Research article

Dual-function coatings to protect absorbent surfaces from fouling

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Abstract: Fouling of surfaces caused by pollution, contamination, humidity and microorganisms is one of the major sources of the degradation of mineral and composite materials. The inhibition of foulant growth is essential for the prevention of different kinds of damage, ranging from aesthetic, mechanical and chemical, to risks concerning human and environmental health. This study proposes a new approach for the development of a transparent preservative material with water-repellent and biocide attributes through the use of a sol-gel method. It was found that Si–O–Si dense networks can effectively grow into the micro-pores of mineral and cellulose-based materials, promoting self-cleaning properties as well as sufficient protection against bio-fouling.

Keywords: water-repellent coatings; antifungal; self-cleaning; wood preservation; marble and stone protection; bio-fouling

1. Introduction

Water-repellent strategies to limit the fouling of porous substrates, including mineral and cellulose-based surfaces, are of immense interest for many industrial applications. Mineral surfaces usually employed in cultural heritage constructions and building materials, such as marble, mortar, cement, granite, stone, ceramics and natural rocks, suffer from several attacks. Environmental pollutants, including chemical agents (i.e., acid rain, atmospheric aerosols, SO_2, NO_x, etc.), physical factors (such as humidity and temperature variations), biological agents (i.e., bacteria, fungi, algae) and other weathering effects are common threats causing direct or indirect degradation to mineral

porous surfaces. Furthermore, composite materials, such as wood consisting of cellulose, hemicellulose and lignin, can also quickly degrade, especially when exposed to humid air. Water is the primary natural factor that triggers the swelling and shrinking of wood substrates owing to their porous structure and increased polarity from the hydroxyl groups of hemicelluloses and cellulose. Similarly, water penetration inside of the stones can cause irreversible chemical or mechanical damage due to the intrinsic properties of building materials, such as roughness and porosity. The presence of polar groups inside of porous surfaces promotes microorganism colonization, thus leading to biofilm formation [1,2].

Throughout the years, several techniques have been employed to monitor the fouling of porous substrates. Within this context, protective coatings can change the surface morphology and wetting properties of bare porous substrates and inhibit water uptake [3] and bacterial colonization by promoting preservative attributes.

Sol-gel [4] is extensively used in the fabrication of such coatings. Sol-gel is a flexible, cost-effective and environmentally friendly method which can generate highly cross-linked networks between organic and inorganic components on a variety of substrates, especially hydroxylated ones. Typical sol-gel precursors are organo-functional silanes. These can deeply penetrate and fill surface microcracks with breathable Si–O–Si nanostructures, which provide preservative properties to the substrate.

Porous substrates can be treated by sol-gel coatings in various ways [5–8]. They can be impregnated either with colloidal solutions consisting of silicon oxide nanoparticles (NPs), or with hybrid structures forming polyhedral oligomeric silsesquioxanes, or with solutions consisting of silane-siloxane oligomer mixtures [4,9]. For example, Chang et al. [10] prepared superhydrophobic hybrid coatings, for the protection of wood substrates, from a mixture of aggregated particles of hexadecyltrimethoxysilane with colloidal silica particles, formed by tetraethoxysilane (TEOS) hydrolysis and subsequent condensation. Szubert et al. [11] fabricated hydrophobic wood protective coatings by using a low-surface tension fluorocarbonsilane (OFTES). Treated samples were impregnated with a TEOS-based silica gel, thus promoting wood-O–Si (siloxane) bonds, and they were coated with a solution containing 5% OFTES and 22% TEOS, which improved hydrophobicity. Manoudis et al. [12] fabricated superhydrophobic coatings for the protection of marble substrates by modifying commercial siloxane compositions with silica NPs. The coatings demonstrated durable superhydrophobicity after five months of exposure to outdoor conditions. Salazar-Hernandez et al. [13] formulated a stone consolidation hybrid material consisting of TEOS, colloidal silica and hydroxyl-modified polydimethylsiloxane (PDMS-OH). Results showed increased hardness, effective pore-sealing and resistance to salt crystallization.

However, the use of sol-gel silane-based coatings has often been associated with the impairment of surface transparency and crack formation, which occur as a result of increased capillary pressure [5], especially in marble and stones. Hence, various research efforts have focused on the development of crack-free xerogels with enhanced water-repellent properties. To this end, a common approach is to introduce into the coating's solution low-surface tension components or lipophilic surfactants. Moreover, the use of silicon-based polymers such as TEOS and polydimethylsiloxane (PDMS) can enhance flexibility, accelerate penetration into the pores and assist in the creation of a strong cross-linked network between substrate silanol groups and short siloxane-based reactive chains in order to promote the formation of crack-free structures [14]. For example, Kapetanaki et al. [7] synthesized water-repellent coatings for mortar and concrete by using TEOS, PDMS and calcium oxide-based NPs. The coatings exhibited good hydrophobic properties with water contact angle (WCA) values on the order of 90–100º. Aslanidou et al. [15] fabricated superhydrophobic self-cleaning

coatings by preparing an aqueous emulsion of alkoxysilanes which contained silica NPs and a fluoropolymer. The coatings were applied on marble and stone, yielding good water resistance. Liu and Liu [16] synthesized a sol-gel hydrophobic stone consolidant by incorporating a mixture of TEOS, PDMS-OH and cetyltrimethylammonium bromide. The latter was used to prevent crack formation. Adamopoulos et al. [17] prepared TEOS-based superhydrophobic structures for a stone-built cultural heritage by introducing into the coating's solution a fluoroalkoxy-modified agent. The obtained coatings generated water-repellent properties on various substrates, including marble, wood, paper, silicon wafers, etc.

Nevertheless, water-repellent, conservation or consolidation coatings alone are unable to inhibit the biofouling of surfaces. For example, Nascimbene and Salvadori [18] evidenced the recolonization of lichens on selected statues which had been previously restored with consolidation materials. Therefore, antimicrobial agents, i.e., biocides, are often employed. Among the most efficient biocides are silver compounds, including silver nitrate ($AgNO_3$) [19], silver NPs (Ag NPs) [20,21], zinc oxide NPs (ZnO NPs) [22], titanium oxide NPs (TiO_2 NPs), green biocides from natural sources [23], copper NPs (Cu NPs) [24,25] and quaternary ammonium compounds [26]. Mu et al. [2] fabricated a durable AgCl/ZnO nanocomposite for the protection of stone-based building materials. A 60-day microbial inhibition was recorded, achieved through the release of Ag^+ and Zn^{2+} ions. Hegyi et al. [27] developed photoactivated TiO_2-based NPs on the surface of cementitious composites for the inhibition of microorganism growth. Coated samples were found to be resistant to bacterial contamination for at least 21 days. Koziróg et al. [28] investigated the efficacy of several microbiocides on wood substrates, including quaternary ammonium compounds, N-(3-aminopropyl)-N-dodecylpropane-1,3-diamine (APDA), boric acid and others. Among them, APDA and didecyldimethylammonium chloride proved to be the most effective against bacteria and mold.

