with high penetration in porous materials and ability to form siloxane (Si-O-Si) bonds with silicon atoms of the stone substrates. Moreover, the siloxane bond which has relatively high bond dissociation energy shows chemical stability, heat resistance as well as stability under UV radiation [3]. Tetraethoxysilane (TEOS), a kind of alkoxysilanes with four reactive silyl-ethoxy groups, is widely used as a cross-linker for inorganic materials as well as a stone consolidant due to its ability to form a three-dimensional network through a sol-gel process, a two-step reaction containing hydrolysis and condensation in water media [4].

Polydimethylsiloxane (PDMS) has high hydrophobicity and low coefficient of friction due to the presence of silicone and methyl groups in its structure [5]. Hydroxy-terminated polydimethylsiloxane (PDMS-OH) can be chemically modified TEOS for improvement of elasticity of dry film, water repellency, and film-forming ability. The incorporation of PDMS into TEOS network can be prepared via the sol-gel process that hydroxyl groups in PDMS-OH form siloxane bonds with Si-OH of hydrolyzed TEOS [6]. According to previous works, the addition of PDMS-OH to TEOS network could reduce the cracking of the silica film due to the increase in structural flexibility [5]. Moreover, the limestone treated with TEOS/PDMS-OH consolidant showed a markable increase in water contact angle compared to pure TEOS consolidant [7]. It was found that the TEOS/PDMS-OH solvent-based coating with the weight ratio of TEOS:PDMS-OH at 80:20 provided the optimum performance of hydrophobic improvement on the tiled facade of cultural-historical building. This coating ratio was able to maintain the original appearance with high transparency of the coating film. However, the coating media used was solvents which may be harmful to applied substrates and operators [8].

To obtain the environmentally friendly coating product for stone-built cultural heritage, we have focused on the preparation of a protective coating with water as a main medium because of its low toxicity, low volatile organic compounds (VOC), and no cause of damage to the substrates. However, the disadvantage of waterborne coating is a slower drying time compared to a solvent-based coating which delays the overall coating process. Moreover, the stability of the waterborne coating is a challenge to overcome for the long shelf life of the coating product [9]. Thus, our study aims to develop the waterborne hydrophobic coating using TEOS and PDMS-OH where chemical reaction proceeded via sol-gel process. The concentration of the waterborne coating was studied to optimize the formulation that provide the highest protective performance. The functional groups of the coatings were investigated by Fourier-transform infrared spectroscopy (FT-IR), and their stability was studied by measuring viscosity and pH values. Furthermore, the coatings obtained were applied on the limestone surface, which is a substrate widely found in stone-built cultural heritage. After completely drying, the microstructure of the coated limestones was investigated and then their protective performances, i.e., water contact angle, capillary water absorption, adhesion, color, gloss, and dirt pick-up resistance were evaluated comparing with the uncoated sample.

2. Methodology

2.1 Materials

Tetraethoxysilane (TEOS) was supplied by BRB International b.v. (Ittervoort, the Netherlands), and Hydroxy-terminated polydimethylsiloxane (PDMS-OH) (Mn = 550) was supplied by Sigma-Aldrich Pte., Ltd. TWEEN 80 (polyoxyethylene sorbitan monooleate) and SPAN 80 (sorbitan monooleate) were received from Colossal International Co., Ltd. Analytical grade ethanol was purchased from RCI Labscan Co., Ltd. All chemicals were used as received.

2.2 Methods

Preparation of waterborne TEOS/PDMS-OH coatings

In this research, the coating was prepared from the optimum weight ratio of TEOS and PDMS-OH at 80:20 [8]. Since PDMS-OH exhibits a hydrophobic characteristic that is insoluble in water; thus, emulsifiers were utilized to prepare an oil-in-water emulsion. For the preparation of the PDMS-OH emulsion, a combination of emulsifiers that closely match the hydrophile-lipophile balance (HLB) value of PDMS-OH would be used. A blend of TWEEN 80 (4.39% by weight ratio of PDMS-OH) and SPAN 80 (5.61% by weight ratio of PDMS-OH), which provides a similar HLB value to PDMS-OH (HLB = 9), had been used as emulsifiers in this emulsion system. Firstly, TWEEN 80 and SPAN 80 were mixed in deionized water using magnetic stirring and sonication (VC-505 Ultrasonic Processor, Sonics & Materials, CT, USA). Then, PDMS-OH was added dropwise into the previously prepared emulsifiers in water. In another beaker, TEOS and ethanol (weight ratio of TEOS and ethanol at 1:2) were vigorously stirred for a few minutes; after that, it was slowly added into the prepared PDMS-OH emulsion. The TEOS/PDMS-OH mixture was sonicated with 500 watts for 2 min to obtain homogeneous coating. After that, the pH of coating was adjusted to neutral (approx. 7) by adding a diluted ammonium hydroxide (NH_4OH). The optimum concentration of the coating was determined by studying different concentrations at 5, 10, 15, and 20 wt% (solid content).

