Performance Improvement of Tetraethylorthosilicate Consolidated Andesite Rock by Adding Titanium Tetraisopropoxyde and Silica Particles

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Abstract: *A study to improve the performance of andesite mortar and rock consolidated with tetraethylorthosilicate (TEOS) sol and a solvent of ethanol in the presence of titanium tetraisopropoxyde (TTIP) and silica particles has been conducted. The improvements include minimizing the shrinkage using silica particles from rice husk ash, rheological property suitability of the consolidant, and mechanical properties of the consolidated mortar and rock. The effect of TTIP concentration, ethanol volume, and addition of the silica particles on rheological properties of TEOS-based consolidant, and also mechanical properties of the consolidated mortar and rock were evaluated. The results showed that the increase of TTIP content in the consolidant shortens the gelling time, and the weight percentage ratio of TTIP:TEOS:ethanol of 5%:55%:40% was the optimum composition for the consolidation. Consolidation of andesite block using that composition significantly increased the compressive strength up to 57.61% (0.58 kgf/mm^2). The addition of 2% of silica particles into the consolidant decreased the gel shrinkage and increased the Young modulus of the mortar. The presence of water in the andesite matrix reduced the consolidation performance, and 0.5% was the maximum percentage of water content acceptable for the consolidation.*

Keywords: *andesite; consolidant; silica-titania; composite*

■ INTRODUCTION

Consolidants widely used in rock conservation for many purposes are not only for consolidation of the deteriorated rock but also for repairing mortars. Andesite rock is commonly used for heritage buildings in Southeast Asia, especially in Indonesia. However, the study on the consolidation of andesite rock is still limited. Alkoxysilane based consolidants are the most widely used materials for rock consolidation. Those penetrate easily into porous materials and give less impact compared to other organic-based consolidants. Organic-based consolidants will decrease water and vapor permeability of the consolidated rock and has a glossy appearance. Two compounds, namely tetraethoxysilane (TEOS) and methyltrimethoxysilane (MTMS), are generally used in oligomer form. In the application, those consolidants are adsorbed by a rock to be consolidated, hydrolyzed by water to form silanols, and followed with condensation to form polymer leading to increase strength [1-2]. Many types of heritage rock, such as sedimentary stone [2], sandstone [3], limestone [4], and calcarenite [5], were conserved with TEOS-based consolidant, but a limited study on andesite rock consolidation was reported.

Consolidation is induced by hydrolysis and condensation reactions of TEOS in the presence of water and catalyst. The hydrolysis of TEOS is generally carried out under acid or alkaline conditions. The acid hydrolysis procedure is commonly employed for the production of silica coating and binder. The quantity of water and acid catalyst used for partial hydrolysis reaction is an important factor for formulating an ethyl silicate binder system. The relatively short shelf life of acid hydrolyzed ethyl silicate solution leads to difficulty in the application [6]. Therefore, the consolidant sol

with a non-aqueous catalyst is developed for the deteriorated rock consolidant to make shelf life longer.

One of the widely used catalysts is dibutyltin dilaurate (DBTDL). This catalyst is used for a TEOS-based consolidant to accelerate the consolidation [7]. The consolidation of TEOS into the rock substrate depends on the gelling time. Typically, TEOS hydrolysis and condensation rate is very slow. The presence of DBTDL in the initial sol increases the rate of hydrolysis, and DBTDL undergoes before hydrolysis to initiate polycondensation reactions [8]. The use of DBTDL as the catalyst in consolidation has been developed to evaluate the effect of a particle on the consolidant performance [2,6-7].

Due to the toxicity of organotin compounds, the application of DBTDL in industrial sectors tends to be decreased to reduce the risk of the negative effects [9]. Organotin compounds are environmental pollutants and endocrine disruptors [10]. Organotin compounds, even in low concentrations, may result in harmful effects on living organisms in the environment [11]. The development of a consolidant without DBTDL catalyst is currently a challenge.

The deficiency of the alkoxysilane-based consolidant is the tendency to crack and shrink during aging. Several studies have modified consolidant by introducing particles into TEOS-based consolidant, a so-called particle modified consolidant (PMC) to minimize the shrinkage. Two types of particles that have been studied as modifiers are nanoparticle silica [2,7] and titania [6].

