Organic−Inorganic Hybrid Compounds Containing Polyhedral Oligomeric Silsesquioxane for Conservation of Stone Heritage

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ABSTRACT Alkoxysilane solutions based on tetraethoxysilane (TEOS) have been widely used for the consolidation of decaying heritage stone surfaces. TEOS-based products polymerize within the porous structure of the decaying stone, significantly increasing the cohesion of the grains of stone components. However, they suffer from practical drawbacks, such as crack formation of the gel during the drying phase due to the developing capillary force and dense gel fractures left inside of the stone. In this study, a TEOS-based stone consolidant containing functional (3-glycidoxypropyl)trimethoxysilane (GPTMS) and polyhedral oligomeric silsesquioxane (POSS) has been prepared in order to reduce gel crack formation during the drying phase. The addition of nanometer-sized POSS and/or GPTMS having a flexible segment reduces the capillary force developed during solvent evaporation. The properties of the TEOS/GPTMS/POSS composite solutions were compared with those of commercial products (Wacker OH and Unil sandsteinfestiger OH 1:1). The gelation time was similar to that of commercial consolidants, and the TEOS/GPTMS/POSS solution was stable over a period of up to 6 months. The addition of POSS and GPTMS provided a crack-free gel, while the gel from the commercial consolidants exhibited cracks after drying. The surface hydrophobicity of the treated decayed granite increased with the addition of POSS and GPTMS, and it was higher than that of the commercial product, implying the possibility of POSS and GPTMS as barriers to the penetration of water. This result implies that the TEOS/GPTMS/POSS solution showed a high suitability for the consolidation of granite heritage.

KEYWORDS: stone consolidation • tetraethoxysilane • polyhedral oligomeric silsesquioxanes • (3-glycidoxypropyl)-trimethoxysilane • sol−gel reaction

INTRODUCTION

Surface treatment materials for the conservation of stone monuments located outdoors need to have certain properties such as good coagulation between grains comprising the stone monument to restore its strength and hydrophobicity to block water penetration. Treatment with such materials decreases the risk of the monument being irreparably lost as a result of degradation by natural weathering and air pollution (1, 2).

Alkoxysilanes, such as tetraethoxysilane (TEOS), are commonly used for consolidating weathered stone (3−5). TEOS-based products polymerize in situ inside the porous stone by means of a sol−gel reaction with environmental moisture, providing strength to the structure. In order to optimize the consolidation effect, the consolidants must penetrate deeply into the weathered stone. Unless the consolidant penetrates into the weathered stone until it reaches the intact stone, an internal weakness will be created, which will eventually lead to additional decay phenomena, such as detachments and scaling. From that point of view, the very low viscosity of TEOS-based products is an advantage for stone consolidation. While TEOS increases the cohesion of the grains of the decayed stone via a sol−gel reaction, the gel obtained from TEOS has two drawbacks: crack formation during the drying phase and formation of dense fragments of gel inside the stone (6−9). As reported in several previous studies (6−11), TEOS consolidated materials tend to form brittle gels that are highly susceptible to forming cracks inside the stone, which leads to secondary degradation. Cracking occurs as a result of a differential capillary pressure produced within the gel pores during its drying phase (12). Because the capillary pressure is inversely proportional to the gel network pore radius, it is obvious that the dense microstructure having very small

pores promotes high pressures and subsequent cracking of the network.

Recently, several trials have been carried out to enlarge the gel network pore radius inside the gel through the addition of nanomaterials such as silica nanoparticles (7, 13−20) because larger pores form in the presence of nanomaterials by reduction of the capillary pressure. The other approach is to enhance the ductile properties of the network, as in the new perfluorurate polymers (21, 22), organosilicone-modified polyurethanes (23) and organic segments, to obtain additional flexibility (24), which leads to a smoother transition in the drying phase.

Another drawback of the dense gel debris inside the stone is that the debris blocks the pores of the stone. This may promote a significant reduction in the water vapor evaporation through the stone, preventing the desirable removal of the moisture condensed inside the stone. Therefore, the appropriate way to avoid deterioration is to prevent water from penetrating into the stone, as well as to allow the water vapor inside the stone to easily move out because condensed water is mainly responsible for stone decay.

Although the addition of nanoparticles reduces crack formation in the gel, it still may act as a barrier to water vapor movement. Therefore, we prepared a new consolidant material in order to improve the transport of the water vapor, using a material having nanometer-sized pores. We selected polyhedral oligomeric silsesquioxanes (POSSs), clusterlike oligomers of the type $(R-SiO_{1.5})_n$, with the aim of improving the permeance. The POSSs resemble nanosized particles of SiO_2 having well-defined voids, where small molecules such as water can be easily transported (25).

The study presented here is aimed at the development of TEOS-based consolidants that give improved properties compared to existing commercial products for the preservation of cultural stone monuments. We have prepared and characterized TEOS-based consolidants containing (3-glycidoxypropyl)trimethoxysilane (GPTMS) having flexible segments and nanomaterials. The moderate condensation rate of silanol on GPTMS in the sol−gel process effectively prevented macrophase separation during gel formation. In order to evaluate the suitability of the new materials as stone consolidants, the formation of the gel and characteristics of the treated Korean granite stone were used to preliminarily evaluate their efficacies as conservation materials.

