

# Coagulation Strength of Some Adhesives for Conservation of Cultural Heritage

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## 文化遺産の保存に用いる接着剤の凝固強度

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### 1 Introduction

Various adhesives or coating agents are utilized for the restoration of cultural assets depending on the type of asset [Fitzner 2016]. Alkoxy silane is used for the consolidation of stone cultural assets [Fitzner 2016; Wheeler 2005; Bracci *et al.* 2008], such as OH100 (Wacker Chemie AG), which reacts with weathered stone surfaces to impart hydrophobicity and prevent further weathering. The silica formed by the condensation reaction fills tiny cracks on the stone surfaces. Epoxy resin is used for the filling of larger cracks or for the adhesion of broken stone fragments [Fitzner 2016]. Acrylic resin coatings are used to prevent the exfoliation of paints on mural paintings or to reinforce wooden cultural assets by impregnation and solidification of a solvent solution of acrylic resin. For example, Paraloid B72 (Rohm and Haas, random copolymer of methyl acrylate and ethyl methacrylate) is widely used as an acrylic resin [Träistaru *et al.* 2011; Milanesi *et al.* 2009]. Nanorestore (CSGI) [Natali *et al.* 2014; Baglioni *et al.* 2014], which is a solution of calcium hydroxide, Ca(OH)<sub>2</sub> in 2-propanol, is used to repair gypsum or lime plaster in mural paintings. However, the relation between the formulation of

these adhesives and the performance are not clarified yet. For example, Wacker has OM25 and OM50 as alkoxy silane in addition to OH100. It has not clarified the reason, although OM25 and OM50 are known to be high strength. First aim of this study is to solve this point.

Furthermore, there is also the restoration of remains that do not respond to the adhesives and coating agents mentioned here, e.g., the mastaba (tomb) of Princess Idout near the step pyramid of Saqqara in Egypt. The ancient and beautifully colored mural paintings drawn 4400 years ago are in an underground burial chamber. The preservation and restoration of these mural paintings have been advanced mainly by Kansai University [Yasumuro *et al.* 2016]. Fig. 1 shows a photograph of the burial chamber. This ancient tomb is located in the underground of a desert area, so this mother rock is weak and likely to collapse. Therefore, not only restoration of the mural paintings but also reinforcement of mother rock is required. The main characteristics required for this restorative adhesive are:

- 1) High permeability
- 2) High strength
- 3) Solvent-less

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Fig. 1 Mother rock of the Idout mastaba in Saqqara, Egypt.

The solvent-less is required because of a narrow underground burial chamber. The volatilization of solvent may do damage to the mural paintings and to the health of those who do repair work. However, there are presently no adhesives that satisfy all of above three characteristics.

The second aim of this study is to investigate about how to design the adhesives for such an application. In our previous studies [Yamazaki *et al.* 2016; Fukuda *et al.* 2013], the reactivity of silane coupling agent on a silica particle surface was investigated using thermogravimetric (TG) analysis [Yamazaki *et al.* 2016] and the molecular mobility of the treated layer on silica particle surface was measured using  $^1\text{H}$  pulse nuclear magnetic resonance ( $^1\text{H}$  pulse NMR) [Fukuda *et al.* 2013]. These techniques were also utilized in the present study.

## 2 Experimental

### 2.1 Materials

OH100, OM25, OM50 (Wacker Chemie AG, Germany, we received from ACT Corp., Japan) and TOT (Tanaka Geological Corp., Japan) alkoxy silanes were employed. Uniepo 01 (Konishi Co., Ltd., Japan) was used as an epoxy resin. This epoxy resin consists of the diglycidyl ether of bisphenol-A epoxy resin and ketimine as a hardener. Methyltrimethoxysilane (MTMS; KBM-13), dimethyldime-

thoxysilane (DMDMS; KBM-22) and an oligomer of MTMS (KR-500, it was termed as "oligomer") were also used as alkoxy silane and were kindly donated by Shin-Etsu Chemical Co., Ltd. (Japan). Toyoura standard sand (Toyouura Keiseki Kogyo Co., Ltd., Japan), which has a particle size of 100 to 200  $\mu\text{m}$  with a mean size of 180  $\mu\text{m}$ , was used as model sand. The main component of Toyoura standard sand is  $\text{SiO}_2$  (> 92%).

### 2.2 X-ray Diffraction Analysis of Rock

The component of rock taken near the Idout mastaba of Sakkara in Egypt was analyzed by X-ray diffraction (XRD; XRD-6000, Shimadzu Corp., Japan) method. This analysis was entrusted to Matsutomi Museum of Geoscience, Kyoto, Japan.

### 2.3 Permeability Test

Model sand (80 g) was added to a polypropylene (PP) cup and alkoxy silane (20 g) was added to the cup. The permeability of alkoxy silane from the upper surface of the sand to bottom was observed with the naked eye.

### 2.4 Compression Test

Model sand (80 g) was added to a PP cup and alkoxy silane (20 g) was added to the cup. The model sand with alkoxy silane was stored at 23°C for seven days. The solidified model sand was re-

moved from the cup and a simple compression test was conducted using a universal testing machine (AG 5kNIS MS, Shimadzu Corp., Japan) with a test rate of 5 mm/min to record the force-displacement curve. A simple compression test was also done for the mixture of alkoxy silane/epoxy resin.