The consolidation is effective in improving the physical property of deteriorating rock when it can penetrate the rock pores [3]. Therefore, rheological properties such as viscosity, density, and surface tension of the sol are important parameters for consolidant development. It is generally accepted that the penetration of the consolidant mainly depends on its viscosity [8]. An appropriate solvent is added to decrease the viscosity of the mixture to achieve the optimum penetration into the rock pores. However, the solvent addition should be limited since the higher content (34%) of silica gel in the consolidant mixture is necessary [1].

The study reported here is the improvement of TEOS-based consolidant performance by adding silica particles and titanium tetraisopropoxyde (TTIP). Silica particles added into the system acts as a filler in generating particle reinforced composite to reduce gel shrinkage during aging in the consolidation. Silica particles produced from rice husk ash are chosen since, as agricultural solid waste, it has been commonly reported as the precursor for silica particle production [12]. TTIP is used to replace toxic DBTDL as a catalyst to increase the hydrolysis rate and shorten the gelling time [13].

■ EXPERIMENTAL SECTION

Materials

Tetraethylorthosilicate (TEOS, analysis grade with > 99% purity), ethanol (absolute pro analysis grade) were purchased from Merck and used as the consolidant precursor and solvent, respectively. Titanium tetraisopropoxyde (TTIP, pro analysis grade with > 99% purity) used as a titania source was purchased from Aldrich. Silica particles were extracted from rice husk ash in the laboratory of Borobudur Conservation Office using a procedure reported by Zulfiqar et al. [14]. Andesite rock similar to the material used as heritage temples was collected from Magelang, Central Java, Indonesia.

Instrumentation

The instruments used for the analysis included a viscometer Amtast Type NDJ-55, SEM (JEOL 8000-upgraded with Semaphor Image processor) and Image-J software, XRF (Handheld type, Olympus DP-2000), FTIR spectrophotometer (Shimadzu 8201 PC), X-Ray Diffraction (Philips, Ultrasound velocity instrument, Geotron Elektronik type USG40, and Lighthouse DW Ver. 1.3 software for data processing), and Universal Testing Machines (UTM, Cometech model QC-508).

Procedure

Preparation of TEOS/TTIP based consolidant

TEOS/TTIP-based consolidants were prepared by mixing the TEOS, TTIP, and ethanol in various compositions, as presented in Table 1.

The effect of solvent and TTIP concentration on the rheological properties were evaluated from the consolidants C1-C4 and C5-C10, respectively. These rheological properties include viscosity (using viscometer Amtast Type NDJ-55), density, surface tension with capillary method [15], the capillary rate on andesite specimen, and density measured with the gravimetric method using a 25 mL pycnometer.

The surface tension (σ) was calculated using the following formula [15]:

$$\sigma = 0.5\rho ghr[N/m]$$

where ρ = liquid density [kg/m^3], g = gravitational acceleration (9.80665 m/s^2), h = average height of liquid column in capillary [m], and r = capillary radius [m]. The capillary rate was performed on a prismatic andesite specimen of 2.5 × 2.5 × 5.0 cm [1]. One face of 2.5 × 2.5 cm was placed in contact with a thin layer of the consolidant sol in a jar to minimize the solvent evaporation during observation. The capillary rate was calculated based on the time needed by consolidant to diffuse completely in the specimen. The gelling time of the sample was observed visually in an interval time of 6 h. The gelling time is equal to the time needed for a consolidant to stop flowing [13].

Consolidation of andesite mortar and rock with TEOS/TTIP consolidants

Andesite powder used for mortar was made from rock block. The sample was grounded with crusher and separated into different sizes by particle siever. The particle size of the andesite powder used for the mortar test followed Fuller law with a maximum size of 2 mm. The particle size distribution of andesite powder tested in this investigation is shown in Table 2.

Consolidation was performed by mixing the 3 mL of consolidant sample to 100 g of andesite powder and put the mixture in a 1.5 × 1.5 × 5 cm cast. After two weeks, the solidification of mortar samples was observed. The result was noted with "negative (-)" if the substrate was still in powder form, positive (+) if the mortar became solid but fragile, (++) if the mortar became solid but not compact, and (+++) if the mortar became solid and compact.

The consolidation effectivity test of the andesite rock was performed using andesite prism samples with a size of 1.5 × 1.5 × 3 cm. The samples were immersed in the consolidant and then air-dried for three weeks for consolidation reaction. The compressive strength of the samples was measured with UTM.