Application of coatings on limestones

After the preparation step, the coatings were aged at room temperature for 7 days prior to use. The limestone samples with a size of $5 \times 5 \times 2$ cm^3 were used for water contact angle measurement, capillary water absorption test, dirt pick-up resistance test, and a size of $15 \times 5 \times 2$ cm^3 was used for adhesion performance test, and color and gloss measurements. The coatings were applied on the limestone surface by brushing with a controlled weight of 200 g/m^2. Then, the coated limestones were dried at 60 °C for 7 days before further characterization.

2.3 Characterization and property tests

Chemical structure of coatings

Chemical bonds and functional groups of coatings were characterized using a FT-IR with ATR accessory (ALPHA II, Bruker, MA, USA) at 64 scans with a spectra resolution of 8 cm^{-1} in the wavenumber range of 550-4000 cm^{-1}.

Stability of coatings

The stability of the coatings was investigated by measuring viscosity using a viscometer (DV-II, Brookfield, MA, USA) and pH using a pH meter (SP-2100, Suntex, Taiwan) from day 0 of the coating until day 60.

Microstructure of coated limestones

The microstructure of limestones was investigated by a scanning electron microscope (SEM, JSM-6480LV, JEOL, Japan). The cross-section samples of uncoated and coated limestones were gold sputter-coated for 90 s and viewed at 5,000x and 10,000x magnifications under an accelerating voltage at 15 kV.

Hydrophobicity of coated limestones

The hydrophobicity of coatings was evaluated by water contact angle measurements using a goniometer (PGX+, Rycobel, Belgium). The test was carried out following ASTM D7334-08. 5 µL of deionized water droplets were sessile on five different positions of limestone surface. The average water contact angle value of five replicates was reported in each sample.

Adhesion performance of coated limestones

The tape peel test was used to investigate the adhesion performance of coated limestones. The 3M Scotch® transparent tape #600 (18 mm width) from 3M was attached on the coated limestone surface for 90 s, and then perpendicularly pulled off. The tested surfaces were evaluated by water contact angle measurement after tape peel test to prove the adherence of the coating [10].

Color and gloss of coated limestones

The colorimetric analysis of coated surfaces was measured using a spectrophotometer (CM-700d, Konica Minolta, Japan) with 8 mm spot diameter and illuminant D65 at observer angle 10°, through the determination of L*, a*, b* coordinates of the CIELAB color space, and the color difference (ΔE^*) between before and after coating was reported using Equation 1. The ΔE^* result was averaged from five replicates in each sample.

$$\Delta E^* = \sqrt{(L_2^* - L_1^*)^2 + (a_2^* - a_1^*)^2 + (b_2^* - b_1^*)^2} \tag{1}$$

The gloss measurement was evaluated using a gloss meter (Micro-gloss 75°, BYK-Gardner, CT, USA). Three replicates were evaluated in each sample.

Capillary water absorption

The capillary water absorption was performed following ASTM C1403-15. The limestones were placed on the specimen supports and partially immersed (the immersion level was controlled at 3.0 ± 0.5 mm) in a 25 × 35 × 12 cm water container. The amount of uptake water was evaluated by weighing the specimen after the different period of time and calculated using Equation 2.

$$M_i = \frac{m_i - m_0}{S} \tag{2}$$

Where M_i is an amount of absorbed water per surface unit at specific time t_i (sec), m_0 is a mass (g) of dried specimen, m_i is a mass of specimen at specific time t_i (sec) and S is a surface area in contact with water during the test (cm^2). The capillary water absorption curve was obtained by plotting M_i values against the square root of time (s$^{1/2}$), according to the equation $Q = Kt^{1/2}$, where Q or M_i is the amount of water uptake, and t is time (sec). The test was performed in three replicates in each sample [1].

Dirt pick-up resistance

The dirt pick-up water resistance test was performed by using carbon black as a pollutant model. The test was performed following the method described by Lu et al. [11]. The carbon black was sprinkled on the limestone surface, and then the limestone was placed in a petri dish with an inclination angle of 10°. Three water droplets were dropped on the top of the surface, then the droplets rolled away and removed the carbon black particles off the surface. Finally, the surface was rinsed with distilled water about 90 sec to remove the carbon black residue.

3. Results and discussion

Chemical structure of coatings

The chemical structures of the coatings were investigated by FT-IR as the results shown in Figure 1. The broad band in the 3200-3500 cm^{-1} represents O-H stretching vibration. The peaks located at 2962 and 1261 cm^{-1} are assigned to C-H stretching and C-H bending of -CH_3 in PDMS-OH, respectively. The peak located at 1020 and 785 cm^{-1} are attributed to the stretching vibration of Si-O-Si and Si-O, respectively. These two peak positions are typically found in both PDMS and TEOS. An evidence of copolymerization between Si-OH of hydrolyzed TEOS and Si-OH of PDMS-OH appeared at 851 cm^{-1}, where does not present in both unreacted TEOS and PDMS-OH spectra, indicating the achievement of condensation reaction conducted in our process [7,8].