## 2.5 Solidification of Alkoxy Silane

Alkoxy silane (20 g) was added to a PP cup and solidified by storage at 23°C for seven days. The solidified sample was ground by the mortar for TG and pulse NMR measurements. The solidification of mixture of alkoxy silane/epoxy resin was also done by the same procedure.

## 2.6 Polycondensation of Alkoxy Silane

Alkoxy silane (MTMS, DMDMS, oligomer and MTMS/oligomer and DMDMS/oligomer mixtures) and ion exchanged water (1/2, w/w) were mixed and stirred at 23°C for 24 h. The mixture was poured into a vessel made from poly (tetrafluoroethylene) sheet and heated at 80°C for 24 h in an oven.

## 2.7 TG Analysis

TG analysis of alkoxy silane was performed us-

ing a thermogravimetric/differential thermal analyzer (TG/DTA-6300, SII NanoTechnology Inc., Japan). The samples were heated to 1000°C at a heating rate of 10°C/min in an air atmosphere (flow rate: 300 mL/min).

## 2.8 Pulse NMR Analysis

The molecular mobilities of the alkoxy silanes before and after solidification were measured using  $^1\text{H}$  pulse NMR (JNM-MU25, JEOL. Ltd., Tokyo, Japan, resonance frequency of 25 MHz) with the solid echo method at 25°C. The sampling time was 2 ms, integration was conducted 128 times, the pulse width of the radiofrequency wave was 2.2  $\mu\text{s}$ , the pulse interval was 8.0  $\mu\text{s}$ , and the pulse repetition time was 4.0 s.

The free induction decay (FID) curves obtained were analyzed according to the method proposed by Urahama [Urahama 2010], as in our previous report [Fukuda *et al.* 2013]. The FID amplitude (signal intensity at 0 ms) was normalized, i.e., the FID curves were corrected to maintain a constant FID amplitude, and the normalized FID curves were then differentiated.

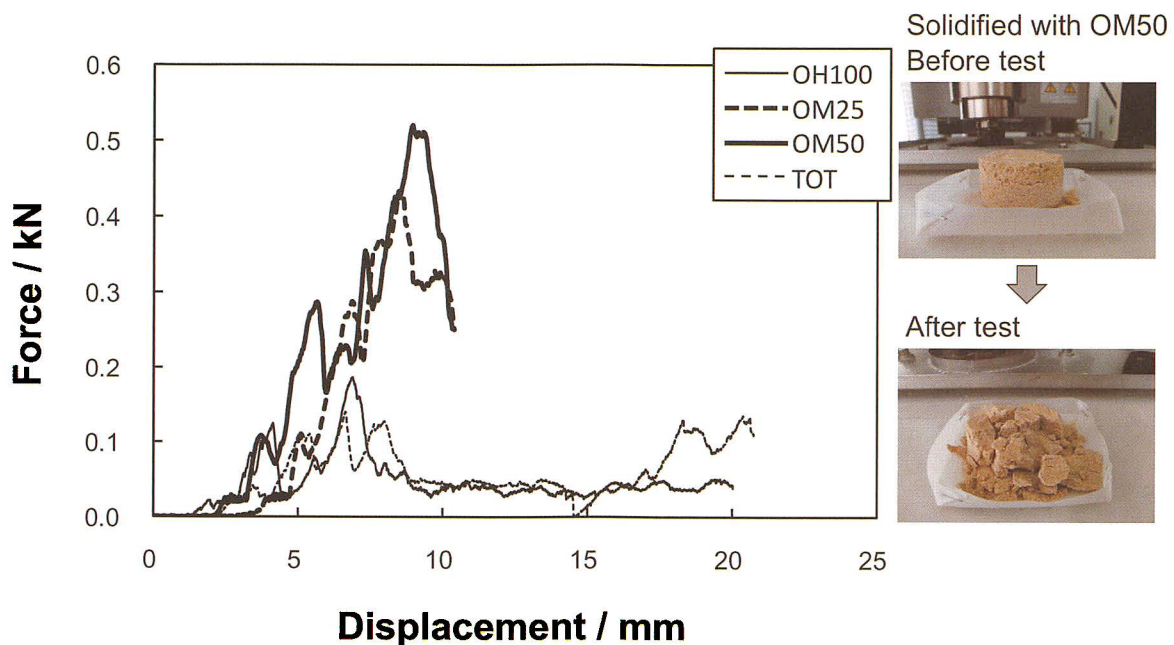


Fig. 2 Force-displacement curves measured by compression test of Toyoura standard sand solidified with alkoxy silanes, and the sand specimen solidified with OM50 before and after compression test. Solidification was achieved by storage at 23°C for 7 days after alkoxy silane addition.