Compared to preservative materials, antimicrobial agents are, in general, more effective against biofilm formation. However, their efficacy over time is often compromised. To mitigate this problem, the development of bifunctional systems which combine both water-repellent and antimicrobial properties has been proposed. For example, Moreau et al. [29] investigated the deposition of a biocide on a water-repellent coating for mineral substrates. The samples were first coated with an alkylpolysiloxane (Rhodorsil H224) and, after a 28-day curing, they were treated with a ready-to-use quaternary ammonium salt. It was found, that the biocide increased the surface energy of the underlying coating. Moreover, although its biocidal efficacy was sufficient, it could not provide long-term protection due to its gradual leaching out from the coating. In another effort, Pinna et al. [25] mixed traditional consolidants and water-repellent products with biocides to inhibit microbial growth on sandstone, marble and plaster. Tributyltin oxide, dibutyltin dilaurate and Cu NPs were used as biocides. It was found that, when Cu NPs were combined with a solvent-based consolidant (Silo 111), the resistance of coated marble substrates against colonization was improved. Eyssautier-Chuine et al. [30] developed a preventive coating with the aid of an environmentally friendly biocide to protect stones used in buildings and monuments. Samples were first treated with a water-repellent silane-siloxane emulsion (Tegosivin HE 328), and then with the biocides, with the latter being chitosan, silver nitrate or mixtures of them. It was suggested that the treatment positively affected colonization prevention. However, the hydrophobicity of coated specimens decreased significantly. Furthermore, Aldosari et al. [31] developed a biocidal and consolidating self-protective coating for exposed marble columns. It was proved that the combination of an acrylic polymer (Paraloid B44) and ZnO NPs provided adequate antifungal activity. Continuing with wood substrates, Palanti et al. [19] investigated the antifungal

activity of an alkoxysilane mixture consisting of TEOS:APTES (APTES: 3-aminopropyltriethoxysilane) in two different ratios of 10:1 and 1:1, with and without the addition of copper chloride. Results showed that, by the addition of copper at a ratio of 5:1 APTES:Cu, the biocidal activity improved. However, when the ratio of TEOS to APTES was 10:1 the treatment appeared to be ineffective in the absence of copper. Wu et al. [32] fabricated superhydrophobic antibacterial coatings through the use of Ag NPs on poplar wood samples. The latter were first treated with a silver-ammonia complex solution, and then with stearic acid, to achieve superhydrophobicity. It was found that fouling resistance was enhanced.

It should also be noted that, instead of depositing a biocide before or after the water-repellent coating-treated surfaces with one-component coating systems, possessing a dual functionality may be a more advantageous approach. Such attempts [25,33] have been performed on porous substrates by combining several alkoxysilanes to promote both preservation and biocidal properties. However, facile fabrication of protective coatings with strong water repellency, long-term durability and broad-spectrum antibacterial efficacy still remains a significant challenge.

Therefore, the primary aspect of this study is to propose an innovative strategy toward the fabrication of multifunctional sol-gel coatings for both stone and wood surfaces. Within this scope, focus was given to the endurance of the coatings, as well as to the facility of the synthetic procedure. The coating solutions were applied to pine wood and Karystos stone, as well as to both polished and unpolished marble.

2. Materials and methods

2.1. Materials

TEOS 98% and a quaternary ammonium compound, namely, 3-(trimethoxysilyl) propyldimethyloctadecyl ammonium chloride, 72% in methanol, were used as precursors. They were supplied by Gelest, Inc. and used without purification. Ethyl alcohol, acetone (purchased from Sigma Aldrich) and deionized water were used as solvents. Hydrochloric acid fuming 37% (Sigma Aldrich) was used as a catalyst. Two white (Thassos) marbles, one polished and one unpolished ($20 \times 20 \times 2$ cm^3), two Karystos stones ($20 \times 30 \times 2$ cm^3) and four pine wood boards ($10 \times 10 \times 30$ cm^3) with straight grains and without knots were used as substrates. Bromophenol blue (BB) powder by Sigma Aldrich was used as a dye indicator to detect in situ residual quaternary ammonium complexes dried on tested surfaces.

2.2. Preparation and application of coatings

First, TEOS and a quaternary ammonium silane (Si-QUAT) were separately dissolved in deionized water at 50% w/w and 20% w/w, respectively. The two solutions were acidified by using 37.5% hydrochloric acid (pH = 2.7), and they were stirred vigorously for 3 h until homogeneous liquid solutions were formed. Both solutions were stored inside closed glass vessels and left to age for 48 h at room temperature. Then, the TEOS-based concentrated solution (TEOS-C) was split into four parts. Three of them were further diluted with ethyl alcohol to final concentrations of 7%, 10% and 15%, respectively. To each of the three solutions, a certain amount of the separately hydrolyzed quaternary ammonium silane was added in order to produce sols with final TEOS/quaternary ammonium silane (Si-QUAT) ratios ranging between 5:1 and 7:1, based on the dry actives' contents. The pH of the end solutions was adjusted to 4 with the addition of a few drops of an aqueous KOH (0.1 M)

solution. Then, they were stirred for 10 min and left for 24 h to complete aging. Finally, the fourth part of TEOS-C was diluted with deionized water to a final concentration of 15% w/w of TEOS, and it remained in this state, i.e., without being mixed with the Si-QUAT. The four coating solutions were denoted as Sol-1, Sol-2, Sol-3 and Sol-4, respectively (Table 1).

Pine wood samples were each ultrasonically cleaned with ethyl alcohol and water for 10 min. Then, they were dried in an oven for 4 h at 90 ℃ to reach a totally dry state. The marble and stone samples were washed with tap water and then rinsed with a mixture of deionized water and acetone (70:30 v/v). They were left to dry under ambient conditions for three days before they were placed in an oven for 24 h at 90 ℃ to complete drying. Sol-1, Sol-2 and Sol-3 coating solutions were deposited onto both wood and mineral substrates by simple spraying. Coated specimens were then left to cure under ambient conditions for three days. Sol-4 was deposited only on wood and served as a control sample in order to evaluate the antifungal efficacy of coatings.

Table 1. Chemical composition of coating solutions.

Solution	TEOS (dry content, %)	Si-QUAT (dry content, %)	Water, %
Sol-1	7	2	14.82
Sol-2	10	2	20.83
Sol-3	7	1.4	31.64
Sol-4	15	0	15

2.3. Characterization

Coated samples were subjected to a series of tests. For most of them, WCA measurements were applied to examine the coatings' properties with respect to the variation of the sample's surface energy prior to and after the test. Different coated samples were used for each test. In all cases, the static contact angles of coatings were measured at the ambient temperature by using an OCA 15EC video-based optical contact angle-measuring instrument (DataPhysics Instruments GmbH, Germany) equipped with SCA 20 software. Testing was performed with deionized water with an initial conductivity of less than 5 μS/cm. The contact angle was averaged over six measurements on the same surface. The coating thickness was determined by performing cross-sectional imaging of the coated samples using scanning electron microscopy (SEM; JEOL JSM 6610LV). The parameters used for imaging are reported elsewhere [34]. Only coated polished marble was evaluated via this method since the rest of the substrates examined were not smooth; thus, coating thickness might interfere with substrate roughness. Since the application method was the same for both mineral and wooden substrates, it was assumed that the same amount of coating was deposited on the surface, regardless of substrate type. It should be pointed out, though, that the porosity of wooden substrates was higher than the porosity of mineral substrates; therefore, the thickness of coatings on wood was assumed to be less than the thickness of coatings deposited on marble and stone. Therefore, the thickness of coatings on rough substrates was also indirectly evaluated in terms of the difference in weight between uncoated and coated samples and the coating's density, as determined via the SEM analysis mentioned above.

2.3.1. Characterization of coatings on mineral substrates

Hydrophobicity was determined by measuring the static contact angles of deionized water on the surface of coated samples. The retention of water-repellent attributes under capillary pressure was also evaluated after conducting a water absorption test. More specifically, the coated sides of two pre-weighted mineral specimens (the unpolished marble sample and the Karystos stone sample) were immersed into a vessel of distilled water for 150 min under ambient conditions. The amount of absorbed water per unit area was recorded at time intervals of 15 min. The WCAs were also recorded. Chemical resistance of the coatings was evaluated through the reduction of hydrophobicity, as recorded after subjecting the samples in aqueous solutions of various pH values for 24 h. Different samples were used for each test. All samples were then rinsed with copious amount of water and left to dry at ambient temperature for 24 h. Furthermore, coated samples were subjected to 200 cycles of wet abrasion scrub testing according to the EN ISO 11998:2006 standard with the aid of a BYK 5063 Gardner-scrub wipe tester (BYK-Gardner Gmbh, Germany). A silicon carbide pad (Scotch-Brite pad, No. 7448, type S) was used to scour the surface. Deionized water served as the liquid medium. The WCA of abrasively worn surfaces was then measured in order to assess the abrasion resistance of the coatings. Again, the contact angle was averaged over six measurements on the same surface. Salt crystallization effects were examined by immersing the mineral substrates in a warm (60 °C) saturated solution of sodium sulfate for 4 h. Samples were then left to cool at ambient temperature and the WCAs were recorded. Finally, the fungistatic activity of coatings was qualitatively evaluated only on coated marble by using an aqueous solution (0.1% w/v) of BB. Specifically, 0.5 mL of the dye was dropped onto the coated substrate via a syringe and left to dry for 5 min under ambient conditions. Then, the substrate was rinsed with tap water to remove all traces of the residual dye. Assessment of the antifungal activity was verified by visual inspection of the treated sample. The results were largely indicative, i.e., the test was used to verify that the coatings had an inherent antifungal activity rather than to accurately assess their efficacy.