Addition of silica particles in Consolidation

Preparation of silica particles from rice husk ash.

Silica particles were prepared from rice husk ash (RHA) using sodium hydroxide solution followed with a sol-gel process. The rise husk sample was washed with deionized water and dried at 110 °C for 2–3 h [9]. The dried sample was powdered by mortar grinding and sieved for 60 mesh [16]. Approximately 25 g of the sample was mixed with 150 mL of 10% citric acid solution and transferred into an autoclave and maintained at 120 °C for 2 h. The acid pretreated rice husk was washed several times with distilled water to remove citric acid. The residue of rice husk was dried and incinerated at 650 °C for 1 h in a muffle furnace [17-18] to produce RHA. The produced ash was mixed with 100 mL of 2 M NaOH solution, and the mixture was heated at 90 °C with continuous stirring

Table 1. The various compositions of prepared consolidants

Consolidant code	Composition (g)		
	TTIP	TEOS	Ethanol
C1(7.3:72.7:20)	7.3	72.7	20
C2(6.4:63.6:30)	6.4	63.6	30
C3(4.5:45.5:50)	4.5	45.5	50
C4(3.6:36.4:60)	3.6	36.4	60
C5(1:59:40)	1	59	40
C6(2:58:40)	2	58	40
C7(3:57:40)	3	57	40
C8(4:56:40)	4	56	40
C9(5:55:40)	5	55	40
C10(6:54:40)	6	54	40

Table 2. Particle size distribution of andesite rock powder 100 g used for mortar consolidation

Particle size (mm)	< 0.063	0.063–0.125	0.125–0.25	0.25–0.5	0.5–1	1–2
Weight (g)	35.44	8.09	10.06	12.39	15.25	18.77

for 2 h to obtain silicate solution. To obtain the desired particle size of silica, the concentration variation of silicate in the solution was 0.05, 0.1, 0.2, 0.3, and 0.4 M, and 10 mL ethanol was added as co-solvent [19]. The silicate solution with various concentrations was then neutralized with 1 M HCl under continuous stirring to allow the gel to be formed. The suspension was centrifuged, and the silica particles were separated, washed with hot water, and dried [8]. The powder was put into crucible porcelain and was pre-heated to 15–200 °C, heated to 650 °C for 2.5–3 h. The silica was grounded in an agate mortar. Ethanol was added and followed with an ultrasonic fragmentation for 2 h. The mixture was left for 10 min at room temperature and centrifuged at 7000 rpm for 5 min. The deposit was refrigerated for 1–2 h, and the silica particles were obtained. Particle size was determined based on the data observation measured with SEM (JEOL 8000-upgraded with Semaphor Image processor). Image-J software was used for the SEM data processing to determine the particle size, and the silica purity of the samples was analyzed with XRF (Handheld type, Olympus DP-2000), and the effect of silicate concentration on particle size was evaluated.

Effect of silica particle addition on the silica-titania gel properties. Silica particle modified silica-titania gel was prepared by adding silica particles to the consolidant C9 (TEOS/TTIP sol with the composition of 55% TEOS, 40% ethanol, and 5% TTIP) at various percentages (0, 1, 2, 3, and 4% (w/w)). The mixtures were put in the open petri dish and located in the open space at room temperature. After 48 h, the solid deposit was obtained, and the shrinkage and crack were observed visually. Additionally, the deposit was characterized by XRD and FTIR spectrophotometer to identify crystallinity and the presence of the functional groups, respectively.

Effect of silica particles on andesite rock consolidation. Analog to the previous work, the mortar was made by mixing 100 g andesite powder and 3 mL consolidant at various percentages of silica particles (0, 1, 2, 3, and 4% (w/w)). The mixture was in a 1.5 × 1.5 × 5 cm cast. The composition of the consolidant sol used for this test was C9. After two weeks, the mortars were characterized by measuring ultrasonic velocity and Young Modulus with Geotron Elektronik type USG40 and Lighthouse DW Ver. 1.3 software for data processing.

■ RESULTS AND DISCUSSION

Rheological Properties of TEOS/TTIP Consolidant

The rheological analysis results of the consolidants, including viscosity, density, surface tension, and capillary rate, are shown in Table 3. In addition, the gelling time and consolidation results are also shown in this table. The mortar samples produced from the consolidation are visually displayed in Fig. 1.