### 3 Results and Discussion

#### 3.1 Strength of Alkoxy Silane

According to the safety data sheet (SDS) for OH100 [Wacker Chemie AG], the composition is a mixture of tetraethoxysilane and its oligomer. OH100 also contains a catalyst and small amount of solvent (ethanol). The compositions of OM25, OM50 and TOT appear to be similar to OH100. To confirm these coagulation strength, the simple compression test was done. Toyoura standard sand was used as model sand. It is widely utilized as a standard sand in the civil engineering field in Japan. The specimen was simply prepared by solidification of model sand with alkoxy silane in a PP cup, and the sample shape was thus irregular. Therefore, only the shape of the force-displacement curve was compared without calculation of the compression strength. The compression test was conducted with  $n = 5$ ; however, there was no significant difference in the shape.

Fig. 2 shows force-displacement curves for the model sand solidified with alkoxy silanes. The spec-

imens solidified with OM25 and OM50 showed higher fracture forth than those with OH100 and TOT. The reason for the high strength was investigated next.

These alkoxy silanes are liquids, but they became solid after being stored at 23°C for 7 days. This solidification is caused by a self-condensation reaction and the formation of a network structure. TG and pulse NMR analyses of the alkoxy silanes were performed before and after solidification.

Fig. 3 shows TG curves of the alkoxy silanes (a) before and (b) after solidification. Prior to solidification (a), weight loss was observed below 300°C, and then became constant above 300°C. Even at 1000°C, the weight loss was not completed, except for MTMS. Yang conducted pyrolysis gas chromatography (PGC) analysis at 250 and 600°C for inorganic particles treated with 3-methacryoxypropyltrimethoxysilane [Yang *et al.* 2003]. They observed flash evaporation of physisorbed silane at 250°C and thermal decomposition of chemisorbed silane at 600°C. The dotted line in Fig. 3a shows the TG curve of MTMS, where weight loss was completed

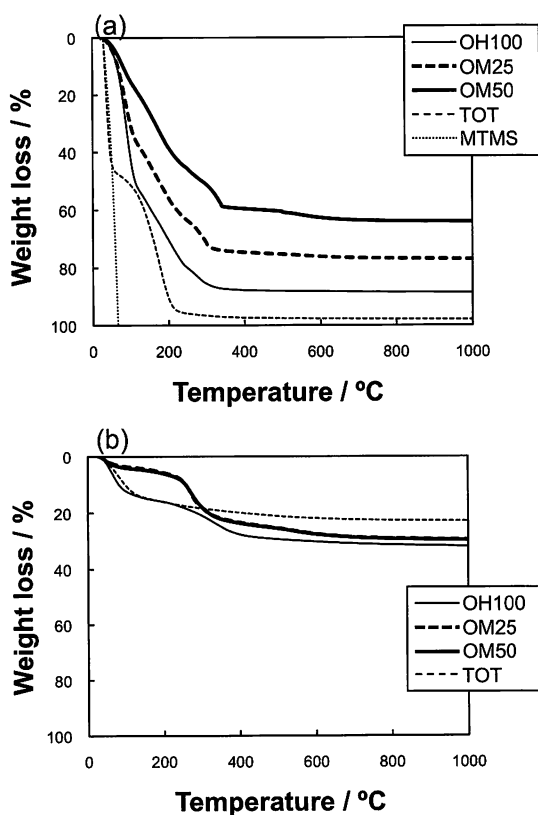


Fig. 3 TG curves for alkoxy silanes (a) before and (b) after solidification by storage at 23°C for 7 days.

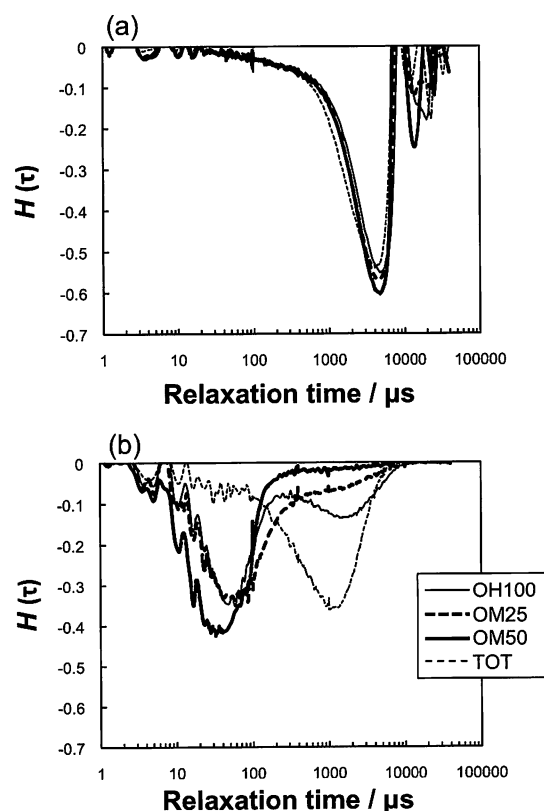


Fig. 4 Pulse NMR spectra of alkoxy silanes measured at 23°C (a) before and (b) after solidification by storage at 23°C for 7 days.

below 100°C. Therefore, the weight loss for MTMS is considered to be evaporation. The alkoxy silanes are a mixture of the silane monomer and oligomer; therefore, the weight loss below 300°C is considered to be evaporation. On the other hand, evaporation of the oligomer does not occur, because of higher molecular weight and the oligomer is considered to become silica (SiO<sub>2</sub>). After the TG analysis, a fine white powder was present in the crucible, which was confirmed to be silica particles. Based on these results, the oligomer content in the alkoxy silanes is expected to be in the order of OM50 > OM25 > OH100 > TOT.