EXPERIMENTAL SECTION

Materials. TEOS and GPTMS were purchased from Sigma-Aldrich Co. Inc. Two POSSs, TriSilanolIsooctyl POSS (SO1455) and TriSilanolPhenyl POSS (SO1458), were purchased from Hybrid Plastics, Hattiesburg, MS. The chemical structures of the POSSs are shown in Scheme 1. Ethanol and dibutyltindiauate (DBLT) were purchased from Samchun Pure Chemical Co. Ltd. and Aldrich, respectively. DBLT, which is also included in the commercial consolidants, was used as a catalyst for the gelation reaction at a neutral pH. A red dye (DyeRed 33, Hyundai Chemical) was used for visual observation. Naturally weathered granite samples from Namsan, Korea, were cut into $3 \times 3 \times (2−3)$ cm³ cubic blocks for the capillary rise application and $(1−2) \times (1−2) \times (5−6)$ cm³ cubic blocks to test the consolidation effect on the stone by immersion as determined by

Scheme 1. Chemical Structures of POSSs (a) SO1455 and (b) SO1458
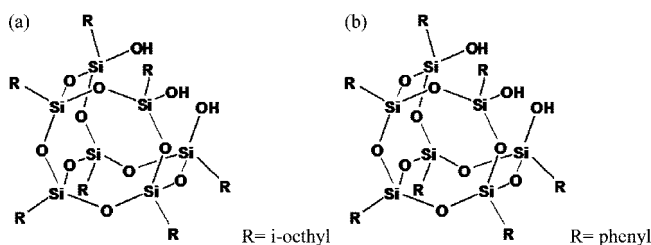
ultrasonic velocity and shore hardness measurements. All stone samples were obtained from one rock specimen for consistency, and the data here are the average of 2−5 samples. The specimens were rinsed with deionized (DI) water for 1 h with ultrasonic agitation and dried in an oven at 150 °C. Commercial consolidation agents (Unil sandsteinfestiger OH 1:1 and Wacker OH) were used as received. The amounts of ethyl silicate of Unil sandsteinfestiger OH 1:1 and Wacker OH are 37% and 100%, respectively.

Preparation Methods. Different molar ratios of TEOS/GPTMS (1:1 and 1:2) solutions were prepared, and an appropriate amount of POSS (1, 3, and 5 wt %) was added. The total silicate weight percents were 35 and 50. DI water was added for stoichiometric content with respect to the amount of hydrolysis of the alkoxy groups in TEOS and GPTMS, and then ethanol was added to reach the final silicate solid content. DBLT (1 wt % of solid content) was added as a catalyst. The solutions were mixed by ultrasonic agitation for 1 h and then magnetically stirred for 24 h at room temperature. The notation 1T1G and 1T2G refers to the 1:1 and 1:2 TEOS/GPTMS solutions, respectively. The gels were prepared at room temperature by pouring the solution into polypropylene dishes. The gelation time was similar for all samples (ca. 2−3 days), and the drying time was determined gravimetrically when the treated stone specimens reached a constant weight ($\Delta M < 0.001$ g); it was completed after 10 days at room temperature.

Consolidation solutions were applied to granite by a capillary rise by placing the samples into a solution of 1 cm in depth (or using the immersion method depending on the characterization measurement). The stone was put into a sealed bottle for 5 days. In all cases, the solution then was distributed evenly through the stone. The treated stone was taken out of the bottle, dried at room temperature until a complete reaction occurred (ca. 2 weeks), and vacuum-dried at 35 °C for 24 h to remove the residuals.

Characterization. The viscosity of the solution was measured with a vibro viscometer using a sine-wave vibro viscometer SV-10 (A&D Co. Ltd.) at 28 °C. Fourier transform infrared (FT-IR) spectra of the gels were measured on a Spectrum 100 (Perkin-Elmer, Inc.) instrument equipped with an attenuated total reflectance detector at a resolution of 4 cm⁻¹. The surface and cross-sectional morphologies of the stone were investigated using a JSM-6300 scanning electron microscope (JEOL Ltd.). The contact angle (θ) of the surface of the stone was measured by a Phoenix 300 contact angle analyzer (SEO Surface Electro Optics Co. Ltd.). Wide-angle X-ray diffraction (WAXS; Rigaku D/Max-2000, Cu Kα) measurements were performed using a conventional diffractometer employing Ni-filtered Cu Kα radiation. Dried sample membranes were used in which the scanning angle was varied from 5° to 55° at a scanning rate of 5°/min. All spectra were measured at ambient temperature and mounted onto an aluminum sample holder.

