

EFFECT OF PRETREATMENT FOR TEOS BASED STONE CONSOLIDANTS

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Abstract

Consolidants based on alkoxysilanes, such as tetraethoxysilane (TEOS), have been applied widely in Korean stone heritages because they penetrated inside of the decayed stone and they polymerize within the porous structure of the decaying stone by means of a classic sol-gel process, significantly increasing the cohesion among the decayed stone grains. The study presented here is aimed to provide the interaction between the TEOS-based gels and the surface of the decayed grains, which give improved properties for the preservation of cultural stone monuments. We developed the interaction between the stone and the consolidants by the pretreatment with the functional alkoxysilanes, and have characterized them for the application of Korean granite stone consolidants. The effect of the pretreatment with the functional alkoxysilanes was compared with TEOS based solution including the commercial products such as Wacker OH 100. For the model study, functional alkoxysilanes were used to treat SiO₂ particles and we obtained crack-free dried gel for all TEOS based consolidants. The surface attachment test for Korean granites showed improved interaction with the TEOS based consolidants including commercial products. The properties and the applicability of the developed pretreatment process for the decayed Korean granites are also investigated.

Keywords: consolidants, tetraethoxysilane, pretreatment, granite, sol-gel

1. Introduction

Wacker OH, based on alkoxysilanes such as TEOS, are commonly used for consolidating weathered stones in Korea (Cnudde 2007; Tsakalof 2007; Wheeler 2005), especially outdoors. TEOS-based consolidants polymerize inside the weathered stone heritage, by means of a sol-gel reaction with environmental moisture, providing strength to the structure. While TEOS increases the cohesion of the grains of the weathered stone via a sol-gel reaction, the gel obtained from commercial materials based on TEOS has two drawbacks: crack formation during the drying process and formation of dense fragments of gel inside the stone (Wheeler 1992; Mosquera 2002, 2003), which could block the pores of the stone. This may promote a significant reduction in the water vapor transmission through the stone, preventing the desirable removal of the moisture condensed inside the stone.

Cracking occurs as a result of a differential capillary pressure produced within the gels during its drying phase (Mosquera 2008) inside and/or outside of the pores of the decayed stone. Because the capillary pressure is inversely proportional to the radius of pores filled with the gel network, it is obvious that the dense microstructure having very small pores promotes high pressures and subsequent cracking of the network of the gels.

Several trials have been carried out to obtain crack-free consolidating materials through the addition of nanomaterials such as silica nanoparticles (Escalante 2000, 2002; Agglakopoulou 2002; Alessandrini 2000; Zendri 2007; Mosquera 2005) because larger pores form in the presence of nanomaterials, which reduce the capillary pressure. The other approach is to enhance the ductile properties of the network, as in the new perfluorate polymers (Puterman 1996; Toniolo 2002), organosilicone-modified polyurethanes (Mazzola 2003) and organic segments, to obtain additional flexibility (Kim 2007, 2009), which leads to a smoother transition in the drying phase.

On the other hand, there is no specific interaction between the surface of the decayed stone grains and the consolidants, which would also reduce the consolidation effect of TEOS-based solution. The study presented here is aimed to provide the interaction between the TEOS-based gels and the surface of the decayed grains, which give improved properties for the preservation of cultural stone monuments. We chose (3-aminopropyl) triethoxysilane (ATEOS) as a pre-treatment reagent, which would be suitable for Korean granite. The formation of the gel and characteristics of the treated Korean granite were used to evaluate their efficacies as conservation materials.

2. Experimental

2.1 Materials

TEOS, (3-glycidyloxypropyl) trimethoxysilane (GPTMS), ATEOS, dibutyltindilaurate (DBLT) were purchased from Sigma-Aldrich Co. Inc. Aerosil® OX-50 (SiO₂, 40 nm) was purchased from Degussa Chemical Co. Ethanol was purchased from Samchun Pure Chemical Co. Ltd, 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 used, and all stone samples were obtained from one rock specimen for consistency. The specimens were rinsed with deionized (DI) water for 1 h with ultrasonic agitation and dried in an oven at 100 °C. Commercial consolidation agents (Wacker OH 100) were used as received.