2.3.2. Characterization of coatings on wood substrates

Pine wood specimens treated with TEOS:Si-QUAT and TEOS 15% solutions were subjected to a contamination resistance test. Specifically, 3 mL of three common liquids (milk, coffee, tea) were dropped onto the test surface via a syringe and left to dry for 1 h under ambient conditions. The specimens were then thoroughly rinsed with distilled water and visually observed. When dried, the WCAs were measured. The stain-repelling properties of the coatings were evaluated by comparing their WCA values with the ones recorded after performing the above procedure on an untreated pine wood specimen. Moreover, changes in the hydrophobicity of coatings after heating were determined by placing treated wood specimens in an oven and heating them at moderate temperatures ranging from 25 to 100 °C for 6 h. After cooling the samples to ambient temperature, the WCA values were recorded. The durability of treatment was assessed through the variations in measured WCA after repetitive water submersion test cycles and the leaching tendency of coatings in an aggressive chemical environment. More specifically, water submersion testing took place by placing treated samples into a vessel of deionized water, which was 10 times the volume of the wood specimens, for 10 h and heating them in an oven for 8 h at 105 °C until complete drying was achieved. The cycles were repeated 10 times and followed by a measurement of WCA. The leaching stability of coatings was also determined by

performing a chemical resistance test. Two aqueous solutions, one with pH = 2 (adjusted with an aqueous hydrochloric acid solution (1 M)) and one with pH = 12 (adjusted with sodium hydroxide aqueous solution (1 M)), were used as test solutions. Coated wood samples were immersed into the test solutions for 24 h. At certain time intervals, they were dried in the oven at 105 °C for 8 h before the WCA was recorded. Furthermore, the water uptake of treated samples was evaluated by immersing them into water. After 30 days of continuous immersion, the change in their weight was recorded. The fungistatic activity of coatings was qualitatively evaluated on flat pine-wood tongue depressors by using the above-mentioned aqueous solution (0.1% w/v) of BB. Again, 0.5 mL of the dye was dropped onto the coated substrates via a syringe and left to dry for 5 min under ambient conditions. Then, the substrates were rinsed with tap water to remove all traces of the residual dye. Assessment of the antifungal activity was carried out by visual inspection of the sample and verification of the depth of the blue color remaining on the substrate, as according to a color standard from BIOSAFE (Gelest, Inc.). Finally, the resistance against fungal decay was determined through a decay resistance test by the use of the brown-rot fungus Coniophora puteana (BAM Ebw. 15, DSM 3085) in a mini-block test. Before testing, the coated samples were left to cure under ambient conditions for three days. Then, they were weighed to determine their dry mass. Prior to fungal exposure, the coated specimens were subjected to a standardized leaching process (EN 84). Then, they were kept at 26 °C and a relative humidity of 55%–65% in a conditioned room for 1 week. Sterilization at 60 °C for 60 min inside of a dry-heat sterilization oven followed. Subsequently, the samples were aseptically inoculated on 3% malt extract agar (Sigma Aldrich) in Petri dishes (9 cm in diameter, 15 mm deep) according to the EN 113-1 standard. In each Petri dish, three treated samples and three controls were exposed to the fungi. The exposure time was 6 weeks. The effectiveness (and durability) of treatment was assessed through the mass loss of coated samples.

3. **Results and discussion**

3.1. Effectiveness of coatings on mineral substrates

After curing was completed, the hydrophobicity and water repellency were examined by measuring the coatings' WCA values. As can be observed from the results (Table 2), the nature of the substrate induced significant variations in the recorded surface energy for the same coating solution.

In the case of Karystos stone, the initial WCA values were hard to record prior to the coating's deposition due to the quick absorption of water, which resulted from their increased porosity and increased surface energy. In contrast, the wetting properties of coated samples had dramatically changed since the strong hydrophobic behavior manifested, regardless of the amount of solids contained in the coating solution. In addition, an increased fluctuation in the measurements of samples coated with Sol-1 and Sol-3 was observed. In the case of Sol-1 particularly, WCAs up to nearly 120° were recorded. Despite the reduction of the Si-QUAT weight ratio, Sol-2 was also highly hydrophobic due to an increase in the solids' content. On the other hand, samples treated with Sol-3 exhibited much weaker water repellency with WCA values on the order of $91 \pm 2.5°$. The above findings indicated that the total amount of solids in the coating solution, as well as the weight ratio between TEOS and Si-QUAT, had a great impact on the final wetting behavior of the substrate and, thus, on its potential self-cleaning ability.

Table 2. Static WCAs of coatings applied on mineral substrates.

Substrate	Coating solution	Static WCA
Unpolished Marble (untreated)	-	$39.7 \pm 1°$
Unpolished Marble	Sol-1	$114.0 \pm 1.5°$
Unpolished Marble	Sol-2	$106.0 \pm 2°$
Unpolished Marble	Sol-3	$88.5 \pm 1°$
Karystos Stone (untreated)	-	$24.5 \pm 1°$
Karystos Stone	Sol-1	$118.5 \pm 1.5°$
Karystos Stone	Sol-2	$111.5 \pm 2.5°$
Karystos Stone	Sol-3	$91.0 \pm 2.5°$
Polished Marble (untreated)	-	$30.1 \pm 1°$
Polished Marble	Sol-1	$98.0 \pm 2°$
Polished Marble	Sol-2	$97.0 \pm 1.5°$
Polished Marble	Sol-3	$73.0 \pm 1°$

Furthermore, as compared to Karystos stones, marble substrates had, in all cases, lower WCA values (Figure 1). This was attributed to the marble's chemical composition. Marbles were composed of recrystallized carbonate minerals, mainly calcite or dolomite; therefore, the hydrolytic stability of the resulting bonds with silanes was rather poor. However, they were found to exhibit hydrophobic characteristics after being treated with the TEOS:Si-QUAT solutions, probably due to the penetrating ability of the latter. In other words, impregnation with the silica-rich encapsulated structure was supposed to be the primary adhesive mechanism, regardless of the ability of available silanols to crosslink with anchor sites of the substrate. In addition, it was evident that polished marble had to be coated by solutions with higher concentrations of the active components in order to achieve sufficient hydrophobicity, and this is due to their low surface roughness. The thicknesses of the coatings on the polished marble substrates were approximately 300, 450 and 200 nm for the Sol-1, Sol-2 and Sol-3 coating solutions, respectively.