After solidification (Fig. 3b), the amount of weight loss became much less and there was only a small difference for the alkoxy silanes because all alkoxy silane monomer and oligomer reacted and formed a network structure within seven days of storage. The structure that never evaporating increased and almost all of the alkoxy silane became silica during TG analysis.

The molecular mobility of the alkoxy silanes before and after solidification was investigated using pulse NMR, which is based on the nuclear spin of protons in the polymer oriented in a magnetic field followed by measurement of the relaxation time of the nuclear spin. The spin-spin ( $T_2$ ) relaxation time obtained by measurement of the FID is dependent on the molecular mobility; longer relaxation times indicate a more flexible polymer chain. In this study, the FID curves were normalized (the signal intensity for a relaxation time of 0 was made constant), differentiated, and presented as relaxation spectra, which can show the distribution of components having different relaxation times.

Fig. 4 shows pulse NMR relaxation spectra for the alkoxy silanes measured (a) before and (b) after solidification. Before solidification, a clear peak appeared between 1000 and 10000  $\mu$ s, which indicates that the alkoxy silanes possess high molecular mobility before solidification, and there was no difference between the alkoxy silanes. After solidification, the major peak appeared at a shorter relaxation time (between 10 and 100  $\mu$ s) for OM25 and OM50, but appeared at a longer relaxation time (at ca. 1000  $\mu$ s) for TOT, while two peaks at shorter and longer relaxation times appeared for

OH100. These results indicate that a network with high crosslinking density was effectively formed for OM25 and OM50. A higher content of silane oligomer is thus useful for network formation with a high crosslinking density. This is the reason why OM25 and OM50 showed a higher fracture forth in the compression test (Fig. 2).

### 3.2 How to Strengthen the Brittle Wall

Next, the designing of higher strength adhesive for brittle wall such as Idout mastaba was investigated based on the above mentioned alkoxy silanes. Danehey investigated the condensation reaction of MTMS in the presence of silica or calcium carbonate particles using <sup>29</sup>Si NMR [Danehey *et al.* 1992]. The results revealed that the condensation reaction did not occur easily in the presence of calcium carbonate particles, which indicates that the reactivity of alkoxy silane is affected by the type of rock. The silanol (Si-OH) group of hydrolyzed MTMS reacts easily with Si-OH of silica, whereas it does not react readily with calcium carbonate (calcite) [Plueddemann 1991]. Therefore, the type of rock is important when using alkoxy silane. The chemical component of rock sampled near the Idout mastaba was analyzed as an example.

Fig. 5 shows the XRD analysis results for (a) the rock taken near the Idout mastaba and (b) pure Egyptian limestone. The spectrum of the rock near the Idout mastaba showed various peaks and a quartz (silica) peak that was larger than the calcite (calcium carbonate) peak, whereas the spectrum of the pure limestone showed a large clear calcite peak and no quartz peak. This indicates that the alkoxy silane would react well with the surface of rock near the Idout mastaba.

Fig. 5 also shows the results for (c) the rock taken at Barbar temple in Bahrain, (d) the sand taken at Barbar temple in Bahrain and (e) the Ryukyu limestone. The main peak of the rock of Barbar temple (c) showed calcite. It was relatively pure. On the other hand, the sand of Barbar temple (d) showed various peaks of quartz (SiO<sub>2</sub>), calcite (CaCO<sub>3</sub>) and gypsum (CaSO<sub>4</sub>). It was not pure. Ryukyu limestone (e) was pure limestone.

As mentioned in the introduction section, the high permeability and the solvent-less are also re-