2.2 Preparation methods

ATEOS was applied to SiO₂ nanoparticles (1.21g of ATEOS/1g of SiO₂ nanoparticles) as a model for the Korean granite in order to check the interaction between the stone and the consolidants. A 1:1 TEOS:GPTMS (1T1G) solution was prepared; DI water was added for a stoichiometric content with respect to the hydrolysable alkoxy groups of TEOS and GPTMS. Then, ethanol was added to reach the final silicate solid content of 35 wt.%. 0.08 wt.% of silicate weight of DBLT was added as catalyst. The solutions were mixed by ultrasonic agitation and then magnetically stirred for 24 h at room temperature.

Interaction between the modeled SiO₂ nanoparticles and consolidants was tested by the formation of the gel from the treated SiO₂ and consolidant solution; various concentrations of treated silica nanoparticles were added into 1T1G solution and/or Wacker OH solution. The gels were prepared at room temperature by pouring the solution into polypropylene dishes. The gelation time was similar for all samples (Kim 2007, 2009; Son 2009), 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. In order to see the adhesion interaction between the pretreated fresh granite and the consolidants, the ATEOS solution was coated twice to attach the surface of the granite; a red dye was added for visual observation of the consolidants.

2.3 Characterization

The viscosity of the solution was measured using sine-wave vibro viscometer SV-10 (A&D Co. Ltd.) at 25°C. Fourier-transform infrared (FT-IR) spectra of the gels were obtained on a Spectrum 100 (Perkin Elmer, Inc.) instrument equipped with attenuated total reflectance at a resolution of 4 cm⁻¹. The cross-sectional morphology of the dried gel was investigated using a scanning electron microscope JSM-6369 (JEOL Ltd.). The adhesion interaction of the consolidants on the surface of the pre-treated granite was macroscopically investigated using the ISO 2409 cross-cutting test after one month.

3. Results and Discussion

In order to optimize the consolidation effect, the consolidants must penetrate deeply into the pores of 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 further decay phenomena, such as detachments and scaling. Although the TEOS-based consolidants show excellent properties in the solution phase because the extremely low viscosity of alkoxy silane monomers allows them to penetrate deeply into porous stone, sol-gel reaction is in progress in the presence of water, which increases the viscosity of the solution with time. It is generally accepted that the penetration of a consolidant depends on its viscosity, therefore the viscosity of the solutions were measured with time and the result is shown in Figure. 1.

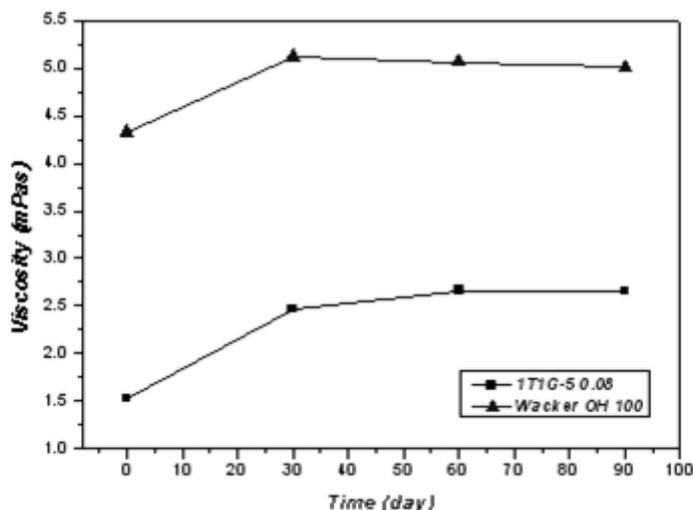


Figure 1. Viscosity change of consolidants with storage time.

The viscosity of the 35 wt.% of 1T1G solution is lower than that of commercial Wacker OH 100 in all time periods, which is reasonable since the solid content of Wacker OH 100 is higher than that of 1T1G solution. The viscosity of the two solutions increased only by ca. 1mPa·s for a period of time of up to three months, showing no significant phase change.

It is well known that the dried gels obtained from the TEOS based solutions containing Wacker OH were brittle and many cracks formed in the dried gels (Kim 2009, Son 2009), while the one obtained from 1T1G solution is clear and crack-free. The crack-free dried gel obtained from 1T1G solution is considered to be helped by the flexible chains of the GPTMS. Small amounts of silica nanoparticles would provide the crack-free dried gels due to the increased the size of pore of the network, the high amount of addition of silica nanoparticles develop the cracks in the gels. Images of the gel obtained from the Wacker OH 100 and 1T1G solutions with 7wt% of silica nanoparticles are shown in Figure 2. Cracks are clearly visible with the addition of 7 wt% of silica nanoparticle for both dried gels.