Capillary water absorption testing was performed only on Karystos stone and unpolished marble. Polished marble specimens were not subjected to testing since the polishing process creates tight scratch patterns that reduce the size of pores and capillaries, thus interfering with the coating's actual ability to reduce water uptake. More specifically, the coated sides of two pre-weighted mineral specimens (i.e., the unpolished marble sample and the Karystos stone sample) were immersed into a vessel of distilled water for a total duration of 150 min under ambient conditions, and the weight of absorbed water per unit area (g/cm^2) was recorded at 15-min time intervals. The results are plotted in Figure 2, which shows the amount of water per unit area absorbed by the two specimens after being in contact with water for each one of the above time intervals (15, 30, 45 min). The test revealed that coated Karystos stones offered enhanced protection against the capillary rise of water. In contrast, coated marble specimens were more susceptible to water uptake despite their strong initial hydrophobicity, thus implying that water absorption and repellency are not necessarily directly proportional to the static WCA. In addition, it was demonstrated that water absorption is affected by the coating thickness. More specifically, it was found that specimens coated with the Sol-2 coating solution absorbed water at a ratio that decreased slightly more than that for the Sol-1-coated samples, especially after about 60 min of immersion. This behavior was attributed to the larger thickness of

Sol-2 coatings, and it was more pronounced on marble substrates, rather than on Karystos stones, probably due to the larger porosity of the former. However, the total amount of water that Sol-1-coated samples absorbed was less than that of Sol-2 coated samples, which highlighted the strong influence that hydrophobicity had on water uptake, especially at the first stages of immersion. Furthermore, Sol-3-coated samples were more prone to water absorption, since both the initial hydrophobicity and thickness values were the lowest among the samples examined. Finally, the static WCAs after the water absorption test are illustrated in Figure 3. Only the Sol-1-coated samples were evaluated since these were the most effective against water absorption. It was found that the initial WCAs were relatively unaffected by potential swelling or other effects.
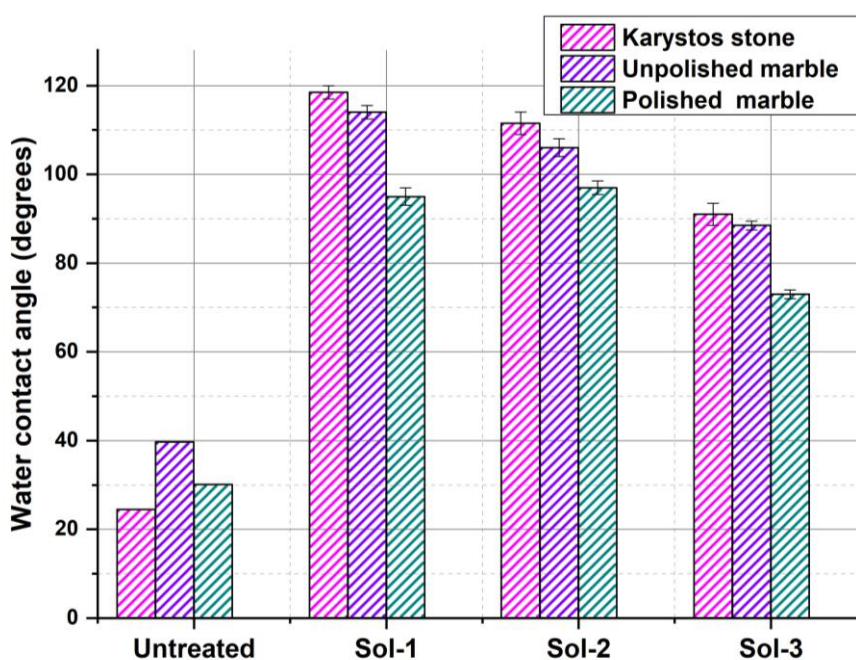
Figure 1. Average of measured WCAs on stone and marble substrates.

With regard to the effect of pH changes on the hydrophobicity of coatings, it was evident (Figure 4) that the samples with increased hydrophobicity, such as the Karystos stone samples, were able to retain their water-repellent properties after being subjected to both acidic and alkaline solutions. On the contrary, the wetting behavior of marble was significantly affected by the pH, especially when the latter was increased at values close to 12, probably due to substrate degradation.
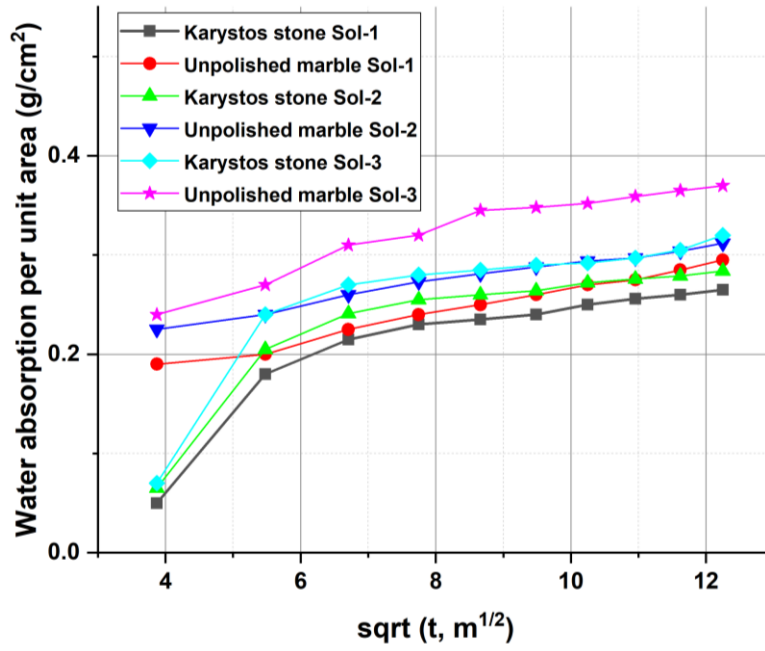
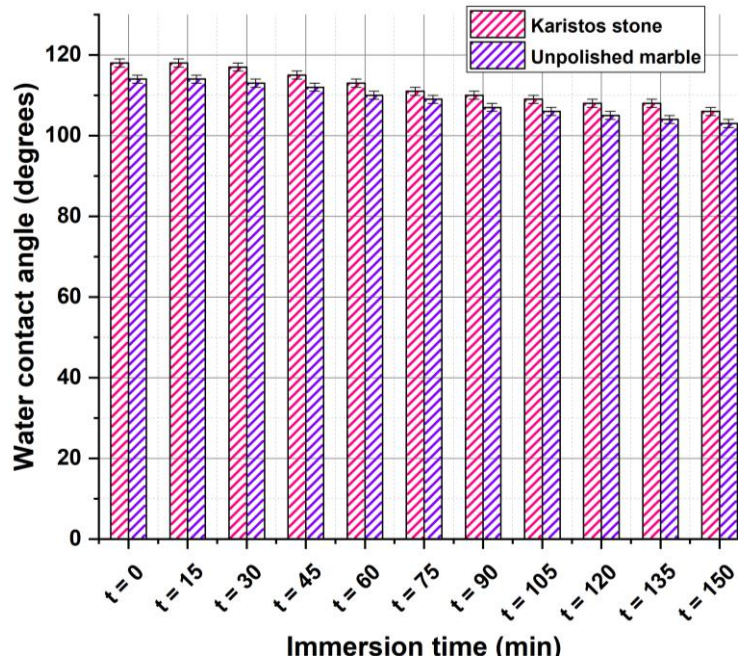**Figure 2.** Water capillary absorption test on Karystos stone and unpolished marble.

Figure 3. WCAs of Karystos stone and unpolished marble after water capillary absorption test.
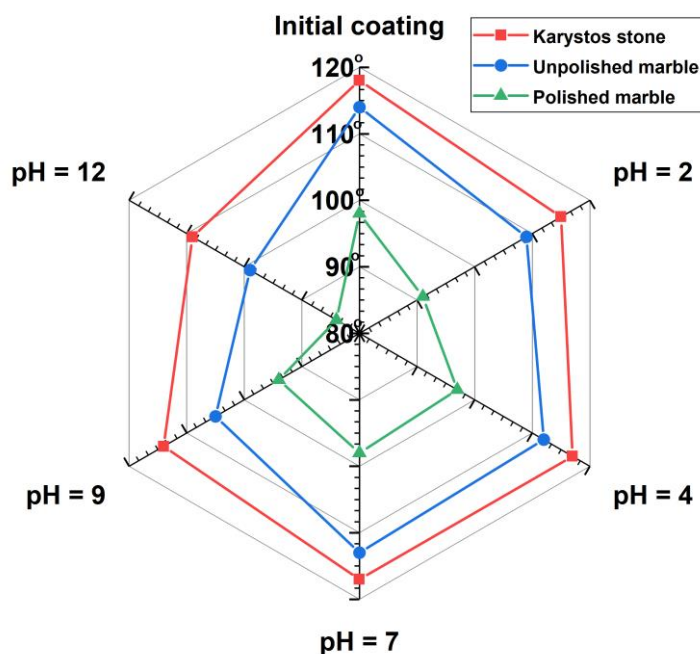
Figure 4. Effect of pH changes on the static WCAs of coatings.