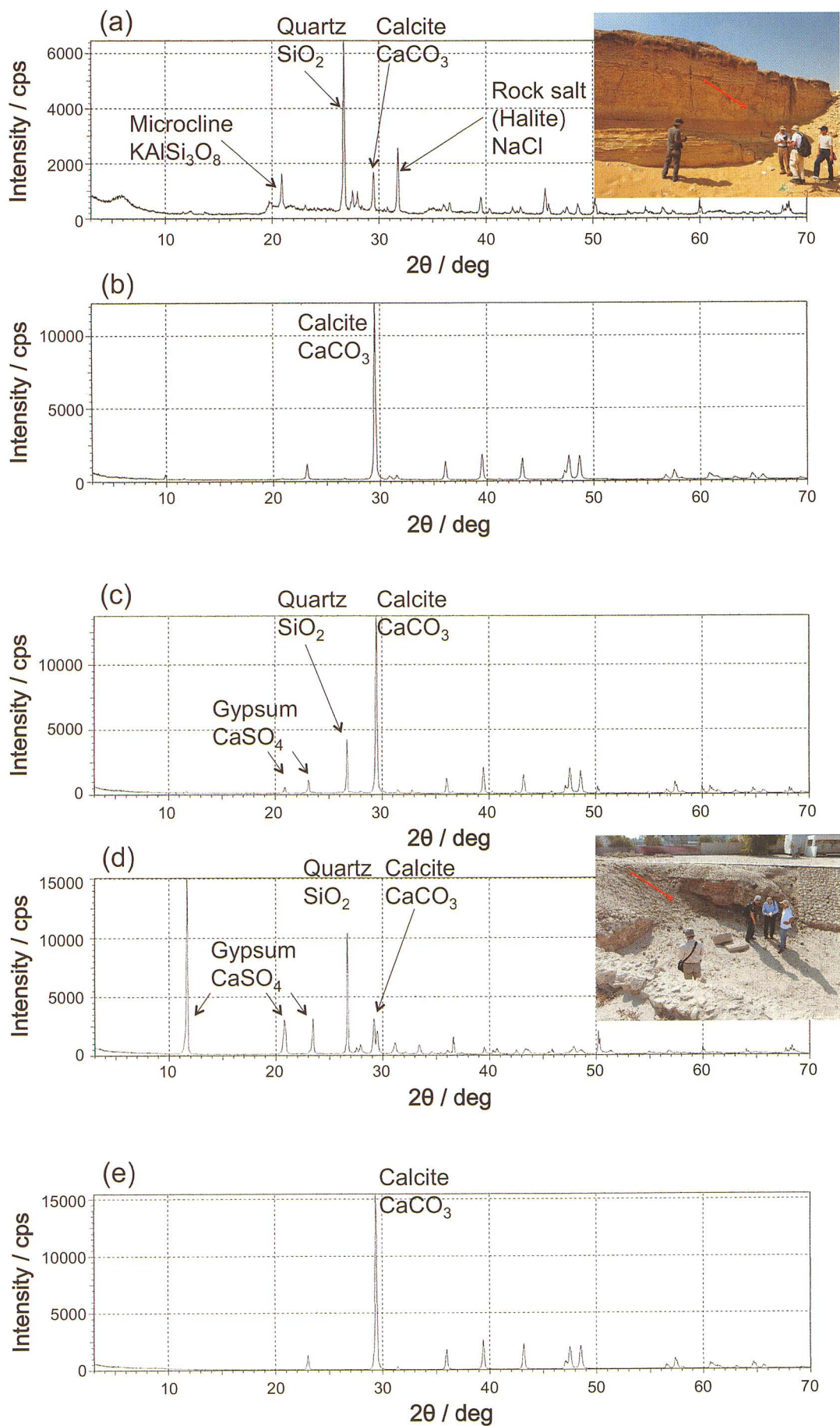


Fig. 5 XRD analysis of (a) rock taken near Idout mastaba in Egypt, (b) pure Egyptian limestone, (c) rock taken at Barbar temple in Bahrain, (d) sand taken at Barbar temple in Bahrain and (e) Ryukyu limestone.

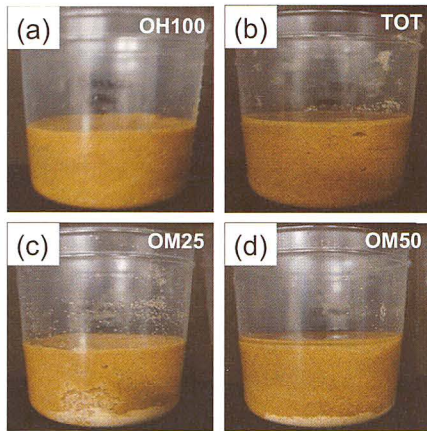


Fig. 6 Permeability test of (a) OH100, (b) TOT, (c) OM25 and (d) OM50 in Toyoura standard sand. The photographs were taken 10 s after the addition of the alkoxy silanes.

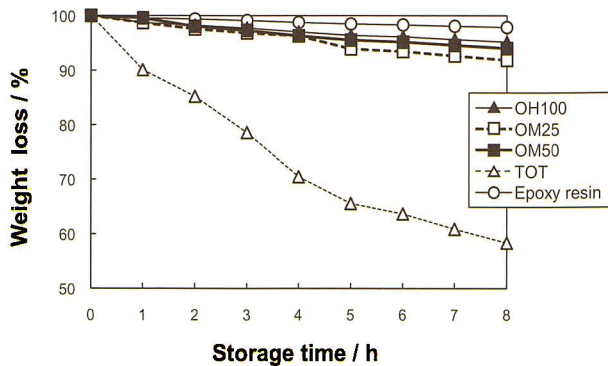


Fig. 7 Weight loss of alkoxy silanes during storage at 23°C.

quired for the adhesives reinforcing the brittle wall such as Idout mastaba. These points were confirmed. Fig. 6 shows the permeability test results for alkoxy silanes. These photographs show the sand samples 10 seconds after alkoxy silane addition. After the alkoxy silane permeated the sand, the color of the sand was darkened. All alkoxy silanes exhibited good permeability, although the permeabilities of OM25 and OM50 were slightly lower.