The consolidant uptake by capillary rise was measured gravimetrically. The pristine stone was weighed (W_0) after being completely dried and then treated with a consolidant solution with the capillary rise method for 5 days. Treated stones were

Table 1. Viscosity of 1:1 and 1:2 TEOS/GPTMS Composite Solutions with Different Amounts of POSS (T1G1 = 1:1 TEOS/GPTMS, T1G2 = 1:2 TEOS/GPTMS; Units = mPa · s)

| | SO1455 | | | | SO1458 | | | |
| | 35 wt % | | 50 wt % | | 35 wt % | | 50 wt % | |
amount of POSS (wt %)	1T1G	1T2G	1T1G	1T2G	1T1G	1T2G	1T1G	1T2G
0	1.98	2.01	3.13	3.32	1.98	2.01	3.13	3.32
1	2.38	2.50	4.10	4.20	2.08	2.26	2.95	3.22
3	2.12	2.24	2.79	2.99	2.27	2.28	3.54	3.53
5	1.99	2.17	2.96	3.26	2.63	2.70	4.45	4.75
WackerOH				1.60				

dried in a vacuum oven at room temperature for 1 day. The treated stone was weighed (W_t) after complete drying at room temperature and vacuum-dried. The applied consolidant uptake was estimated using the expression

$$\text{consolidant uptake} (\%) = \frac{W_t - W_0}{W_0} \times 100 \qquad (1)$$

where W_t and W_0 are the masses of the stone treated with and without consolidants, respectively (in grams).

Ultrasonic velocity measurements were performed to evaluate the efficiency of the consolidants using a measurement device (FUNDIT RS-232). Shore hardness measurements (NSS hardness tester C-2 type) were conducted for the weathered surface before and 1 month after treatment. The treat method was immersion of the sample into the consolidants for both experiments.

The characterization of the stone was conducted by stereomicrophotographs (Nikon SMZ1500), X-ray diffraction (XRD; Rigaku D/Max-2000, Cu Kα), and X-ray fluorescence analysis (Philips PW2400). The size of the samples was less than 0.075 mm. The adhesion interaction of the developed consolidants on the surface of the granite was macroscopically investigated using the ISO 2409 cross-cutting test; a red dye was added for visual observation of the consolidants. The consolidants containing red dye were coated twice to form the film on the surface of the fresh granite, and a tape detachment test according to the ISO 2409 method was conducted after 1 month.

RESULTS AND DISCUSSION

Characterization of TEOS/GPTMS/POSS. All TEOS/GPTMS/POSS solutions were homogeneous and stable in closed bottles for up to 6 months. Because the theoretical sizes of the POSSs are 1.4 and 1.8 nm for SO1455 and SO1458, respectively, which is smaller than the average pore diameter of decayed granite (which is 68.8 nm) (26), the size of the POSS is not a concern for penetration through the pores of the stone. The addition of nanomaterials to a TEOS solution increased the solution viscosity. Because the penetration of the consolidants into the stone depends on its viscosity (27), optimization of the viscosity of the solution is necessary when developing a new consolidant. The solid content and amount of POSS and GPTMS were the other parameters considered in order to optimize the formulation of the new consolidant.

The viscosities of the two different solid content solutions are shown in Table 1, with different amounts of POSS with two different molar ratios of the TEOS/GPTMS solution. The viscosity of commercial solutions is also shown in the table. The viscosity of the solution of 50 wt % of solid content is

higher than that of the 35 wt % solution in all samples. The range of the viscosity change with the addition of POSS is less than 1.5 mPa · s.

The gels obtained from the TEOS solution alone were brittle, and many cracks formed in the dried gels (20). Stereomicrophotographs of the gel obtained from the different solutions are shown in Figure 1. After gelation, cracks were clearly visible in commercial Wacker OH and Unil sandsteinfestiger OH 1:1. We reported that the cracks clearly disappeared with the addition of GPTMS in a TEOS solution (24). The addition of POSS does not change the gelation time (and the drying time) at this concentration or affect the crack-free gel morphology. The gels obtained from a 35 wt % 1T1G solution containing 3 wt % of both POSSs are shown in Figure 1. Both gels were clear and crack-free.

The sol−gel reaction of the 1T1G solution was confirmed via FT-IR, which is shown in Figure 2. For all samples studied here, there was a very pronounced band appearing at 1011 and 1074 cm^{-1}, along with a less pronounced band at 797 cm^{-1}, which corresponded to the asymmetric and symmetric stretching and bending peaks of the Si−O−Si groups, respectively, indicating that all samples were mainly composed of a silica network (28). FT-IR spectra of TEOS/GPTMS with increasing POSSs are also shown in the figure, and the peaks at 1011 cm^{-1} moved to higher wavenumbers, but the other peaks, including those at 903, 850, and 790 cm^{-1}
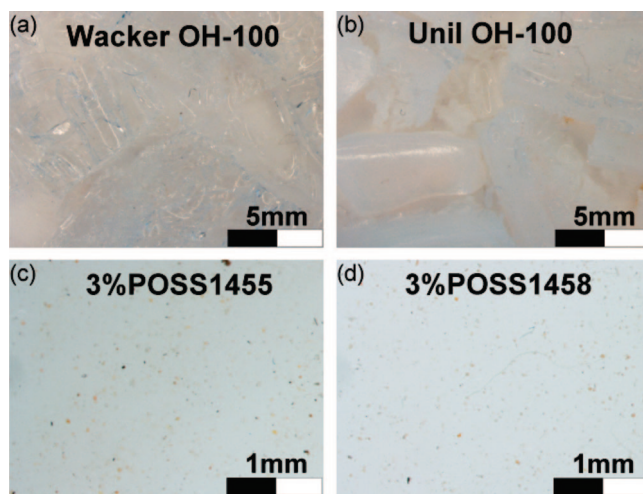