Furthermore, the influence of the abrasion test on the coated marble and stone substrates was strong (Figure 5). Due to the brittle nature of mineral surfaces, the abrasion resistance of coatings deposited on marble and stone is, in fact, dictated by the abrasion resistance of the substrate itself. Therefore, it was no surprise that the WCAs measured on Karystos stones after the abrasion test were significantly reduced. This reduction was pronounced due to the inherent roughness of the uncoated substrate. Similarly, marble stones lost their hydrophobic properties, almost completely, after 150 abrasion cycles. In that case, the coating's inability to remain grafted onto the substrates resulted from the lack of active anchor sites. The best results were obtained in the case of the polished marble specimens, obviously due to the increased substrate smoothness.

Finally, the WCA values after the salt crystallization test are presented in Figure 6. The results demonstrated that the saturated salt solution had only a minor influence on the final coating performance.

In order to qualitatively evaluate the antifungal efficacy of the treated mineral substrates, an aqueous solution (0.1% w/v) of BB was used. Only the Sol-1 coating on marble was evaluated. An uncoated specimen was also used for comparison. Specifically, 0.5 mL of the dye was dropped onto the coated substrate via a syringe and left to dry for 5 min under ambient conditions. Then, the substrate was rinsed with tap water to remove all traces of the residual dye. A dark blue color remained on the coated sample, while no color was detected on the uncoated one. It is known that the blue color indicates the presence of cations, which interact with the anionic dye. As a result, the presence of a large number of immobilized quaternary ammonium compounds, indicating sufficient antifungal activity, was verified.
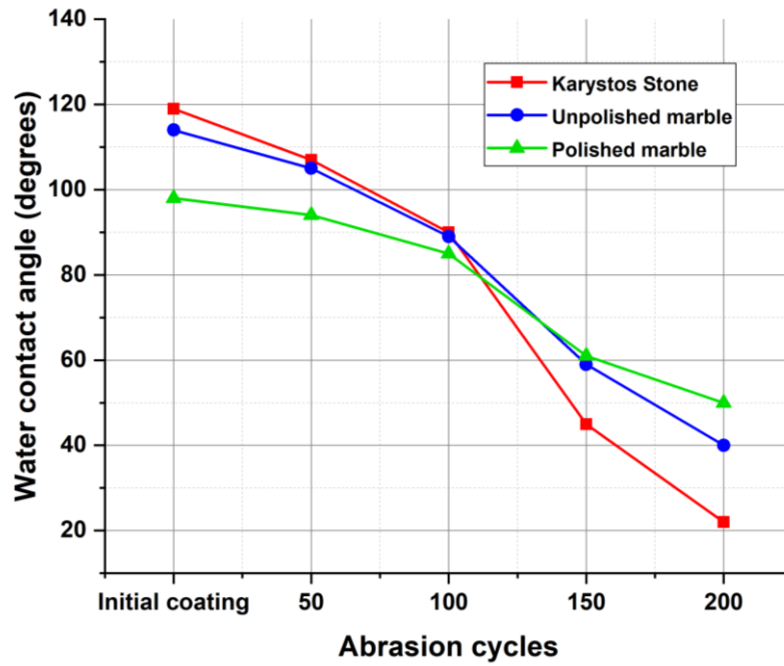
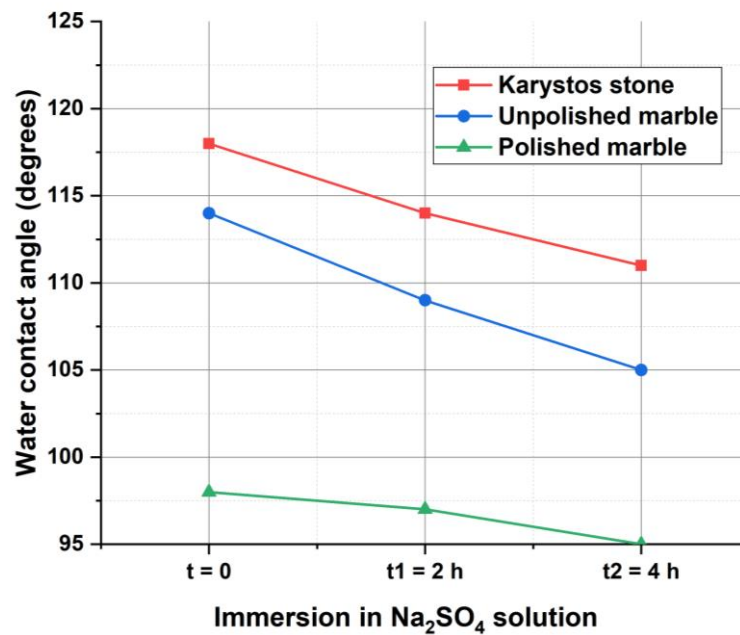**Figure 5.** WCAs of treated Karystos stone and unpolished marble specimens after abrasion.

Figure 6. Results of measured WCAs after immersion of Sol-1 specimens in a saturated Na_2SO_4 solution.

3.2. Effectiveness of coatings on wood substrates

The WCAs of the coatings on wood substrates are shown in Figure 7. Samples exhibited pronounced water-repellent properties, which were attributed to the C-18 aliphatic chain of Si-QUAT. Ethyl alcohol improved the wettability of the surface, thus leading to strongly adhered low-surface energy nanostructures. No visible change or crack formation was noticed on the treated substrates.

Untreated wood samples were hydrophilic, with WCAs on the order of 72º. Among the wood samples coated with Sol-1, Sol-2 and Sol-3, it was proven that Sol-2 yielded higher WCAs, reaching up to 125º. This increase (+5º) in the coating's hydrophobicity was attributed to the additional amount of solids contained in the coating solution. In contrast to the stone substrates, wood specimens were generally more hydrophobic. The latter type was more reactive to alkoxysilanes due to their polar nature, while, at the same time, their decreased porosity inhibited impregnation by the coating's solution. As a result, the formation of a surface hydrophobic monolayer was facilitated.
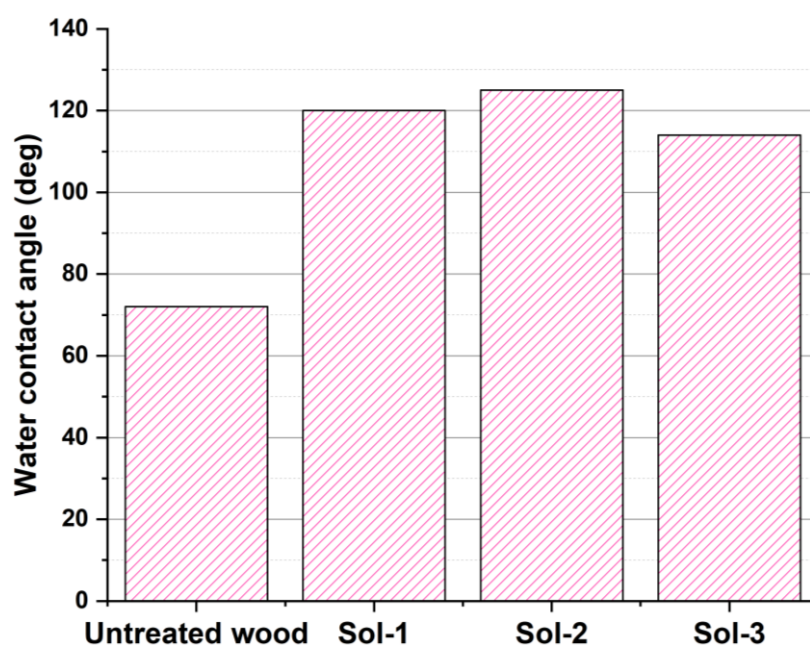

Figure 7. Values of static WCAs measured on untreated pine wood specimens and treated with Sol-1, Sol-2 and Sol-3, respectively.