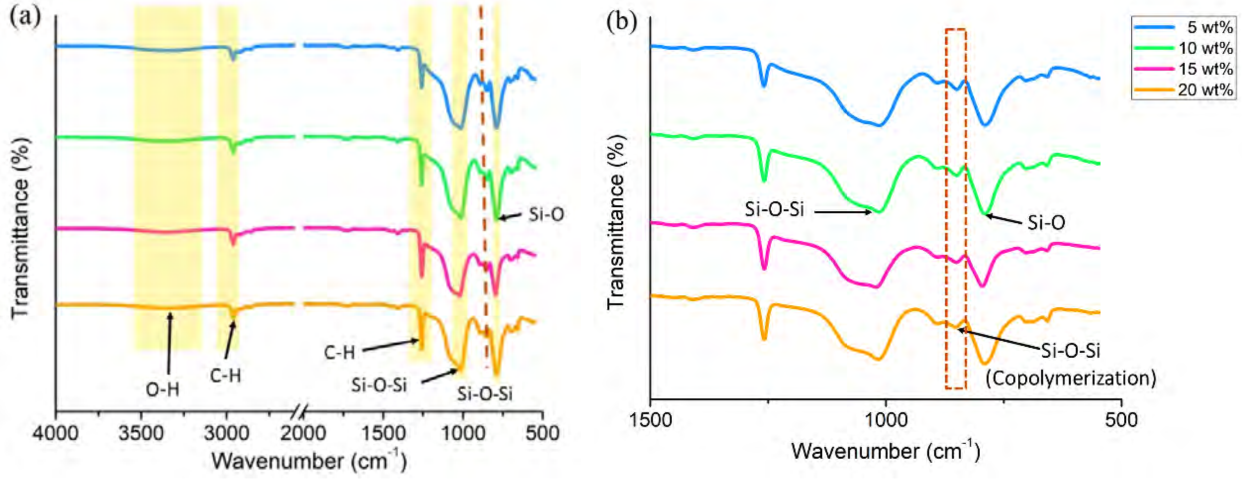

Figure 1 FT-IR spectra of TEOS/PDMS-OH coatings of (a) 4000-500 cm^{-1} and (b) 1500-500 cm^{-1}.

Stability of coatings

An appearance of waterborne coatings with various solid contents at 5, 10, 15, and 20 wt% of TEOS/PDMS-OH is shown in Figure 2(b). All prepared coatings showed low viscosity which is appropriate for deep penetration inside a porous material. The coatings with solid contents at 5 and 10 wt% have exhibited good stability with no significant change of viscosity and pH up to two months (Figure 2), indicating the copolymerization between TEOS and PDMS-OH could thoroughly happen by using our method. On the other hand, an increase of the solid content to 15 and 20 wt% led to poor stability in which viscosity build-up and gelation of coatings could be observed within two weeks (Figure 2(a)). The increase of PDMS-OH and TEOS contents in the coating formulation resulted in the reactive -Si-OH groups remained in the waterborne system; thus, the further condensation reaction could happen after the coating preparation and caused a continuous increase to the viscosity of the finished product [7].

Microstructure of coated limestones

The cross-section images presented in Figure 3(a-b) reveal that the uncoated limestone exhibited smooth surface particles without any substances covering the surface. In contrast, the coated limestone presented in Figure 3(c-d) showed particles with rough surfaces which are attributed to the hydrophobic coating substance penetrating into the stone layer as white arrows shown in Figure 3(c-d). From this observation, it can be inferred that the hydrophobic coating was capable of penetration inside the stone pores, resulting in a reduction of water absorption.