FIGURE 1. Stereomicrophotographs of gel derived from (a) Wacker OH-100 and (b) a Unil sandsteinfestiger OH 1:1 and 1T1G composite solution containing 3 wt % of (c) SO1455 and (d) SO1458, respectively.
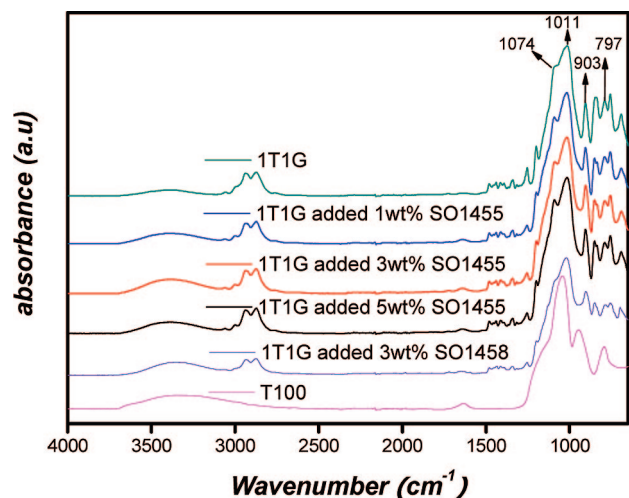
FIGURE 2. FT-IR spectra of gels obtained from TEOS, TEOS/GPTMS, 1, 3, and 5 wt % TEOS/GPTMS/SO1455, and 3 wt % TEOS/GPTMS/SO1458.

FIGURE 3. WAXS curves for a gel obtained from (a) a TEOS solution containing different molar ratios of GPTMS and (b) 1T1G containing a 3 wt % POSS solution.

presenting the epoxy ring of GPTMS, remained during the sol—gel reaction in these conditions.

Because the microstructure of a gel is closely related to its physical properties, WAXS investigations were used to deduce information about the morphological properties of the gels obtained from the TEOS solution with and without GPTMS and/or POSS. The WAXS diffraction patterns for gels from the TEOS solution with the addition of GPTMS are shown in Figure 3a.

The WAXS pattern of the inorganic matrix made from TEOS (Figure 3a, T100) showed two broad peaks at $2\theta < 3$ and 23.6°, which appear frequently in different types of amorphous polysiloxanes (31). The Bragg d spacings, which are usually assigned to the inter- and intrachain distances, were calculated with Bragg's law using the peak maximum, where the intrachain distance was 0.38 nm, implying dense Si—O—Si bond formation. The gel obtained from the 2T1G solution clearly showed two broad peaks at $2\theta = 5.58$ and 21.7°. The inter- and intrachain distances were calculated at 1.58 and 0.41 nm, respectively, showing that the intrachain distance increased with the addition of GPTMS having a γ-glycidoxypropyl group. With the further addition of GPTMS on TEOS, the interchain distance decreased and it was ca. 1.42 nm for the gel from the 1T2G solution, implying interaction formation between γ-glycidoxypropyl groups.

The WAXS diffraction patterns for gels from the 1T1G solution containing 3 wt % POSS are shown in Figure 3b. Although the POSSs are crystalline monomers, the POSS crystallinity is not presented in the figure, implying that the small amount of POSS is not sufficient for developing crystal domains. For all samples, two broad peaks were observed, but the peak at $2\theta = 5.7°$ increased with the addition of 3 wt % of POSS, while the peak at 21.0° remained, implying that the addition of 3 wt % POSS in a 1T1G solution reduces the interchain distance to 1.4 nm from 1.54 nm with the addition of SO1455 and SO1458, while the intrachain distances were maintained. Because the theoretical sizes of SO1455 and SO1458 are estimated to be 1.4 and 1.8 nm, respectively, which are in the range of the interchain dis-
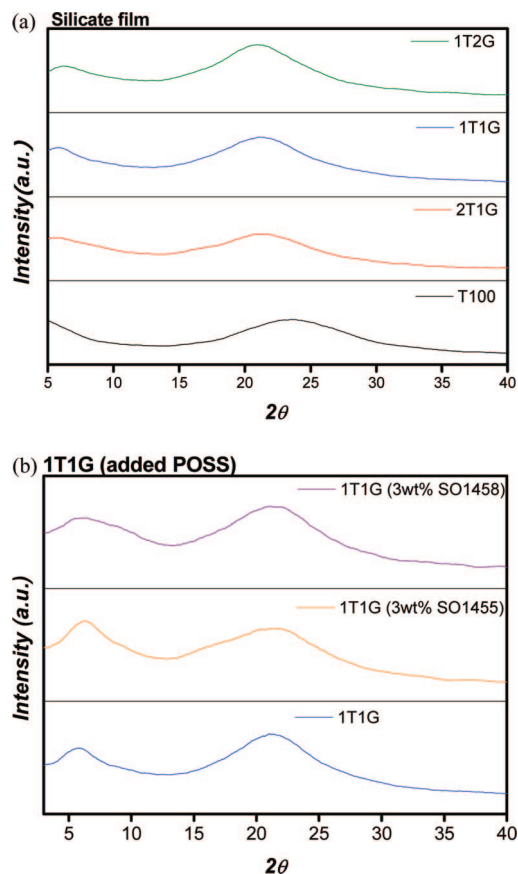
tance measured by WAXS, the distance changes would be due to the addition of POSS affecting the chain—chain conformation.