Table 3 summarizes the results of the qualitative contamination test, i.e., the resistance of pine wood specimens against staining by common liquids (milk, coffee, tea). Since these were organic substances, it was expected that the hydrophobic coatings examined within this work would have limited cleanability. Surprisingly, it was found that TEOS:Si-QUAT-modified pine wood presented good repellent properties, leaving no trace of contaminants on the substrates. In contrast, when the Sol-4 (15% TEOS without Si-QUAT) coating solution was used, the measured WCA was less than the hydrophobicity threshold of 90º. This finding highlighted the fundamental role of Si-QUAT in the development of contamination-resistant attributes. The underlying mechanism for this may be related to the latter's surfactant properties that are triggered by the coexistence of cationic R_3N^+ groups and

non-polar methyl groups which aided in the effective solubilization of both inorganic and organic contamination and their facile removal after thorough rinsing of the substrate with water.

Table 3. Contamination-resistance test with common liquids (milk, coffee, tea) on untreated and treated pine wood samples.

	Sol-1	Sol-2	Sol-3	Sol-4	Untreated
Liquid Contaminants	No-traces	No-traces	No-traces	Traces	Impregnation
WCA	$\geq 100º$	$\geq 100º$	$\geq 100º$	$<90º$	$<80º$

Several TEOS:Si-QUAT-modified pine wood samples were exposed to heating. All wood specimens possessed hydrophobicity after exposure to the heating test. According to the line chart (Figure 8), substrates coated with Sol-1 and Sol-2 showed higher resistance to heat, as compared to those treated with Sol-3, probably due to the increased thickness (approximately 300–400 nm) of the silica matrix.
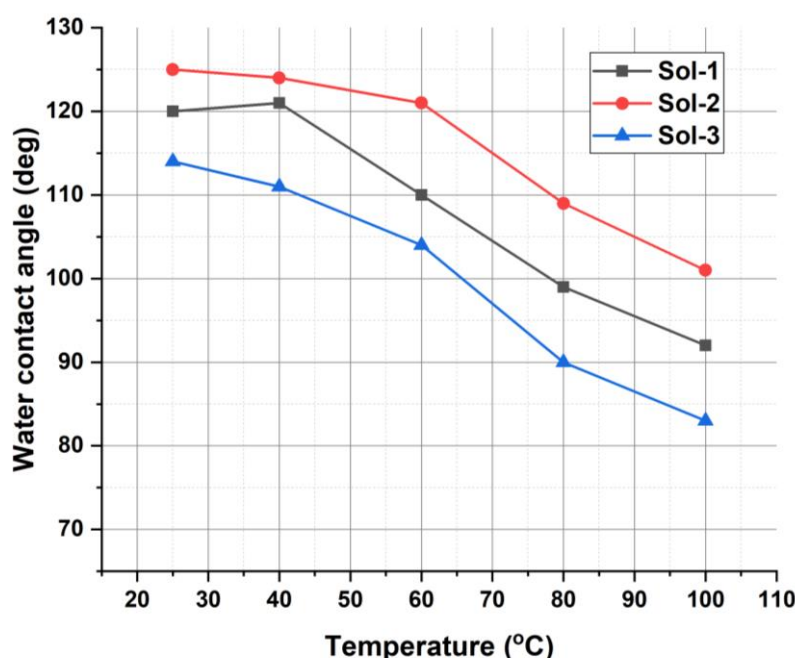

Figure 8. Changes in recorded hydrophobicity of coated samples after heating them at various temperatures between 25 and 100 °C.

In Figure 9, the WCA results associated with the water submersion tests are shown. It was found that, as the number of water submersion cycles increased, the hydrophobicity of the coatings was reduced. The latter remained almost constant for the first four cycles. After the fifth water submersion cycle, an almost linear reduction in hydrophobicity was observed. This was probably due to the onset of a water absorption mechanism. Finally, after 10 submersion cycles, the average WCAs for samples treated with Sol-1 and Sol-3 were $78 \pm 2º$ and $69 \pm 2º$, respectively, while, in the case of specimens coated with Sol-2, the average WCA recorded was $88 \pm 2º$. The latter can almost still be characterized as hydrophobic, indicating longevity and resistance to swelling and shrinking under moist conditions.
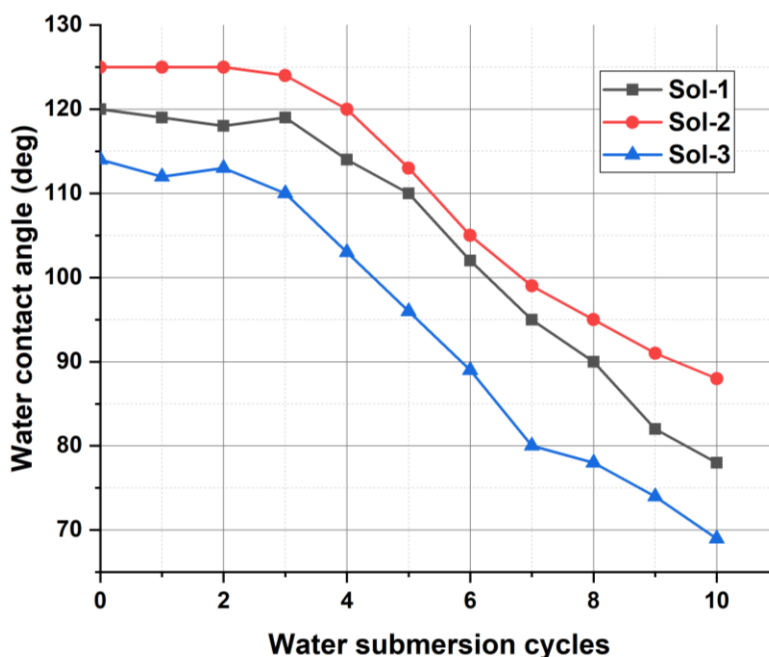
Figure 9. Measured WCAs after 10 repetitive water submersion/drying cycles.

The leaching stability and chemical resistance of the coatings were investigated by submersing the pine wood samples into acidic (pH = 2) and alkaline (pH = 12) aqueous solutions for 24 h. WCAs of the coated samples were recorded every 4 hours for the first 16 h of the immersion; then, one last measurement was recorded during the period of 16–24 h, as can be seen in Figure 10a,b. For pH = 2, it was noticed that samples coated with Sol-2, which demonstrated the highest WCAs before the immersion test, retained their stability and water-repellent properties (WCA ≈ 100º) after the chemical resistance test. Oppositely, the sample treated with Sol-3 had an initial WCA on the order of 114º. This value was reduced to about 70º after 24 h of immersion in the solutions, probably indicating inadequacy of the alkoxysilane molecules in the coating solution. Broadly, a similar behavior was observed for the treated samples submersed in the alkaline (pH = 12) solutions, although the effects of testing were, in this case, somewhat milder. It was only for the Sol-3 treatment that, perhaps, the reduction in WCA a bit more abrupt. This could be attributed to the low density and thickness (150–200 nm) values associated with the silica framework, which accelerated dissolution and deprotonation mechanisms, thus leading to the formation of highly polarized interatomic Si–O bonds, which enhanced silicon leaching.