Table 3. Rheological properties of the consolidants with different composition

Sample	Rheological properties					Qualitative result on mortar
	Gelling time (d)	Viscosity (mPa s)	Density (g/cm^3)	Surface tension (Nm)	Capillary rate (cm/s)	
C1(7.3:72.7:20)	3 d 18 h	2.2760	0.8755	0.0314	0.2021	+++
C2(6.4:63.6:30)	3 d 18 h	2.2138	0.8601	0.0323	0.2136	+++
C3(5:55:40)	3 d 18 h	2.1814	0.8410	0.0332	0.2265	+++
C4(4.5:45.5:50)	3 d 18 h	2.1022	0.8318	0.0343	0.2298	+++
C5(3.6:36.4:60)	3 d 18 h	2.0784	0.8145	0.0355	0.2312	+++
C6(1:59:40)	5 d 18 h	2.1811	0.8406	0.0329	0.2253	-
C7(2:58:40)	4 d 18 h	2.1816	0.8409	0.0329	0.2257	-
C8(3:57:40)	4 d	2.1812	0.8408	0.0332	0.2265	+
C9(4:56:40)	3 d 18 h	2.1815	0.8412	0.0332	0.2259	++
C10(5:55:40)	3 d 12 h	2.1820	0.8411	0.0335	0.2264	+++
C11(6:54:40)	3 d 6 h	2.1821	0.8415	0.0335	0.2260	+++

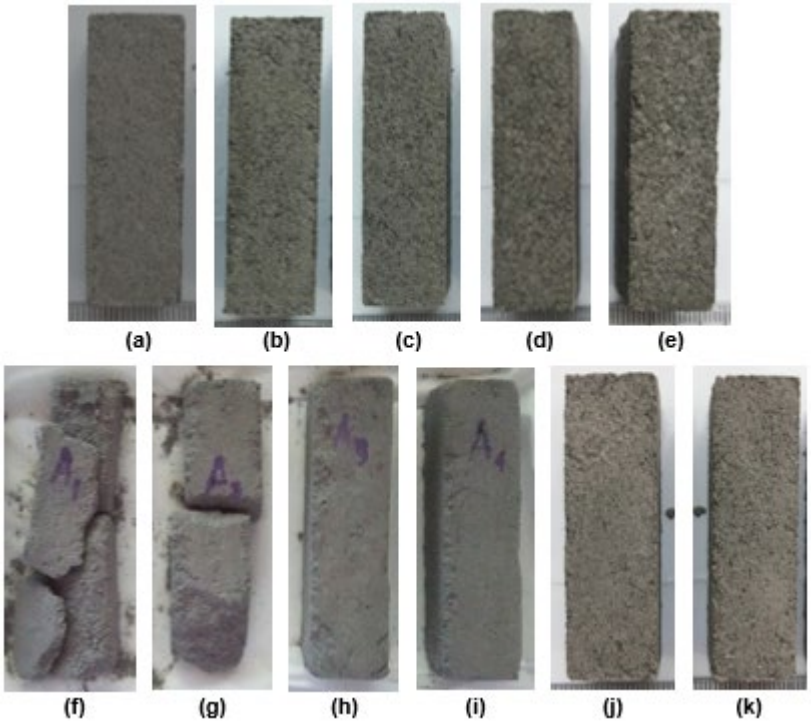

Fig 1. The mortar form andesite and TEOS-base binder with different percentage of TTIP (a) 1%, (b) 2%, (c) 3%, (d) 4%, (e 5%, and (f) 6%

The rheological data of the samples shows that the increase in ethanol content (C1-C5) decreases the viscosity and density, but increases the surface tension and the capillary rate of the sol to andesite rock particles. A high capillary rate of consolidant is expected to ensure the penetration of consolidant material into the rock pore. The consolidant shows different capillary rates in different types of rock, mainly due to the different microstructural characteristics of rock [6]. Andesite rock is a porous material that easily allows the consolidant to penetrate deeply into the porous structure.

From this data, all samples show good rheological properties. The sol can penetrate easily and saturated the andesite rock. In this variation, there is no optimum point since all viscosities are shown in an acceptable range. According to Li et al., commercial consolidant has a viscosity range between 2–3.3 mPa s [8]. Higher ethanol content increases the capillary rate, but the silica content in the mixture is low and not sufficient to attach andesite inter-particles. According to Pinto and Rodrigues, the minimum of silica gel content in the consolidant mixture is 34% [1].