Effect of the Consolidation of Granites. Figure 4 shows photomicrographs of decayed granite located in Namsan, Korea, which is a major stone material for Korean cultural heritage built during the Silla Dynasty (BC 57-AD 935). Highly weathered Namsan granite consists mainly of orthoclase and quartz and minor levels of biotite and clay minerals such as smetite and illite (26).

Compared to the fresh Namsan granite, the amount of clay minerals increased in the rock. The amount of smectite in the Namsan granite increased with weathering grade by XRD analysis (Supporting Information) (26). From the X-ray fluorescence analysis, the amount of Al_2O_3 increased ca. 1.4 % and the amounts of CaO and SiO_2 decreased ca. 0.5 and 3.0 %, respectively, with degradation of the Namsan granite (26, 30).

The 35 and 50 wt % 1T1G solution uptakes in the granite samples by the capillary method with different amounts of POSS are presented in Figure 5. The consolidant uptakes of the granite treated with 35 and 50 wt % 1T1G solutions were 0.34 and 0.47 wt %, and the consolidant uptake was higher for the higher concentration solution. Because the samples we studied here are naturally decayed granite, and there might be a rather large error range, although we prepared the samples from one rock, the difference of the consolidant
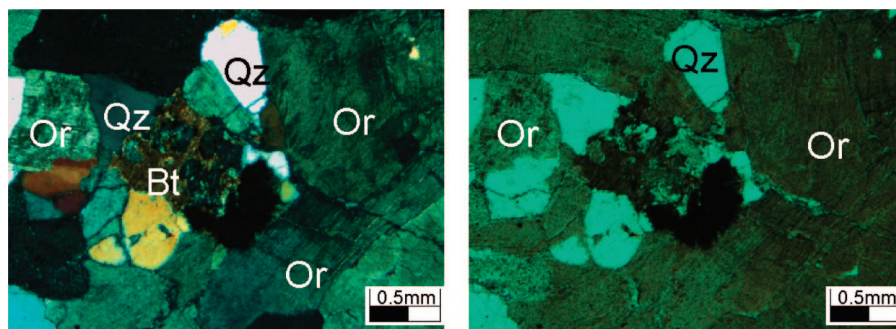
FIGURE 4. Microphotographs of highly weathered Namsan granite (Or = orthoclase, Qz = quartz, and Bt = biotite).
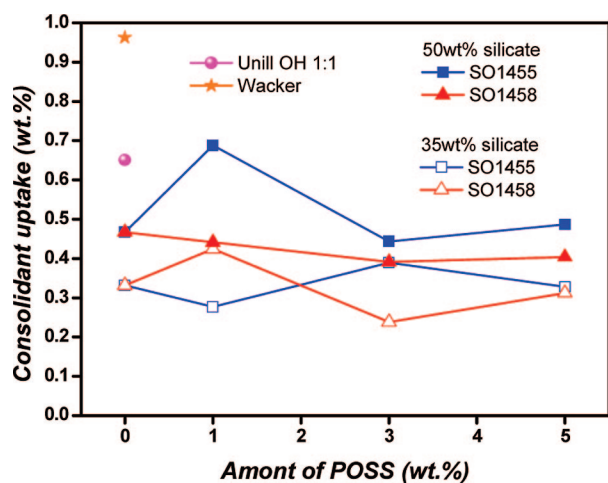

FIGURE 5. Increased consolidant uptake of decayed granite after treatment with 35 and 50 wt % 1T1G composite solutions with different amounts of POSS.
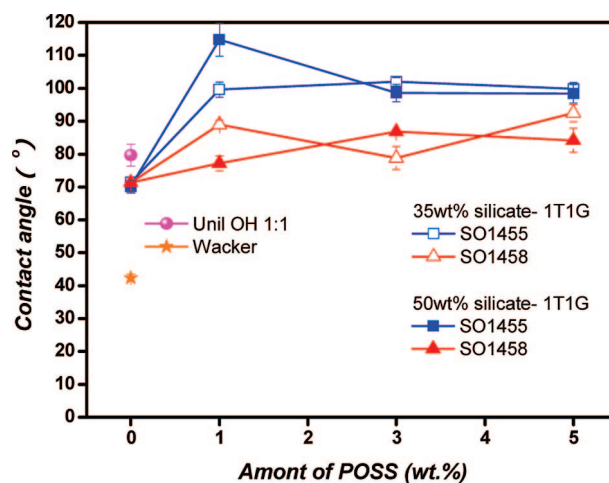

FIGURE 6. Contact angle of the surface of decayed granite after treatment with 35 and 50 wt % TEOS/GPTMS composite solutions containing different amounts of POSS.

uptake of TEOS/GPTMS containing POSS is not significant within the error range. However, in general, the uptake decreased with increasing amounts of POSS, which implies that the increased viscosity affects the amount of uptake of the solution.