Fig. 7 shows the results for the volatilization of the alkoxy silanes. The alkoxy silanes were stored in a PP cup at 23°C and the weight was measured every hour. TOT showed a large weight loss, whereas those of the others were very small. Only TOT contains approximately 60 wt% of ethanol.

There has been much research on organic/inorganic hybrid materials that combine networks of alkoxy silane with epoxy resin at the molecular

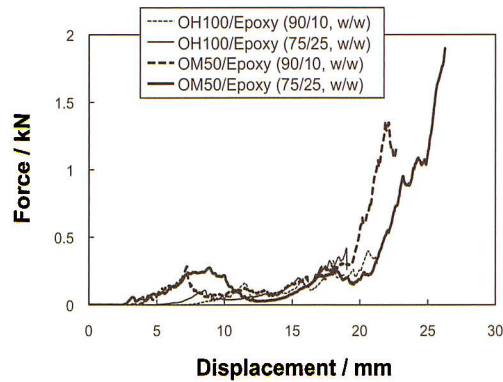


Fig. 8 Force-displacement curves measured by compression test of Toyoura standard sand solidified with OH100/epoxy and OM50/epoxy hybrids. Solidification was achieved by storage at 23°C for 7 days.

level [Ochi *et al.* 2001; Ni *et al.* 2004]. In this study, two networks were also combined to develop the strength of the restoration. The epoxy resin hardener used in this study was ketimine [Okuhira *et al.* 2003], which hydrolyzes with moisture in the air and forms ketone and amine hardeners that react with the epoxy resin. This epoxy resin is thus curable at room temperature without the need for heating, which is suitable for the narrow underground burial chamber of Idout mastaba. Here, this is referred to as the alkoxy silane/epoxy hybrid. However, the viscosity of the epoxy resin is higher than that of alkoxy silane. Therefore, the amount of epoxy resin added was limited to a small quantity so that permeability would not be sacrificed. The alkoxy silane/epoxy ratio was 90/10 or 75/25 (w/w). The OH100 and OM50 were used for these hybrids.

Fig. 8 shows force-displacement curves measured by compression test for the model sand solidified with the alkoxy silane/epoxy hybrids. The OM50/epoxy hybrid exhibited a higher fracture strength, whereas there was no clear improvement for the OH100/epoxy hybrid. The OM50/epoxy hybrid thus effectively improved the fracture strength.

Fig. 9 shows relaxation spectra for the OM50/epoxy hybrids measured by pulse NMR (a) before and (b) after solidification at 23°C for seven days, and (c) after further heating at 80°C for 24 h. Solidification was performed without model sand. Before solidification, the peak for the hybrids appeared at ca. 3000  $\mu$ s. This shows that the hybrids possess

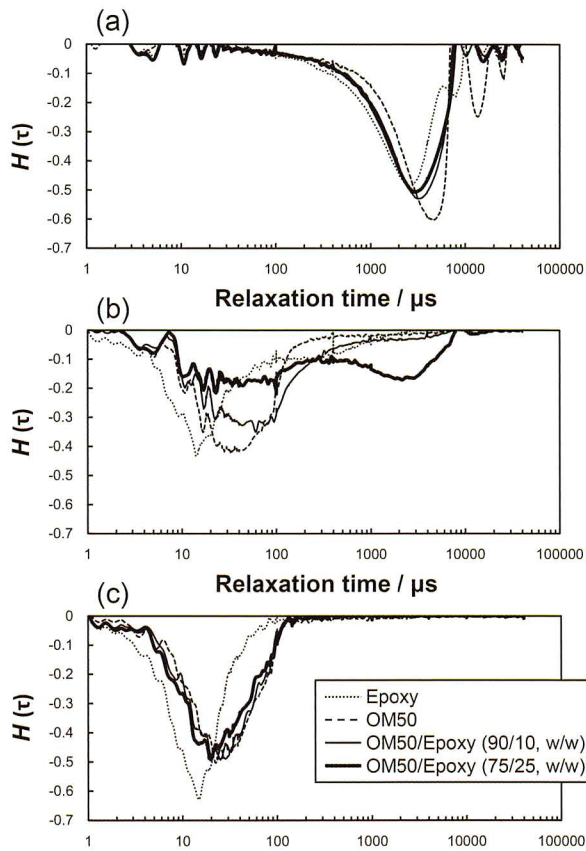


Fig. 9 Pulse NMR spectra measured at 23°C of OM50/epoxy hybrid (a) before solidification, (b) after solidification and (c) after further heating at 80°C for 24 h following solidification. Solidification was achieved by storage at 23°C for 7 days.

good flowability, although the peak shifted slightly to shorter relaxation time. After solidification, a single peak for OM50 appeared at ca. 30  $\mu\text{s}$ ; however, the peak shifted to longer relaxation time with an increase in the epoxy resin content. Two peaks appeared at ca. 20–100  $\mu\text{s}$  and ca. 2000  $\mu\text{s}$  for the OM50/epoxy (75/25) hybrid, i.e., the hybrid became softer with an increase of the epoxy resin