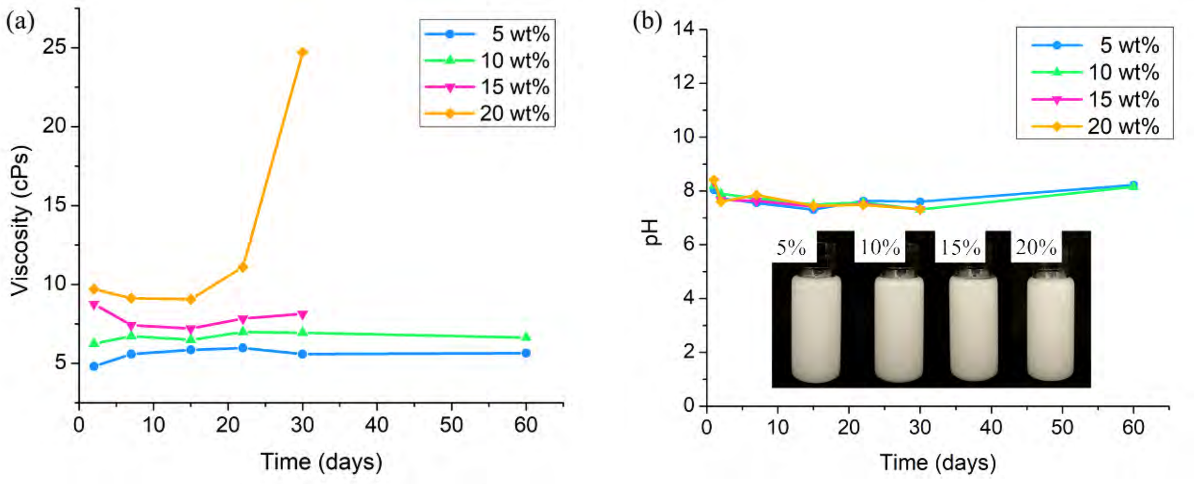

Figure 2 Stability of TEOS/PDMS-OH coatings by investigating of (a) viscosity and (b) pH.

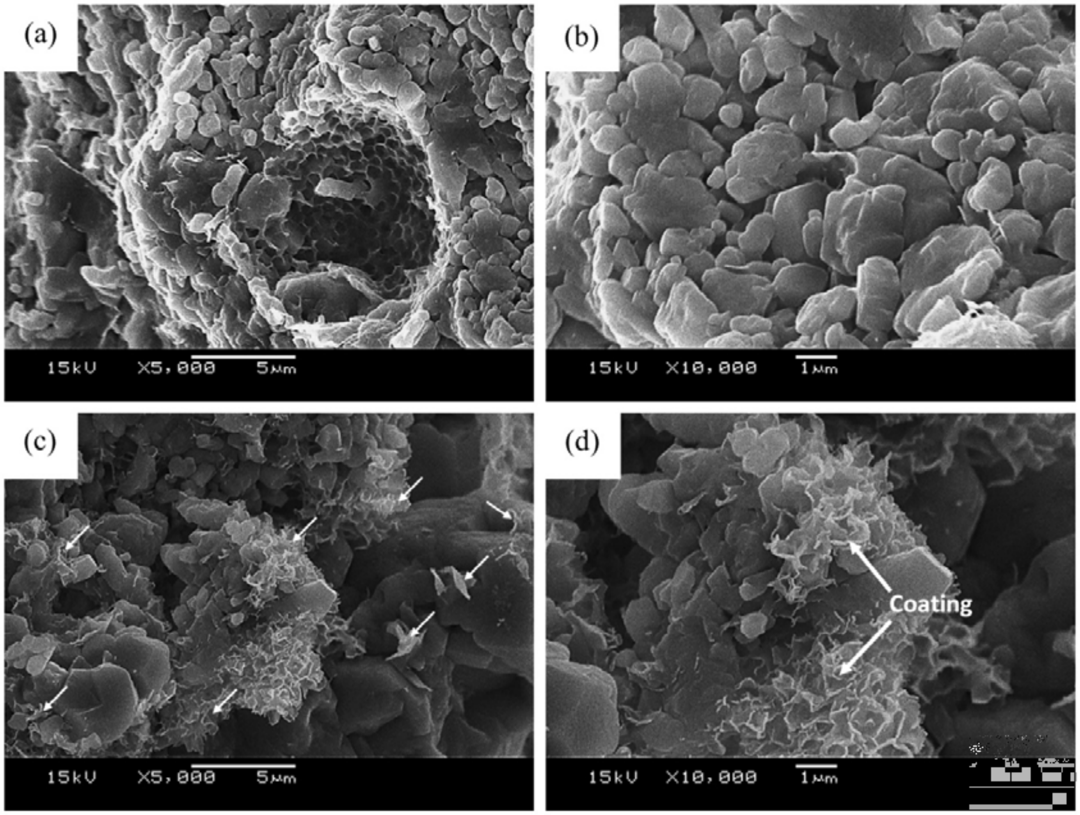

Figure 3 Cross-section micrographs at 5,000x (left) and 1,000x (right) of (a)-(b) uncoated limestone and (c)-(d) limestone coated with 10 wt% coating.

Hydrophobicity and adhesion performance of coated limestones

Figure 4(a) shows the results of water contact angles on uncoated and coated limestone surface. The water droplet on the uncoated limestone rapidly spread on the surface and penetrated into the limestone within a few minutes due to the high porosity of the stone, while an increase of water contact angle values was observed in all coated limestone. The hydrophobic surface was obviously found on the samples with the solid contents at 5 and 10 wt% where their average water contact angle values were 98.8° and 96.3°, respectively. A significant enhancement of the water contact angle of coated limestone is attributed to the characteristic of PDMS chains which have low surface energy and high hydrophobicity [5,12,13]. On the other hand, the limestones coated with higher solid contents at 15 and 20 wt% have a lower water contact angle compared to 5 and 10 wt%. The higher solid content of TEOS/PDMS-OH has covered a porous surface with a thicker coating layer which affected the reduction of rough surface area that has hydrophobic behavior [14]. Therefore, the hydrophobic surface area would be decreased, resulting in a lower contact angle found on those two coated limestones. In addition, the adhesion performance of the coatings was evaluated by a tape peel test and contact angle measurement. The results after the tape peel test in Figure 4(b) showed that the water contact angles of all coated samples were slightly decreased. The 5 and 10 wt% samples still maintained good hydrophobicity with the average water contact angle values of 91.4° and 91.7°, respectively. It can be concluded that the coatings with 5 and 10 wt% of TEOS/PDMS-OH have good adhesion on the stone surface, and they were not only coated on the surface but also penetrated inside the pores of the stone.