The optimum mixture of the consolidant was observed from the consolidation result. The effective consolidation was obtained at the high content of TTIP, from sample C7 to C8. The low TTIP content (sample C5 and C6) shows negative consolidation, there is no consolidation, and the substrate remains in powder form. The minimum content of TTIP composition in the consolidant sample is 5% (with 55% TEOS and 40% ethanol) represented by sample C9. This sample also shows acceptable viscosity (2.1820 mPa s) and capillary rate (0.2265 cm/s).

The consolidation effectiveness relates to the gelling time. Hydrolysis and condensation rates of TEOS are typically low. The consolidation occurs with the high hydrolysis and condensation rate, commonly by catalyst addition. In this study, the increase of hydrolysis and condensation rates due to the addition of TTIP. The TTIP hydrolysis rate is faster than TEOS. The increase of TTIP concentration inclines the hydrolysis and condensation rates and decreases the gelling time. There is no significant effect of the ethanol content on the gelling time.

Silica Particles

Silica particles were extracted from RHA by destructing the sample with sodium hydroxide solution and being followed with the sol-gel process. The silica particle size depends on several factors, including the presence of templates, type of solvent, and concentration of precursor [14]. In this research, the effect of silicate concentration on the particle size was evaluated based on the SEM (with 10.000× magnification) image and measured with Image-J software. The result is shown in Fig. 2.

Based on the Image-J software analysis, the particle size of silica can be determined. The results, including the yield and purity percentages analyzed with XRF, are presented in Table 4.