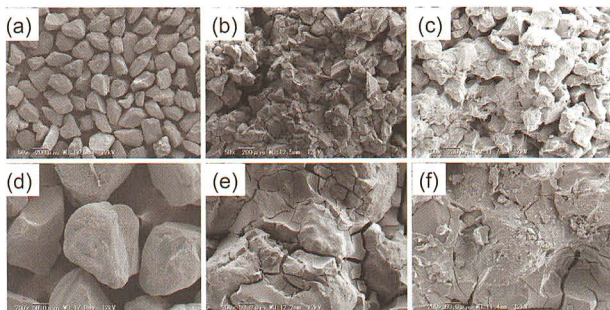


Fig. 10 SEM micrographs of (a, d) Toyoura standard sand and (b, e) fracture surfaces of compression test specimen solidified with OM50, and (c, f) solidified with OM50/epoxy hybrid. Solidification was achieved by storage at 23°C for 7 days.

content. Further heating after solidification shifted the peak for both OM50/epoxy hybrids to ca. 20  $\mu\text{s}$ . This relaxation time was much the same as that for OM50. The longer relaxation times for the solidified OM50/epoxy hybrids were caused by insufficient curing of the epoxy resin. Furthermore, the presence of soft epoxy resin in the hybrid resulted in higher fracture strength determined by the compression tests (Fig. 8). To confirm this point, model sand solidified with the OM50/epoxy hybrids at 23 °C for seven days was further heated at 80°C for 24 h, after which the compression test was conducted. The obtained fracture strength was lower than that for the specimens without further heating.

Fig. 10 shows scanning electron microscopy (SEM) micrographs of (a, d) model sand and fracture surfaces of compression test specimens solidified with (b, e) OM50 and (c, f) the OM50/epoxy (75/25, w/w) hybrid. Many cracks were evident in the adhesive layer for the specimen solidified with OM50. The adhesive was too hard and thus caused brittle fracture in the adhesive layer. On the other hand, the crack formed in the adhesive layer was far smaller for the specimen solidified with the OM50/epoxy hybrid. Therefore, it is important to impart ductility to the adhesive to improve the strength.

An approach to impart ductility to an adhesive layer was considered. From Fig. 9b, ductility was imparted by insufficient curing of the epoxy for the OM50/epoxy hybrid. However, curing advances gradually with time. Ductility is required in the final completely cured state. For this purpose, the addition of a reactive diluent to an epoxy resin is effective [Montserrat *et al.* 1996]. The reactive diluent is a mono-epoxide compound, and the addition of this to the di-epoxide compound lowers the crosslinking density of the epoxy network.

The ductility of alkoxy silane network is also controllable as follows. In our previous reports [Nakamura *et al.* 2011; Nakamura *et al.* 2013], silica particles were treated using silane coupling agent with dimethoxy or trimethoxy structures. A brush-like silane chain formed on the silica surface with the dimethoxy structure, whereas an silane network formed on the silica surface with the trime-



thoxy structure [Nakamura *et al.* 2011]. Furthermore, when silica was treated with a mixture of the di- and trimethoxy structures, a network with various crosslinking densities was formed [Nakamura *et al.* 2013]. The ductility of the alkoxy silane adhesive layer can thus be controlled using this method. Polycondensation of MTMS (trimethoxy structure) and DMDMS (dimethoxy structure) was performed. The OH100, OM25, OM50 and TOT contain the oligomer; therefore, polycondensation was conducted in the presence of the MTMS oligomer. Although a catalyst was also included in the alkoxy silanes, polycondensation in this report was performed without a catalyst. Here, the name of the prepared polycondensed silane has a "P" placed before the name of the base material of polycondensation, e.g., polycondensed MTMS is referred to as PMTMS and the polycondensed MTMS and oligomer mixture is referred to as P(oligomer/MTMS).

Fig. 11 shows pulse NMR relaxation spectra for PMTMS, PDMDMS and those polycondensed with oligomer. The states of obtained polycondensates were solid for PMTMS, P(oligomer) and P(oligomer/MTMS) and viscous liquid for PDMDMS and P(oligomer/DMDMS). The peak for PMTMS appeared at ca. 200  $\mu\text{s}$  and those for P(oligomer) and P(oligomer/MTMS) were shifted to shorter relaxation times, i.e., the crosslinking densities were higher than that of PMTMS. This result is in good accordance with the presence of oligomer and the higher crosslinking density of alkoxy silane ob-

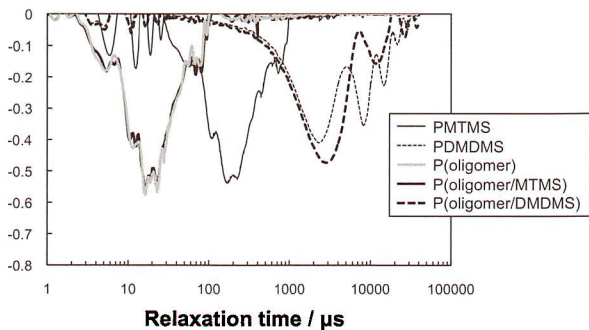


Fig. 11 Pulse NMR spectra measured at 23°C of PMTMS, PDMDMS, P(oligomer), P(oligomer/MTMS), 1/1, w/w) and P(oligomer/DMDMS, 1/1, w/w).

tained from Fig. 3 and Fig. 4. The peaks for PDM-DMS and P(oligomer/DMDMS) appeared at ca. 2000  $\mu\text{s}$ , which indicates that the ductility of the adhesive layer can be controlled by the mixing ratio of di- and trialkoxy silane monomers and oligomer.