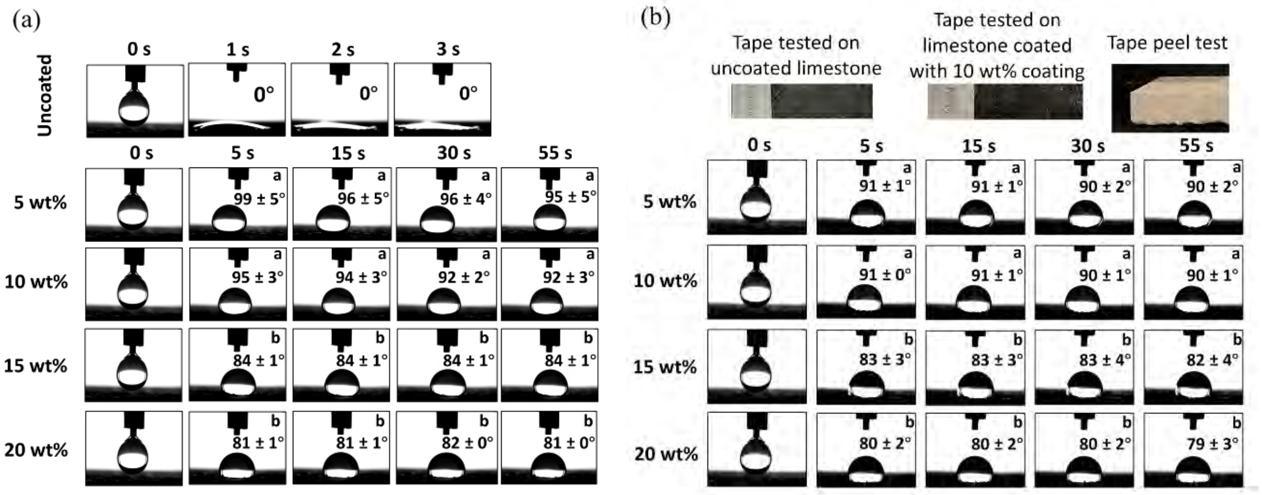

Figure 4 Water contact angles of coated limestone of (a) before and (b) after tape peel test.

Color and gloss of coated limestones

Since the aesthetic point of view must remain for archaeological sites, a protective coating must not change the original appearance of stone after coating. Color and gloss of the limestone before and after coating were investigated. Theoretically, a color difference (ΔE^*) of the coated limestone must be lower than 2 in order to be hardly differentiated by the human eye. As the results displayed in Figure 5(a), all coated stones have ΔE^* less than 2 which implies to the preservation of the stone color after coating. Moreover, it was found that the gloss values between uncoated and all coated samples were not significantly different (Figure 5(b)), where a gloss value difference less than 2 units is not perceptible by the human naked eye [15]. These ΔE^* and gloss results correspond to the previous work of Borhani-Esfahani et al. [8] that their solvent-based coating made of TEOS/PDMS-OH at the weight ratio of 80:20 was colorless and transparent and did not change the appearance of the tile after coating.

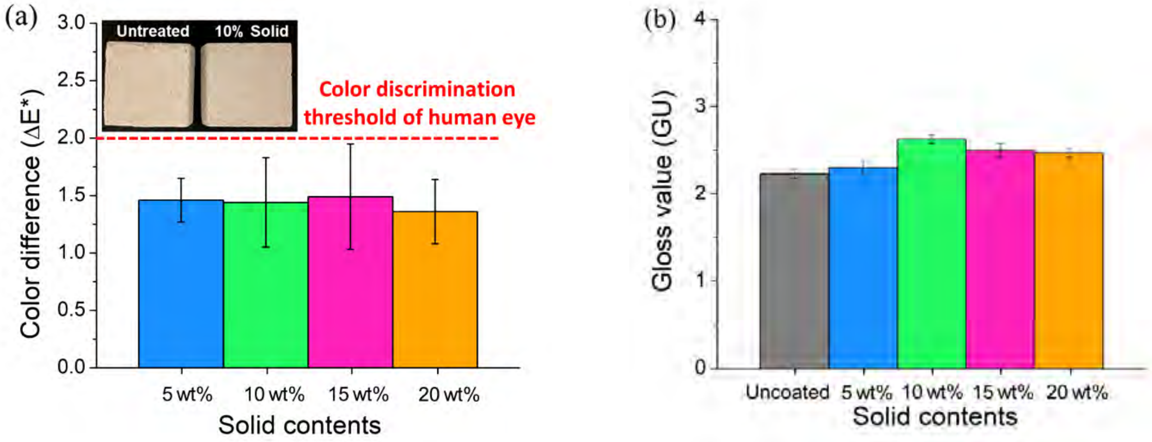

Figure 5 (a) Color difference (ΔE^*) between uncoated and coated limestone and (b) their gloss values.