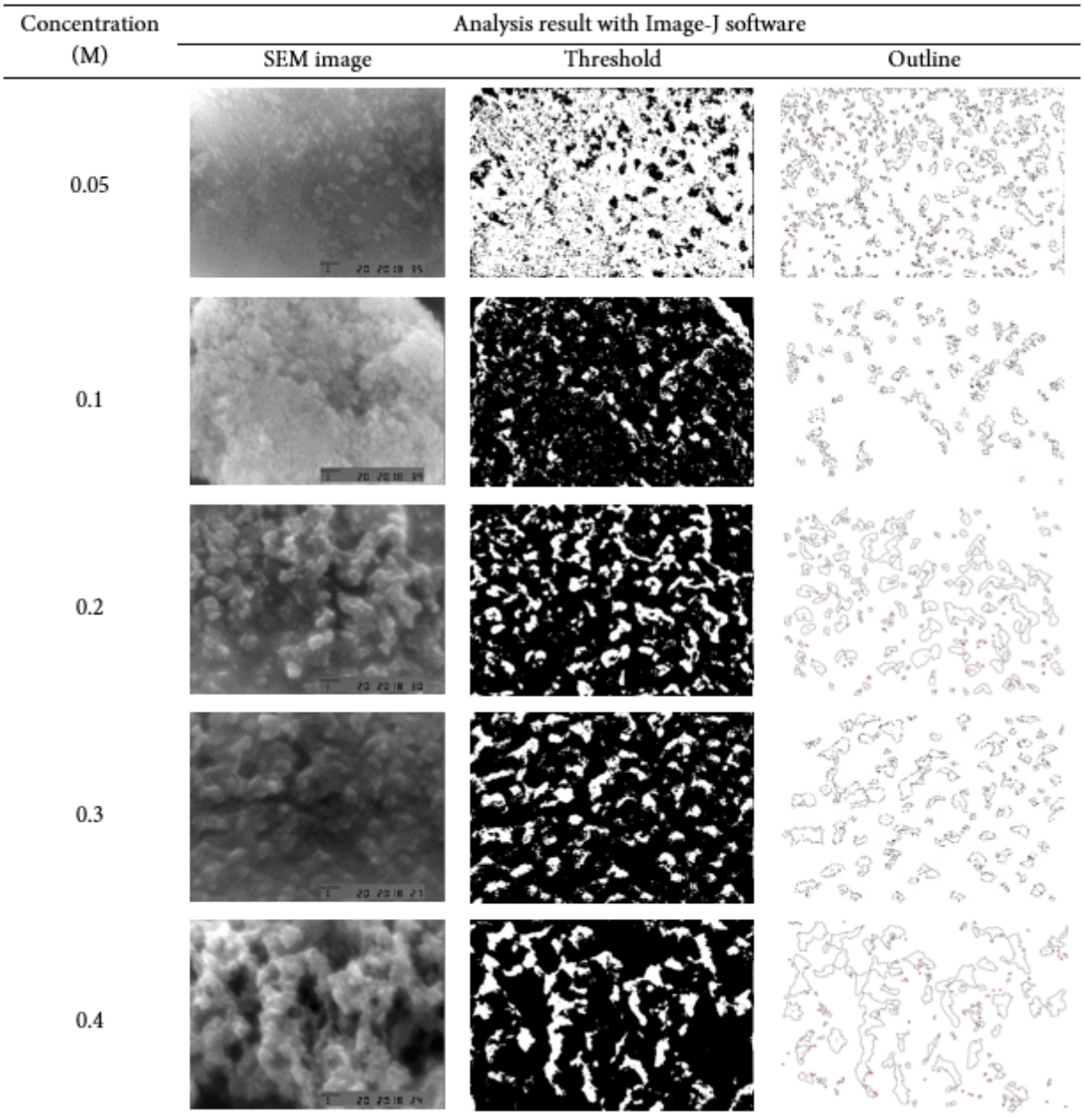

Fig 2. SEM image, threshold, and outline of silica particles extracted from RHA processed with Image-J software at various silicate concentrations

Table 4. Yield, purity, and particle size of silica particles extracted from RHA at various silicate concentrations

Concentration of silicate solution (M)	Yield (%)	Purity (%)	Size (nm)
0.05	55.74	98.99	109 ± 56
0.10	58.05	98.73	119 ± 83
0.20	59.48	99.01	150 ± 88
0.30	62.64	97.87	197 ± 73
0.40	68.91	98.89	211 ± 81

The particle size of the silica is influenced by the concentration of silicate in the solution during the precipitation. The increase in silicate concentration increases the particle size and the yield of the silica. A silicate concentration of 0.05 M shows the smallest particle size with the narrow particle size distribution (109 ± 56 nm). For that reason, this silica particle resulted from silicate solution 0.05 M was chosen as modifier particles in the TEOS/TTIP consolidant for the next step of this study. This particle size is chosen based on previous researches of the particle modified consolidant studies. Liu et al. used silica commercial silica particles with 100 nm size [7], while Ksinopoulou et al. used 150 nm commercial titania particles as modifiers [6].

Effect of the Silica Particle Addition on the Gel Properties

Crack and shrinkage level

The effect of silica particle addition on crack and shrinkage levels can be evaluated from the images of the gel formed from consolidants. Fig. 3 shows the images of the gel formed from TEOS/TTIP consolidant with various additions of silica particles. The gel is formed through hydrolysis and condensation reactions. The hard silica gel is obtained after the condensation of silanols. The silica/titania gel formation tends to shrink and crack, as shown in Fig. 3(a), and the crack decreases with the addition of the silica particles (Fig. 2(b-e)).

Fig. 3 indicates that qualitatively, the optimum percentage of the silica particle addition was 2%. There is a significant decrease in crack formation with increasing the percentage up to 2%, and the crack tends to decrease with increasing the percentage up to 4%.