A water absorption test was also conducted, but only for the samples treated with the Sol-2 composition. In general, the water uptake of wood substrates occurs in the axial (longitudinal) direction rather than in the radial direction due to the wood cell orientation. The uptake of impregnates is also referred to as the weight percent gain (WPG), and it was recorded by using Eq 1:

$$WPG(\%) = \frac{W_t - W_0}{W_0} 100\% \tag{1}$$

where W_0 and W_t express the values of untreated and treated wood specimens, respectively, when they are in a totally dry state.
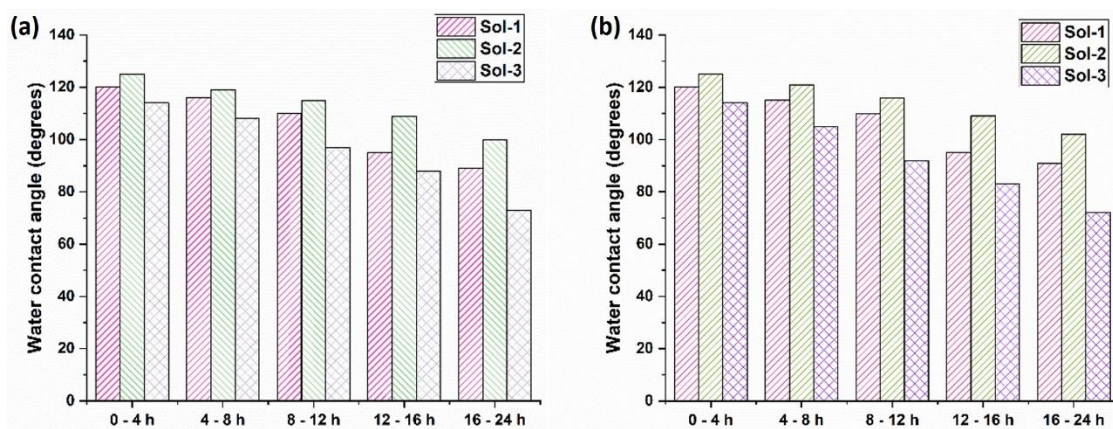
Figure 10. Effects of (a) acid (pH = 2) and (b) alkaline (pH = 12) aqueous solutions on the leaching tendency of coatings.

Figure 11 illustrates the change in weight of both treated and untreated wood specimens after a 30-day immersion period in water. It was observed that the treated samples were almost non-absorbent after the first 15 days. Since the coating was relatively thick (300–400 nm), it was assumed that it could not be penetrated by water. After the 15th day, an upward tendency of the absorption rates, i.e., up to about 58.5%, was noticed, obviously due to the onset of capillarity. Penetration of liquid water in the pore network of wood was more evident in the case of untreated samples, where the absorption rate was periodically increased, ultimately reaching a value close to 76.5%.
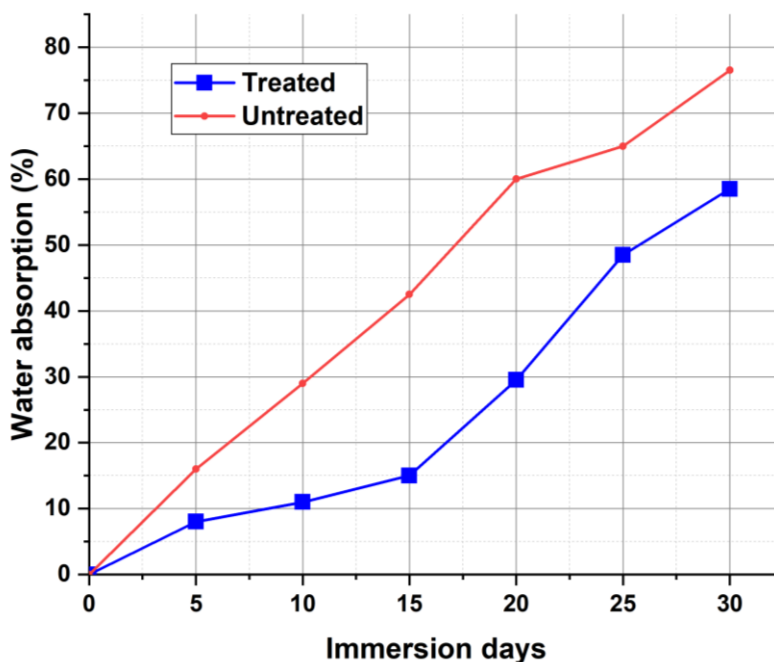

Figure 11. Water absorption comparison between untreated and treated Sol-2 wood specimens after a 30-day immersion period in water.

Continuing with the antifungal activity of coatings, it should be noted that Si-QUAT can offer antifungal attributes to porous surfaces owing to its contact-killing mechanism, which prevents microorganism growth, especially for mosses, algae, lichen and fungi. This activity is based on quaternarized N^+R_3 polar groups which interact with the negatively charged outer membrane of microorganisms. The latter is disrupted by the long aliphatic chain of the silane's hydrophobic tail. As a consequence, the primary functions of the cytoplasmic membrane are destroyed, thus leading to cell death [35]. Moreover, in contrast to the vast majority of antibacterial and antifungal agents, the head group of Si-QUAT, containing terminated silanol groups, facilitates its grafting with other alkoxysilanes or that immediately to the substrates via condensation. As a result, biocide leaching is prevented.

Similar to the marble substrates, the antifungal efficacy of treated specimens was qualitatively evaluated by using the same aqueous solution (0.1% w/v) of BB. When the blue color remained on the surface after being rinsed with water, ionic complexation between quaternary ammonium cations and the anionic dye was indicated. Evaluation of the antifungal activity was then evaluated by comparing the depth of the retained blue color against a color standard. In order to facilitate the handling of samples, the above test was performed on flat pine-wood tongue depressors. Only the Sol-2 and Sol-3 coatings were evaluated, as these performed better than Sol-1 in previous test studies. Untreated samples, as well as substrates coated only with TEOS, were also evaluated.

The presence of residual quaternary ammonium compounds was detected in situ after the dye was deposited onto the surface of the two samples treated with TEOS:Si-QUAT solutions. The blue stains remained on the surface following a rinse with copious tap water, thus indicating the immobilization of Si-QUAT molecules (Figure 12). It was noticed that the TEOS:Si-QUAT samples had darker blue stains than those treated without Si-QUAT. Compared to the untreated wood, the TEOS-treated substrate also had a darker color. However, this was obviously less homogeneous, thus indicating that the blue stain observed was, in reality, the result of dye absorption from the substrate, but without the formation of any complex. Finally, by qualitatively comparing Sol-2 and Sol-3 with the standard color code (Gelest. Inc.), a strong antifungal activity was, in both cases, manifested.
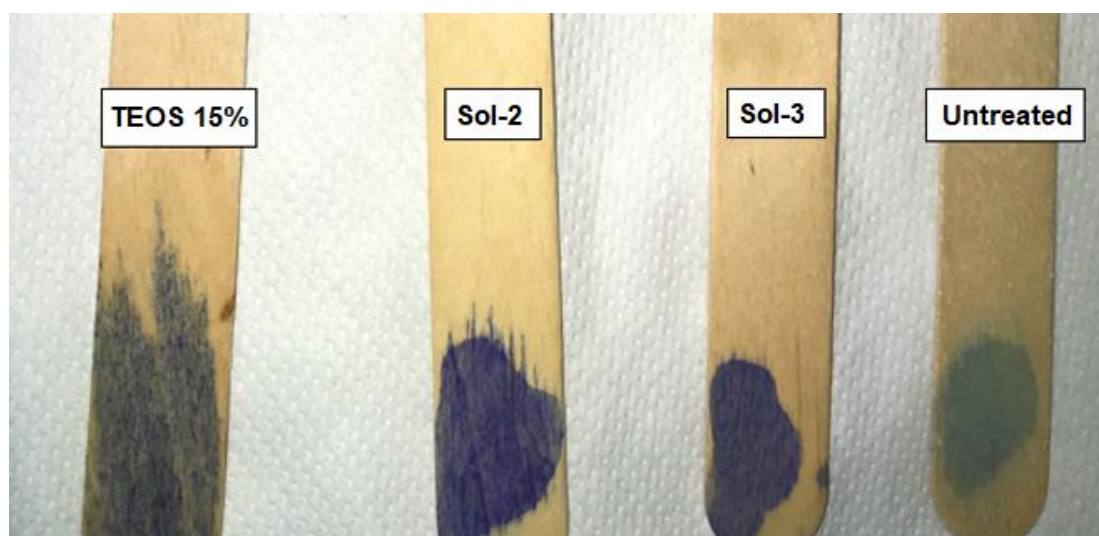

Figure 12. Qualitative BB dye test on four wood samples.