Because the main cause of stone degradation is water inside the stone, surface treatment to avoid deterioration is aimed at preventing water penetration into the bulk of the stone. Therefore, we characterized the contact angle of the surface of the treated stone with a TEOS/GPTMS/POSS solution for its potential use as a stone consolidant.

The contact angles of the granite surfaces treated with the various 35 and 50 wt % TEOS/GPTMS/POSS solutions are shown in Figure 6. These measurements allow a practical evaluation of the water repellency of the surface. The contact angle of the granite treated with Unil sandsteinfestiger OH 1:1 is 79.4°, which is much higher than that of Wacker OH (44.8°). The surface of the treated granite became hydrophobic when the stone was treated with TEOS/GPTMS/POSS solutions. The contact angle increased with the concentration of the consolidants and/or the amount of POSS in the TEOS/GPTMS solution in general, and the granite surfaces were found to be more hydrophobic than those treated with the commercial consolidants, Unil sandsteinfestiger OH 1:1 and Wacker OH. The effect of the chemical group of POSS is clearly shown; that is, the octyl group (SO1455) showed a higher water repellancy that of phenyl (SO1458) in both comparable concentrations of the 1T1G solution.

The surface microstructures of granite treated with Wacker OH, 1T1G, and 1T1G/POSS (3 wt % of SO1455 and SO1458) solutions are shown along with that of untreated granite in Figure 7. The grain structure of the decayed Namsan granite is clearly shown in the surface image (Figure 7a), and the dense gel debris can be seen on the surface treated with Wacker OH in Figure 7b. The debris from the gel was also observed after crack formation due to the low adhesion on the surface of the stone. The surface of the decayed stone was covered roughly with the 1T1G/SO1458 solution (Figure 7d). A well-covered stone surface treated with a TEOS/GPTMS/POSS solution can explain the high contact angle of the surface.

XRD analysis was used for the investigation of mineralogical and surface-coating characteristics of Namsan granite before and after it was treated with consolidant. Namsan granite consists mainly of quartz and orthoclase and minor levels of hornblend, smectite, and illite (Figure 8a). The basal reflection (001) of smectite is very weak and broad. The peak intensity of the smectite basal peak (001) treated with Wacker OH-100 and Unil OH-100 is strong and shifted to a lower angle (Figure 8b,c). Smectite treated with Wacker OH-100 and Unil sandsteinfestiger OH 1:1 resulted in an increase in the basal spacing and volume. On the other hand, the smectite 001 peak, after treatment with a TEOS/GPTMS/POSS consolidant, increased, but the position did not change, implying no change of the crystal structure.
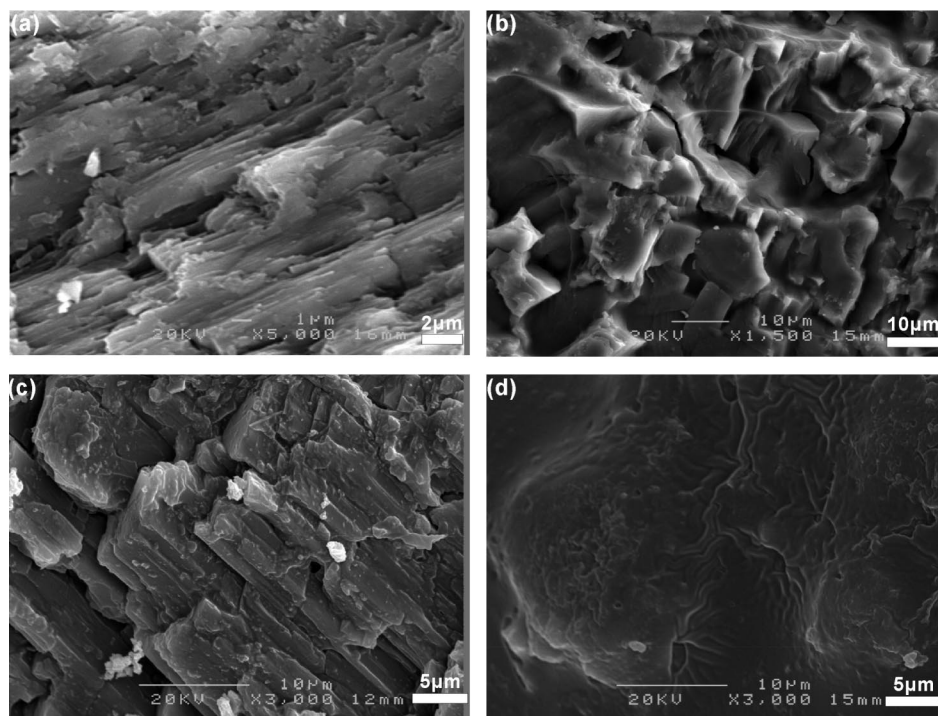
FIGURE 7. SEM photographs of the surface of (a) decayed granite and the same stone treated with (b) Wacker OH and 1T1G composite solutions containing 3 wt % of (c) SO1455 and (d) SO1458.

The peak intensity of illite after treatment with 1T1G containing 3 wt % SO1455 (Figure 8d) became strong, while it was weak for the samples treated with 1T1G containing 3 wt % SO1458 (Figure 8e), showing that TEOS/GPTMS containing 3 wt % SO1458 coats the illite surface better than TEOS/GPTMS containing 3 wt % SO1455.