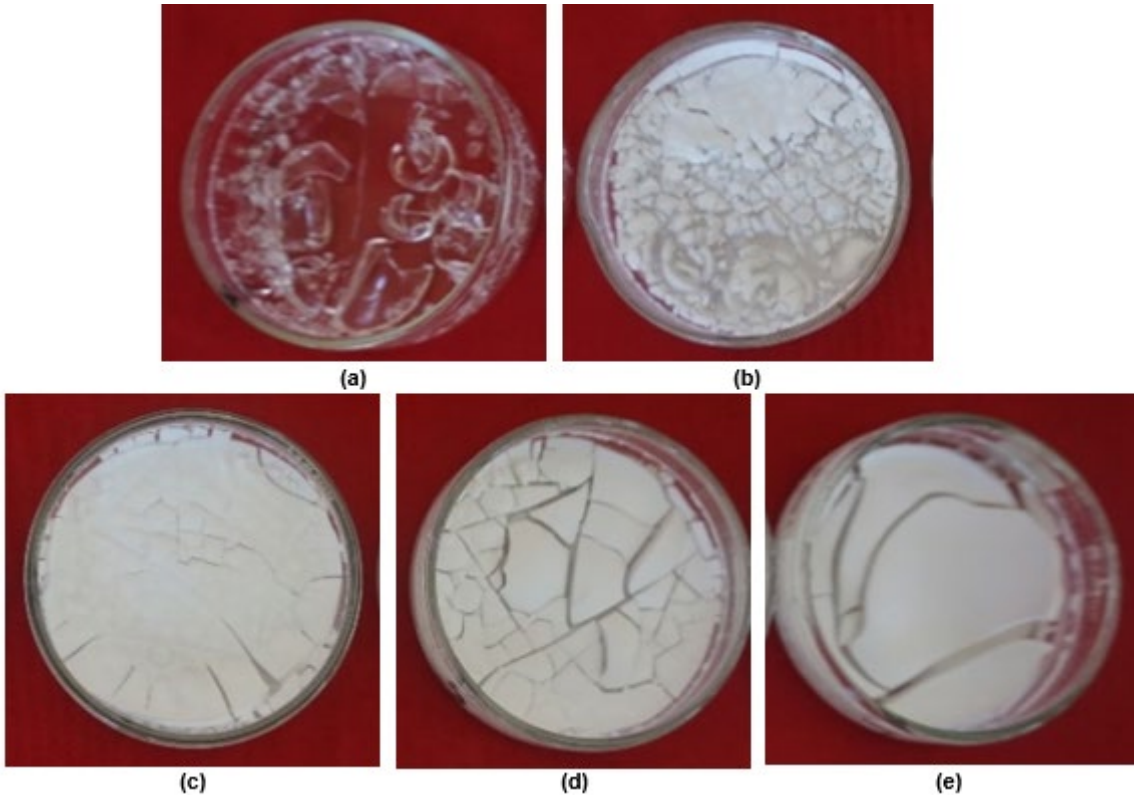

Fig 3. Images of silica-titania gel formed by TEOS/TTIP consolidant with addition of silica particle (a) 0%, (b) 1%, (c) 2%, (d) 3%, and (e) 4%

Functional groups of silica-titania gel

Fig. 4 shows the FTIR spectra of the gel formed from various consolidants.

The FTIR spectra of the silica, both extracted from RHA (Fig. 4(d)) and from TEOS (Fig. 4(e)), shows the peaks indicating characteristic bonds in silica. The peaks at 802 and 462 cm^{-1} indicate Si-O symmetric bending and rocking, respectively. Peaks at 1103 and 802 cm^{-1} indicate the presence of Si-O-Si bond [20], and the broad band around 3433 cm^{-1} is assigned to the superposition of the Si-OH bond stretching [21]. In the FTIR spectra of titania (Fig. 4(c)), peaks at 648 and 1080 cm^{-1} indicate the Ti–O–Ti and Ti–O–C bond, respectively [22-23]. A peak at 941 cm^{-1} in the FTIR spectra of silica-titania (Fig. 4(a)) represents a vibration of Si–O–Ti bond [20-21].

There are two types of interaction between TiO_2 and SiO_2, namely physical (with interaction forces weaker than Van der Waals forces) and chemical (by the formation of Ti–O–Si linkages) interaction. Among the various preparation methods, sol-gel hydrolysis is most widely used due to its possible capability in controlling the textural and surface properties of the mixed oxides. In sol-gel processes, the formation occurs due to the differences in the hydrolysis and the condensation rates of Ti– and Si– alkoxides [13]. According to Marimuthu et al. [24], the formation of Si–Ti mixed oxides through hydrolysis and condensation from TEOS ($(SiOC_2H_5)_4$) and TTIP ($(Ti(OPr^i)_4$) mixture can be presented in the following reaction.

$$Si(OC_2H_5)_4 + H_2O \xrightarrow{EtOH} Si(OH)(Ot)_3 + EtOH$$

$$4\ Si(OH)(OEt)_3 + Ti(OPr^i)_4 \rightarrow Ti[OSi(OEt)_3]_4 + 4\ Pr^iOH$$

$$Ti[OSi(OTe)_3]_4 + 12H_2O \rightarrow -Si-O-Ti-O-Si-+12\ EtOH$$

The crystallinity of silica-titania gel

Fig. 5 shows the XRD pattern of the silica-titania gel modified with and without silica particles, in comparison to titania (from TTIP), and silica (from TEOS and rice husk ash).