Capillary water absorption

Figure 6(a) displays the capillary absorption test for limestones according to ASTM C1403-15. The water uptake of all coated samples decreased compared to the uncoated one as depicted in Figure 6(b) and Figure 6(c). The lowest water uptake was obtained from the 10 wt% sample, its water uptake was reduced up to 36.67% at 147 $s^{1/2}$ (6 h) and 11.60% at 831 $s^{1/2}$ (192 h) when compared with the uncoated sample. The reduction of water uptake in the coated limestone is due to the increase of hydrophobic area inside the porous matrix of the limestone [16]. It indicated that TEOS/PDMS-OH coating could penetrate inside the stone pores and fill the voids between the stone grains as the SEM micrographs shown in Figure 3(c) and Figure 3(d). However, a high-water uptake of the limestone coated with 15 and 20 wt% of TEOS/PDMS-OH was found since 4 h of testing. One possible reason for the higher water absorption observed in the 15 and 20 wt% coatings compared to the 10 wt% coating could be attributed to their high viscosity as depicted in Figure 2(a) which led to a lower penetration inside the stone pores, resulting in lower protecting efficiency. Moreover, a high content of PDMS-OH can cause a lower performance of water protection of coating which was possibly from an increased amount of hydrophilic hydroxyl group in PDMS-OH. The effect of too high PDMS content in a hydrophobic coating on water absorption of stone was also reported in the research of Kronlund et al. [17] that the excessive PDMS amount led to an increase in water absorption of granite. According to Figure 6(b) and Figure 6(c), 10 wt% of TEOS/PDMS-OH would be an appropriate concentration used for a stone protective coating.

Dirt pick-up resistance

A self-cleaning property of the coating was investigated by a dirt pick-up resistance test using carbon black particles to stain the limestone (Figure 7(a)). Firstly, the stone surface was sprinkled with the carbon black. After that, three water droplets were dropped on the top part of the stone. In this step, the droplets on all coated limestones rapidly rolled off from the surface and removed the carbon black in the meantime [18]. In contrast, the droplets on the uncoated limestone spread on the surface and were absorbed into the stone. In the last step, the tested surface was rinsed with water in order to remove the carbon black. The stones coated with 5 and 10 wt% of TEOS/PDMS-OH showed the optimum performance of carbon black removal after rinsing with water as the results shown in Figure 7(a) (right). In Figure 7(b), a water droplet on the coated limestone can remove dirt from the surface because of the hydrophobic characteristic of PDMS. According to this hydrophobic character, surface energy of the coated limestone was reduced, and the dirt would be easily removed by rinsing [19]. The result obtained corresponds to the previous work of Sun et al. [20] that the self-cleaning property was improved when increasing the hydrophobicity of the porous material surface. Therefore, it can be inferred that the organic pollutants on the coated limestones can be removed through rainfall.