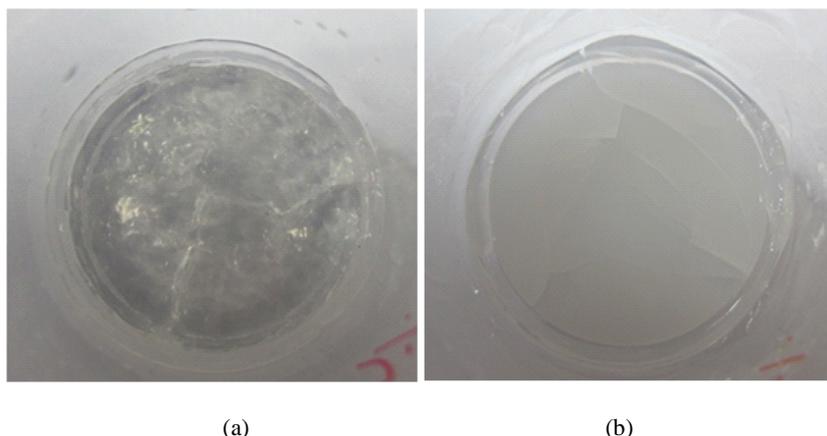


Figure 2. The dried gel obtained from (a) 1T1G and (b) Wacker OH 100 solution with 7 wt% of pristine SiO₂.

From the previous research for the 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), it is known that it consists mainly of orthoclase and quartz (Kang 2007), so a well-controlled size of SiO₂ nanoparticles was chosen as a model for the Korean granite.

With the addition of 7wt% of ATEOS treated SiO₂ particles the cracking clearly disappeared, which is shown in Figure 3a and 3b. However, the color of the dried gels changed to a yellowish color and it is significant for the dried gels obtained from 1T1G containing 7wt% of ATEOS treated SiO₂ particles. It is considered to be the reaction between the epoxide group of GPTMS and amine of ATEOS, which attached to SiO₂ particle, as confirmed by FT-IR.

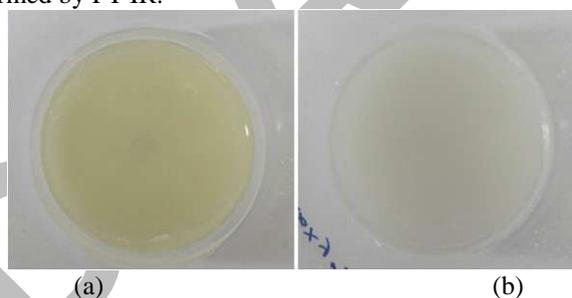


Figure 3. The dried gel obtained from (a) 1T1G and (b) Wacker OH solution with 7 wt% of ATEOS-treated SiO₂ nanoparticles.

For all samples studied here, there was a very pronounced band appearing at 1033cm⁻¹, along with a less pronounced band at 797 cm⁻¹, which corresponded to the vibration absorption of Si-O-Si groups, indicating that all samples were mainly composed of a silica network (Fidalgo 2005). Due to the organic oxirane groups, which are not involved in the sol-gel reaction, a band lying at 906 cm⁻¹ (Innocenzi 2001) is

shown in 1T1G solution, however it decreases with the addition of ATEOS-treated SiO_2 nanoparticles, implying the reaction between the oxide and amine of ATEOS.

The cross-section of the dried gel obtained from Wacker OH 100, 1T1G solution with different amounts of ATEOS treated SiO_2 particles, are shown in Figure 4. As can be seen in the figure, there is no significant heterogeneous segregation inside of the gel matrix. ATEOS treated SiO_2 nanoparticles were covered roughly with the matrix, showing there is an interaction between the SiO_2 nanoparticles and gel matrix, implying positive possibility of the adhesion on the surface of the stone with the gel matrix.