Because the consolidants should have good interaction with the components of the stone in order to bind the isolated grains of the decaying stone, the adhesion interaction of the consolidants on the surface of the granite was macroscopically investigated with the ISO 2409 cross-cutting test. The surface of the granite and the detached tape are shown in Figure 9. We observed that the adhesion interaction increased with the addition of GPTMS in a TEOS solution, and the adhesion decreased with the addition of silica nanoparticles in a TEOS/GPTMS solution (33). The adhesion interaction does not change with the addition of nanomaterials such as POSS in a TEOS/GPTMS solution, implying that the functional group of POSS has some effect on the adhesion with the granite and/or TEOS/GPTMS gel. The interaction between the granite and the gel formed by TEOS/GPTMS/SO1458 is so strong that there is not significant detachment (Figure 9d) from the surface of the granite. The adhesion interaction between the granite and the consolidants is higher for TEOS/GPTMS/SO1458 than for TEOS/GPTMS/SO1455, implying the effect of the phenyl functional group, which is also consistent with the results of the XRD analysis.

This adhesion interaction between the consolidants and the components of the granite affects the conservation efficacy of the intergranular cohesion, which was determined by the ultrasonic velocity change and shore hardness before and after the conservative treatment (32, 33).

The ultrasonic velocity was measured on the decayed granite before and after treatment, and the results are shown in Table 2. The ultrasonic velocity increased ca. 230 % and 150 % for the decayed granite after treatment with 1T1G with 3 wt % of SO1455 and SO1458, respectively. This value is compatible with that for the granite treated with commercial Wacker OH, which shows ca. 170 % improvement. Because the consolidant uptake of TEOS/GPTMS/POSS was in the range of 0.3 wt %, while the consolidant uptake of Wacker OH was 0.96 wt %, TEOS/GPTMS containing POSS has great potential for use in stone conservation.

In general, the degree of degradation of the stone monument at the surface is more significant than that in the bulk of the Korean granite. The shore hardness on the surface of the decayed granite before and after treatment was measured, and the results are also shown in Table 2. The surface hardness increased with consolidant treatment, and it increased ca. 73 % for the surface of the stone treated with a 1T1G solution, a greater improvement than that with commercial Wacker OH (12 %). The surface hardness increased 55 and 82 % with the TEOS/GPTMS consolidants containing SO1455 and SO1458, respectively.

Stone consolidants based on TEOS have been used for stone monument conservation because of their binding effect between the decayed grains of stone. In order to optimize the binding effect, the interaction between the consolidants and the stone grain should be strong enough; otherwise, the independent brittle gel debris formed inside the stone will block the condensed water evaporation from the inside of the stone, which is responsible for the secondary decay of the stone. The composite solution we prepared in this study provides a crack-free gel, which has interactions between the consolidants and the decayed granite grains
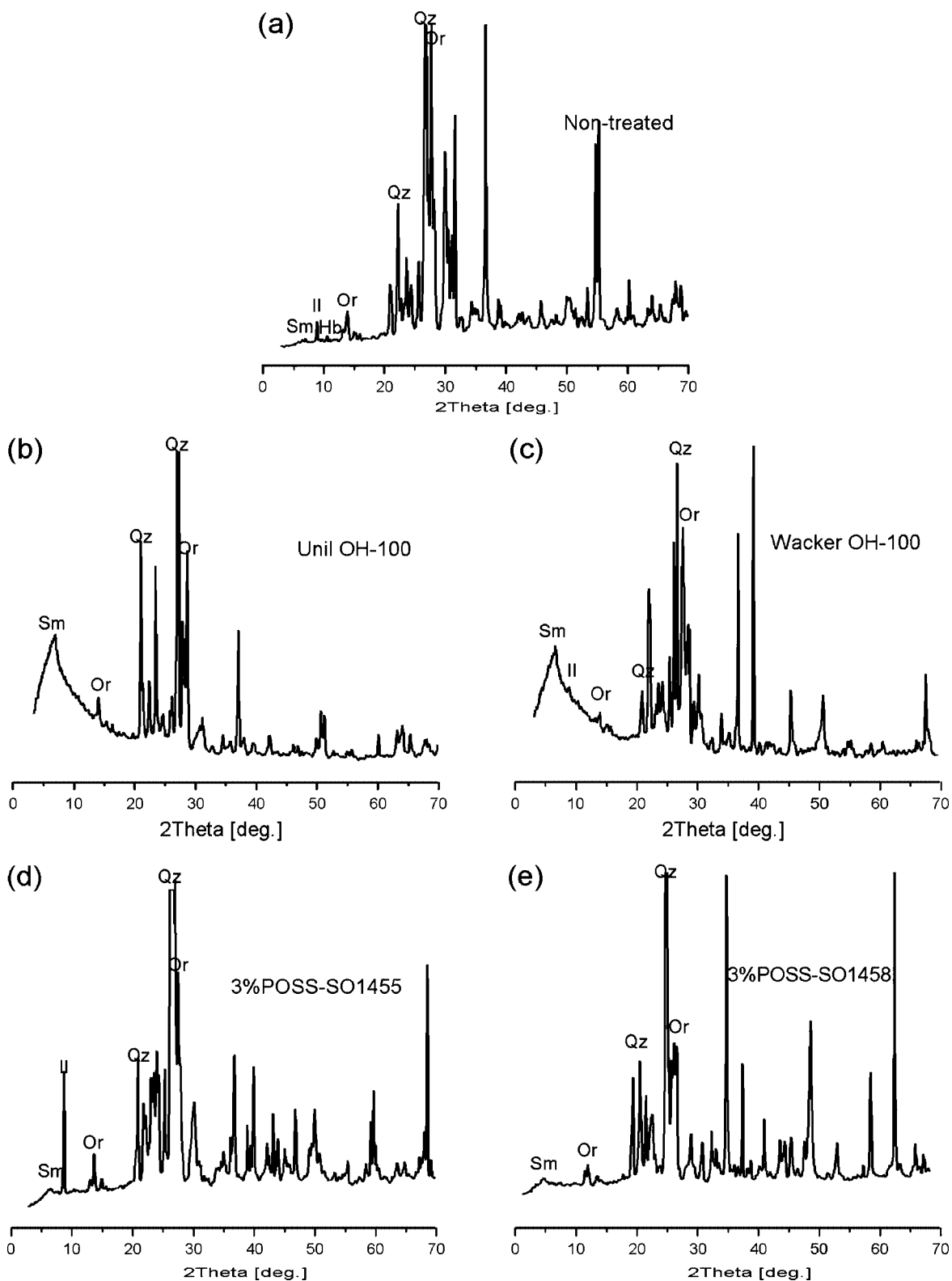
FIGURE 8. XRD patterns of Namsan granite (a) pristine and treated with consolidant containing (c) Wacker OH-100 and (b) Unil OH-100 and 3 wt % of (d) SO1455 and (e) SO1458 (Sm = smectite, Il = illite, Hb = hornblende, Or = orthoclase, Qz = quartz).