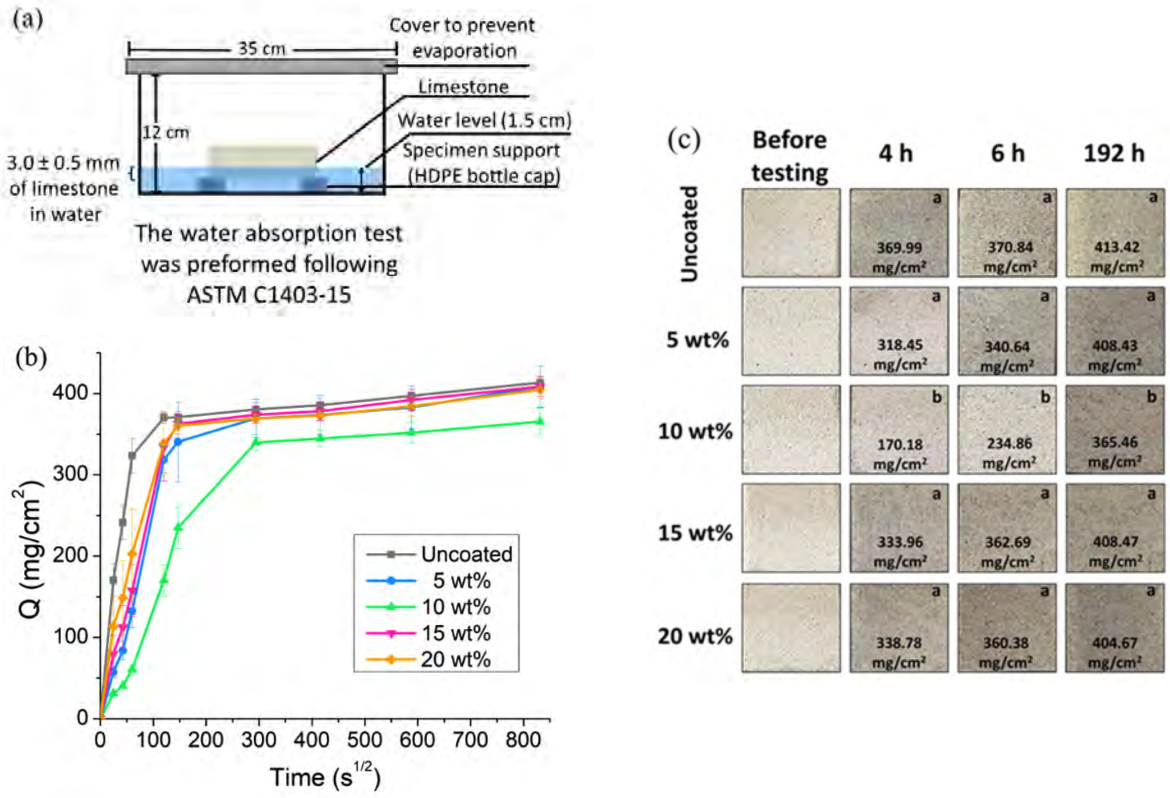

Figure 6 Capillary water absorption; (a) test diagram, (b) water uptake results and (c) limestone samples during the test.

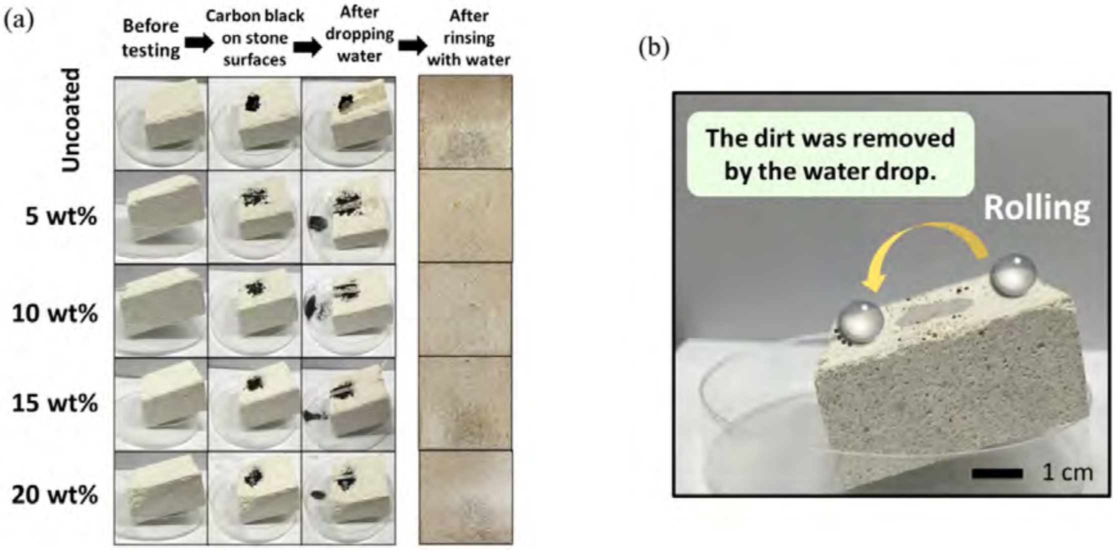

Figure 7 (a) The dirt pick-up resistance test on limestone surfaces and (b) schematic of water droplet on the coated stone surface.

4. Conclusion

The waterborne protective coating for stone-built cultural heritage conservations was successfully prepared from a condensation reaction between TEOS and PDMS-OH with the weight ratio at 80:20. The different concentrations of TEOS/PDMS-OH were studied to find the optimum performance of hydrophobicity, adhesion, and dirt pick-up resistance. The most appropriate concentration of this coating was obtained from a solid content at 10 wt% of TEOS/PDMS-OH where the sample provided good hydrophobicity, well adhesion on the stone surface, the lowest capillary water absorption, and the best self-cleaning property when compared to other concentrations. In addition, good stability of coating was obtained from this 10 wt% concentration in which its formulated coating could maintain viscosity and pH without significant changes for up to 2 months. Furthermore, this coating did not alter the limestone appearance in terms of color and gloss difference. In conclusion, the waterborne protective coating with solid content at 10 wt% of TEOS/PDMS-OH is feasible for use in stone-built cultural heritage conservation.

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References

[1] C. E. Corcione, N. D. Simone, M. L. Santarelli, M. Frigione, Protective properties and durability characteristics of experimental and commercial organic coatings for the preservation of porous stone, *Prog. Org. Coat.* **103** (2017) 193-203.