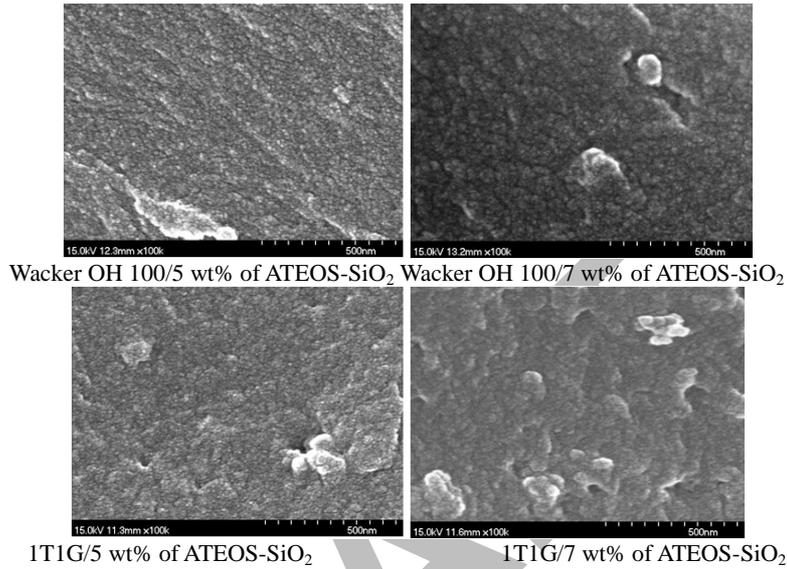


Figure 4. SEM images of cross-sections of dried gel obtained from Wacker OH and 1T1G solution with different amount of ATEOS-treated SiO_2 nanoparticles.

In order to see the effect of the pretreatment of ATEOS on the granite, the adhesion interaction of the consolidants on the surface of the granite was macroscopically investigated with the ISO 2409 cross-cutting test. The detached tapes after the adhesion test of ISO 2409 cross-cutting test are shown in Figure 5. We observed that the adhesion interaction increased with the ATEOS-treated granite for both of consolidant solutions.

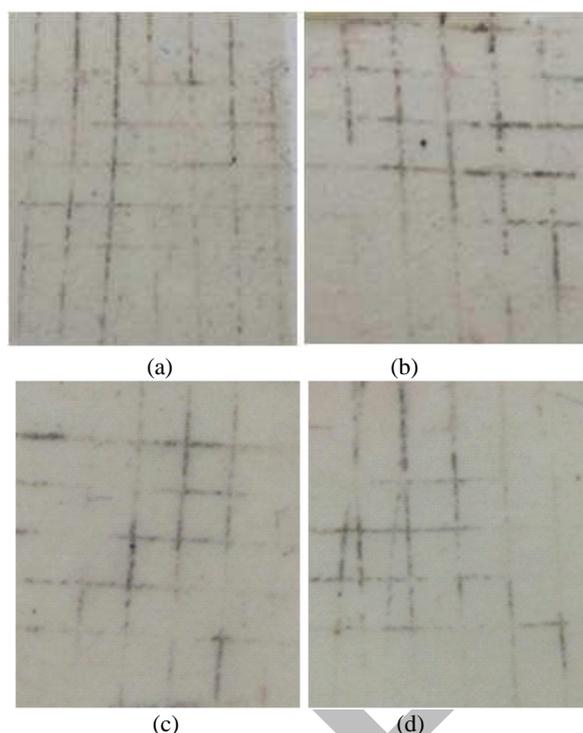


Figure 5. Tape after the adhesion test of Wacker OH 100 (a, b) and 1T1G solution (c, d) with different amount of ATEOS pretreatment on the granite.

The effect of the pretreatment is not clearly seen for the case of 1T1G since this consolidant has an intrinsic ductile properties and showed good interaction with the surface of the granite (Kim 2007, 2008). The adhesion interaction of Wacker OH 100 changed with the addition ATEOS on the surface of the granite. The interaction between the ATEOS-treated granite and the gel formed by Wacker OH (or 1T1G) is strong enough that there is not significant detachment from the surface of the granite.

In order to optimize effect of the stone consolidants based on TEOS, 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. In this research, the interaction was achieved by the pretreatment of granite with functional reagents and the applicability of the developed pretreatment for the decayed Korean granite is under study in the laboratory.

4. Conclusions

The effect of the pretreatment with the ATEOS was compared with TEOS/GPTMS solution and Wacker OH 100 commercial product. For the model study, SiO_2 particles were treated with ATEOS and we obtained crack-free dried gel for two TEOS based

consolidants (1T1G and Wacker OH 100). The surface attachment test showed improved interaction with the TEOS based consolidants including with commercial products with granite. The increased interaction between the grain and the TEOS-based would improve the consolidation on the decayed granite, implying its potential for the preservation of granite heritage in Korea.

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6. References

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