due to the presence of GPTMS (20, 31) and the functional groups of SO1458.

CONCLUSION

TEOS-based consolidants containing flexible GPTMS and POSS were prepared and characterized. The addition of GPT-

MS, which has flexible segments, and nanometer-sized POSS, which has inner voids, reduced crack formation in TEOS-based gels during the drying phase, preventing the secondary deterioration of the stone. The increased surface hydrophobicity and ultrasonic velocity and shore hardness measurements of the decayed Namsan granite showed that treatment with a
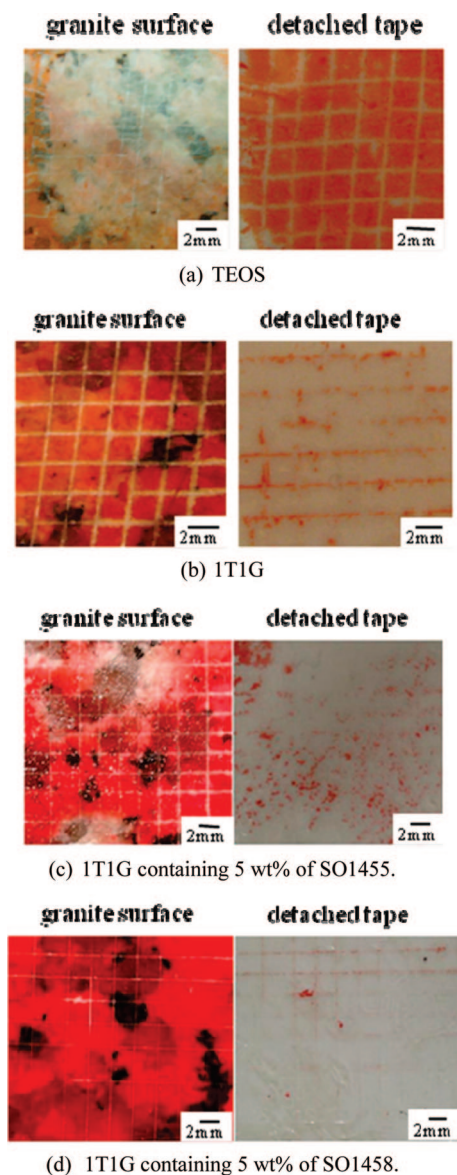
FIGURE 9. Cross-cutting image of the treated granite surface and detached tape after treatment with (a) TEOS, (b) 1T1G, (c) 5 wt % of SO1455 in 1T1G, and (d) 5 wt % of SO1458 in a 1T1G solution.

Table 2. Ultrasonic Velocity and Shore Hardness Measurements Performed on Decayed Namsan Granite Stone Specimens before and after the Solution Treatment

	ultrasonic velocity (m/s)			shore hardness		
	before	after	difference	before	after	difference
1T1G	3371	8333	4962	27.3	47.1	19.8
1T1G/SO1455	2389	7963	5574	24.9	38.6	13.7
1T1G/SO1458	2148	5472	3324	21.1	38.4	17.3
Wacker OH	3258	8788	5530	25.3	28.3	3

TEOS/GPTMS/POSS solution improves the consolidation on the decayed granite, implying its potential for the preservation of granite heritage.

Supporting Information Available: X-ray fluorescence analysis data of Namsan granite. This material is available free of charge via the Internet at http://pubs.acs.org.

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