Finally, the resistance to fungal decay was determined through a decay resistance test by the use of a brown-rot fungus in a mini-block test. The same coated pine wood boards ($10 \times 10 \times 30$ cm^3) used for measuring static WCAs were used as substrates. Decay assessment after 6 weeks of exposure to a wood-destroying fungus (Coniophora puteana) revealed a mass loss of less than 3% for both TEOS:Si-QUAT solutions (Figure 13). In contrast, the recorded mass loss of the TEOS-only sol was on the order of 10%, which indicated the fundamental role of Si-QUAT in the antifungal activity of the treatment. It was assumed that the lack of surface-active quaternary ammonium groups allowed for the onset of biodecay processes more easily. Obviously, the results were dependent on both the duration of exposure as well as the dimensions of the coated samples. Several studies have shown that reducing the dimensions of coated specimens may accelerate the rate of wood biodeterioration, while, in the case of short test periods, the delay of colonization may be long. In addition, the coating's application method was also important to its biocidal activity. It was expected that the impregnation of wood specimens by the coating solution would significantly increase their biodecay resistance relative to spray coating. Nevertheless, some preliminary conclusions regarding the level of protection that the TEOS:Si-QUAT treatment offers to wood samples were easily drawn. It should also be stated that the TEOS-only sol also provided a minor level of protection to pine wood against *C. putaena*. The mass loss was slightly less than that of the untreated sample, especially after 6 weeks of exposure. It was assumed that the penetration of low-molecular-weight diffusible compounds, which is required for fungal degradation, was, to some extent, inhibited by the siloxane matrix, which caused cell wall bulking and micropore blocking.
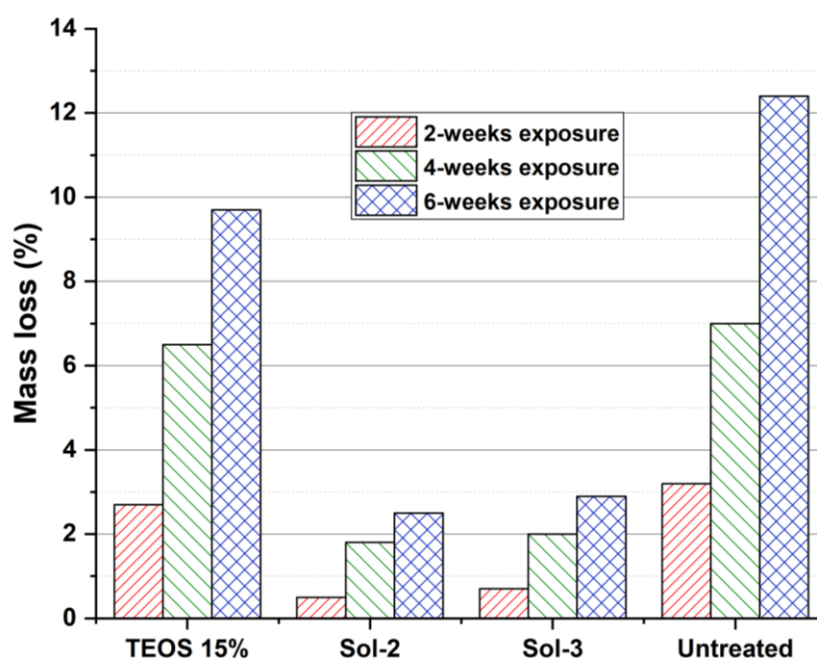

Figure 13. Mass loss of treated and untreated wood samples after 2, 4 and 6 weeks of fungal decay. Samples were exposed to *C. putaena*.

4.   Further discussion

In general, the use of alkoxysilanes, such as TEOS, generates a dense silicic structure with the ability to penetrate the porosity of various substrates, such as mineral and composite substrates. In addition, the primary mechanism of alkoxysilane bonding is the formation of Si–O–Si groups through silanol grafting on surface hydroxyl groups. Alkoxysilanes are widely used for the protection and consolidation of buildings, mainly due to its low viscosity, which facilitates deep penetration into natural stone. On marble especially, the function of alkoxysilanes can be explained as the filling of narrow voids between calcite grains. Furthermore, on wooden surfaces, alkoxysilanes are strongly bounded, providing stabilization to the lignin matrix and minimizing water uptake.

In this work, besides its pore-sealing and impregnation properties, TEOS also promoted the formation of a silica matrix surrounded by anchor sites, allowing the Si-QUAT molecules to graft onto them via siloxane bonding. Therefore, it was expected that blended –Si–O–Si– and –Si–O–R– covalent bonds were sufficiently polymerized, thus creating a three-dimensional, functionalized silicon skeleton within mineral and wood specimen pores.

The formation of the above skeleton was realized by separately pre-hydrolyzing TEOS and Si-QUAT. The addition of hydrochloric acid facilitated an increase of the hydrolysis rate for both TEOS and Si-QUAT molecules. Mixing of the latter led to the formation of hybrid structures, which then co-condense. At this point, condensation seemed to be largely promoted by the increase of pH. At the same time, the rate of hydrolysis decreased. In this way, the polymerization of silane oligomers was accelerated, ultimately reaching a point at which a three-dimensional silsesquioxane system was developed. The lipophilicity provided by alkyl moieties, combined with the stability of the siloxane matrix and the biocidal properties of quaternary ammonium compounds, imparted strong hydrophobization and antifungal properties to both mineral and wooden substrates.

The TEOS:Si-QUAT concentration ratio in the sol coating had a prominent role in the configuration of the resulting structure and its fungal activity. By increasing Si-QUAT concentration, the antifungal activity of the resulting structure obviously increased, too. When the concentration of TEOS was reduced, the spacing among hydrophobic C-18 chains, which was attributable to the mutually repelled cationic groups (R_3N^+), forced Si-QUAT molecules to align themselves like vertical nanopillars, which promoted water-repellent functionality at the expense of a somewhat compromised biocidal efficacy. Accordingly, it should be expected that there would be an optimum ratio at which sufficient hydrophobicity and antifungal activity were simultaneously present.

Concerning conventional quaternary ammonium compounds, it should be stated that these can be directly fixated to wood cell walls via cation exchange interactions with carboxyl and phenolic hydroxyl groups in lignin [33]. In this work, the Si-QUAT molecules were supposed to adhere to the substrate, directly and indirectly, through the siloxane matrix. Moreover, due to the excess amount of TEOS used in all coating sols, it was assumed that the second, indirect configuration was the predominant one. The latter seemed to provide a robust bifunctional structure with strong antifouling properties.

The effectiveness of the proposed approach was particularly evident in the case of coated wood specimens. The mass loss values recorded demonstrated that the TEOS:Si-QUAT coatings prevented the biodecay of wood by fungi. In contrast to conventional quaternary ammonium groups, which are strongly dependent on the surrounding pH, the Si-QUAT molecules used in this study were assumed to be constantly fixed to the siloxane background. This was considered to be an additional benefit of the proposed approach since the resulting structure could not leach out to the environment and thus

posed no threat to human health. Furthermore, in this way, the quaternary ammonium groups cannot be metabolized by the fungus; therefore, the formation of resistant superbugs may be prevented.

The above approach has great potential applicability for smooth, non-porous surfaces as well, as it may be able to effectively address the problem of surface pollution, especially in cases in which the deposition of common water-repellent coatings does not bring significant benefits. It is also possible to incorporate similar compositions into antifouling coatings for metal surfaces, such as the hulls of ships [36]. To this end, a viable strategy could be the development of additive formulations based on the above TEOS:Si-QUAT sols, which would then be incorporated into water-soluble resins via silane coupling agents to produce durable and more efficient marine antifouling paints. This work is currently underway.

5. Conclusions

From this work, a bifunctional hydrophobic and antifungal clear coating has been proposed. For the fabrication procedure, ambient conditions, low-cost laboratory equipment and environmentally friendly materials were employed. A Si-QUAT was integrated into a three-dimensional silica structure in order to develop a robust antifouling coating with enhanced self-cleaning and biodecay-inhibiting properties. It was found that strong antifungal activity, coupled with satisfying water-repellent properties and chemical and mechanical stability, is possible on both mineral and wood surfaces at low concentrations of the Si-QUAT. The proposed strategy has distinct advantages over traditional hydrophobic, antifouling and antibacterial approaches.

Use of AI tools declaration

The authors declare that they have not used artificial intelligence tools in the creation of this article.

Conflict of interest

The authors declare no conflict of interest.

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