### 3.3 Adhesive for Barbar Temple in Baharain

In Bahrain, it often rains. Therefore, the sand flows and the position of the stone changes in Barbar temple in Bahrain. To prevent the flowing sand, the diluted adhesive for wood work was investigated. The adhesive was diluted with water and solidified model sand in the same way as the above mentioned.

Fig. 12 shows force-displacement curves measured by compression test for the model sand solidified with the diluted adhesive for wood work. The adhesive and water was mixed by the ratio of 10/90 and 25/75 (w/w). The adhesive for wood work is the emulsion of poly(vinyl acetate) (PVAc) and the polymer content is 41 wt%, so the PVAc content for the adhesives above two different mixing ratio was 4.1 and 10.3 wt%, respectively. The diluted adhesive with the mixing ratio of 25/75 (adhesive/water) showed the higher fracture force. It was far higher than the fracture strength of OM50/epoxy hybrid shown in Fig. 8. The diluted adhesive with the mixing ratio of 10/90 showed lower fracture force than that with the mixing ratio of 25/75. That is, the coagulation strength can

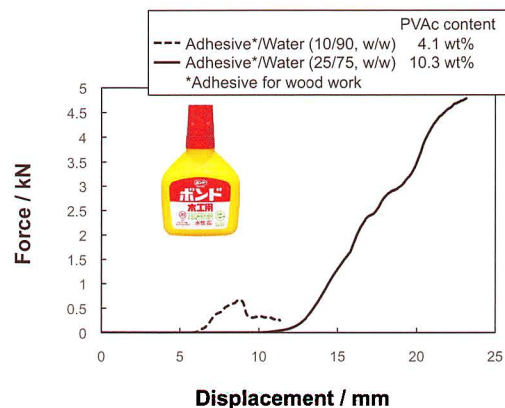


Fig. 12 Force-displacement curves measured by compression test of Toyoura standard sand solidified with the diluted adhesive for wood work with water. Solidification was achieved by storage at 23°C for 7 days.

be controlled by the concentration of adhesive. As shown in Fig. 5d, the sand of Barbar temple contains quartz ( $\text{SiO}_2$ ) component, so the alkoxy silane can be used as the adhesive. However, the diluted adhesive for wood work is far cheaper than the alkoxy silane.

## 4 Conclusions

In the commercial alkoxy silanes for the consolidation of stone cultural assets such as Wacker OH100, the high strength appearance mechanism was investigated. Further, the designing of higher strength adhesive for brittle wall such as Idout mastaba was also investigated based on the commercial alkoxy silane. The following results were obtained.

- 1) Alkoxy silanes were a mixture of silane monomer and oligomer. The oligomer content decreased in the order: OM50 > OM25 > OH100  $\approx$  TOT
- 2) The compression strength of solidified model sand increased with respect to the oligomer content because a high oligomer content forms a network with a high crosslinking density.
- 3) The addition of a small amount of epoxy resin to OM50 was more useful to obtain higher strength. This is caused by the low crosslinking density of epoxy resin with insufficient curing. The introduction of ductility to the adhesive layer was determined to be effective for the development of strength.
- 4) To impart ductility to an adhesive layer, controlling of mixing ratio of di- and trialkoxy silane monomers and oligomer seemed to be useful.

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## Abstract

The coagulation strengths of some commercial alkoxy silanes for the conservation of stone cultural assets were compared using OH100, OM25 and OM50 (Wacker Chemie AG., Germany) and TOT (Tanaka Geological Corp., Japan). Compression tests of solidified model sand were conducted to measure the coagulation strength. The fracture forces for OM50 and OM25 were higher than those for OH100 and TOT, which indicate higher coagulation strength for OM50 and OM25. Thermogravimetric analysis revealed that all the alkoxy silanes examined were a mixture of monomeric alkoxy silane and its oligomer, where the order of oligomer content was OM50 > OM25 > OH100 > TOT. From <sup>1</sup>H pulse nuclear magnetic resonance analysis indicated that the order of molecular mobility in the solidified alkoxy silanes was TOT > OH100 > OM25 > OM50. The degree of crosslinking in the solidified alkoxy silane thus increased with the oligomer content. For this reason, the fracture force determined from compression tests, i.e., the coagulation strength, was higher for OM25 and OM50 than OH100 and TOT. The addition of a small amount of epoxy resin to OM50 was effective to increase the coagulation strength due to a lower crosslinking density caused by insufficient curing of the epoxy resin. The introduction of ductility to the adhesive layer was thus effective to develop strength.

## Keywords

Alkoxy silane / Epoxy resin / Thermogravimetric analysis / Pulse NMR / Conservation