[2] V. Rives, J. G. Talegon, Decay and conservation of building stones on cultural heritage monuments, *Mater. Sci. Forum* **514-516** (2006) 1689-1694.

[3] A. Artesani, F. D. Turo, M. Zucchelli, A. Traviglia, Recent advances in protective coatings for cultural heritage: An overview. *Coatings* **10** (2020) 217.

[4] G. Wheeler, Alkoxysilanes and the Consolidation of Stone, Getty Publications (2005).

[5] R. Zárraga, J. Cervantes, C. Salazar-Hernandez, G. Wheeler, Effect of the addition of hydroxyl-terminated poly dimethylsiloxane to TEOS-based stone consolidants, *J. Cult. Herit.* **11** (2010) 138-144.

[6] G.-D. Kim, D.-A. Lee, J.-W. Moon, J.-D. Kim, L.-A. Park, Synthesis and applications of TEOS-PDMS hybrid material by the sol-gel process, *Appl. Organomet. Chem.* **13** (1999) 36-372.

[7] F. Xu, D. Li, Effect of the addition of hydroxyl-terminated polydimethylsiloxane to TEOS-based stone protective materials, *J. Sol-Gel Sci. Technol.* **65** (2013) 212-219.

[8] S. Borhani-Esfahani, H. R. Salimijazi, M. H. Fathi, A. Ershad-Langroudi, B. Pedram, An environmentally friendly titania–silica core–shell nanoparticles coating for protection of tiled facade of cultural-historical buildings, *Results Surf. Interf.* **2** (2021) 100004.

[9] C. Zhou, H. Zhang, X. Pan, J. Li, B. Chen, W. Gong, Q. Yang, X. Luo, H. Zeng, Y. Liu, Smart waterborne composite coating with passive/active protective performances using nanocontainers based on metal organic frameworks derived layered double hydroxides, *J. Colloid Interface Sci.* **619** (2022) 132-147.

[10] F. Elhaddad, L. A. M. Carrascosa, M. J. Mosquera, Long-term effectiveness, under a mountain environment, of a novel conservation nanomaterial applied on limestone from a Roman archaeological site, *Materials* **11** (2018) 694.

[11] Z. Lu, Q. Ge, Y. Zhang, G. Lian, Preparation and analysis of multi-scale colored superhydrophobic coatings with excellent mechanical strength and self-cleaning properties, *J. Build. Eng.* **64** (2023) 105530.

[12] M. J. Owen, Silicone hydrophobicity and oleophilicity, *Silicon* **9** (2014) 651-655.

[13] D. Kumar, X. Wu, Q. Fu, J. W. C. Ho, P. D. Kanhere, L. Li, Z. Chen, Hydrophobic sol–gel coatings based on polydimethylsiloxane for self-cleaning applications, *Mater. Des.* **86** (2015) 855-862.

[14] Q. Li, C. Liang, Y. Wu, L. Liu, Y. Chen, P. Zhao, L. Lu. Super-hydrophobic hybrid coatings preparation used by methyltrithoxysilane (MTES) and tetraethylorthosilicate (TEOS), In 7th International Conference on the Durability of Concrete Structures (2022).

[15] P. M. Carmona-Quiroga, S. Martínez-Ramírez, H. A. Viles, Efficiency and durability of a self-cleaning coating on concrete and stones under both natural and artificial ageing trials, *Appl. Surf. Sci.* **433** (2018) 312-320.

[16] B. S. da Fonseca, A. P. F. Pinto, A. Rodrigues, S. Piçarra, C. Santos, M. F. Montemor, Effect of the pore network and mineralogy of stones on the behavior of alkoxysilane-based consolidants, *Constr. Build. Mater.* **345** (2022) 128383.

[17] D. Kronlund, M. Lindén, J.-H. Smått, A polydimethylsiloxane coating to minimize weathering effects on granite, *Constr. Build. Mater.* **124** (2016) 1051-1058.

[18] H. Li, Y. Luo, F. Yu, L. Peng, Simple and scalable preparation of robust and magnetic superhydrophobic papers by one-step spray-coating for efficient oil-water separation, *Colloids Surf. A Physicochem. Eng. Asp.* **640** (2022) 128449.

[19] F. Elhaddad, M. Luna, G. M. C. Gemelli, M. L. A. Gil, M. J. Mosquera, Effectiveness and durability assessment, under extreme environmental conditions, of a superhydrophobic coating applied onto sandstone from Carteia Roman archaeological site, *Chem. Eng. Sci.* **265** (2023) 118236.

[20] S. Sun, P. Xu, Z.-H. Chen, Q.-R. Xiao, X.-L. Qiang, X.-L. Shi, "One Stone Three Birds": A multifunctional cotton fabric with favorable self-cleaning, photothermal effect and Joule heating properties, *Appl. Surf. Sci.* **623** (2023) 156961.