The samples used for the measurement is in the same amount. From the diffraction pattern, the amorphous silica is shown by the reflection at around 22.5° [25]. This reflection also occurs at the diffraction of the silica-titania gel samples. The addition of silica particles improves the intensity of the specific peak of amorphous silica. The diffraction pattern of the titania shown in Fig. 5(e) suggests that mainly the anatase phase is obtained [26]. The characteristic reflection corresponding to this phase is observed at 2θ of 25.5°, 38.2°, 48.2°, and 54.3°. This reflection also occurs in the pattern of the silica-titania gel (Fig. 5(a)) and silica-titania gel modified with silica particles (Fig. 5(b)) with a lower intensity. The decrease in the intensity of the titania reflection is due to the lower concentration in the gel. Silica can inhibit the formation of TiO_2 by impeding

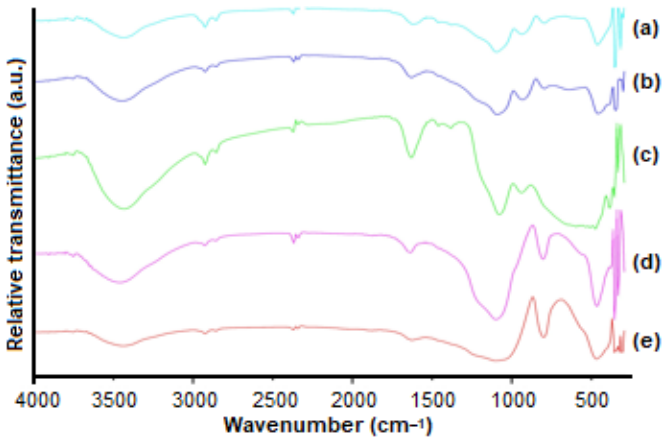

Fig 4. FTIR spectra of (a) silica-titania, (b) silica-titania gel modified with silica particles, (c) titania from TTIP, (d) silica from RHA, and (e) silica from TEOS

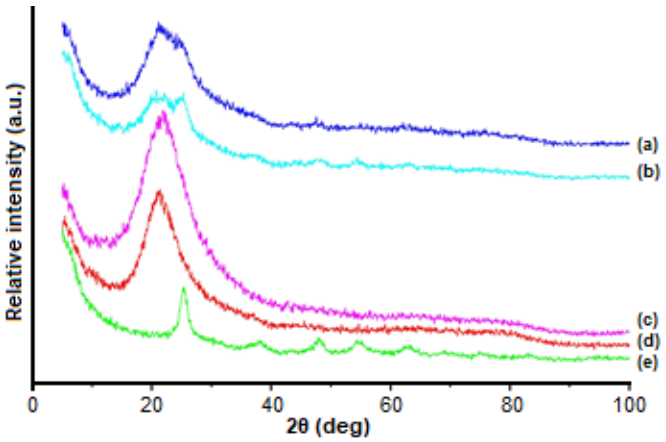

Fig 5. XRD pattern of (a) silica-titania gel, (b) silica-titania gel modified with silica particle, (c) silica gel from TEOS, (d) silica gel from RHA, and (e) titania

direct contact between TiO_2 particles by forming the Ti–O–Si bonding [27].

Consolidation of Andesite Rock

Preparation of TEOS-base consolidant without an organotin catalyst is the main objective of this study. Titanium tetraisopropoxide (TTIP) was tested as a catalyst component on the formation of silica chain during consolidation. Ethanol was used for the solvent to increase the penetration degree of the mixture into the rock pores. The variation of the TTIP percentage in the mixtures were tested to consolidate. Fig. 5 shows the mortar result in consolidation after aging for two weeks at room temperature. The figure shows that mortar consolidation starts from 4% of TTIP, while no effective consolidation occurs at a lower percentage. This relatively higher result, comparing to organotin (normally used at 1%) [28], is due to the double roles of the TTIP in the mixture, acting as a catalyst and being involved in the polymer formation.

Ultrasound velocity measurement of the samples was performed to evaluate the consolidation effectiveness of the sample quantitatively. Table 4 shows the result of ultrasound velocity and the Young modulus data of the samples. Young modulus was one of the important parameters to evaluate the hardness of materials, including rocks [22]. Consolidation is a process of increasing the hardness of the accelerated materials. Therefore, Young modulus could express the effectiveness of the consolidation. The Young modulus data was calculated based on the ultrasound velocity and the density of the samples [21].

At the low percentage of TTIP (1 and 2%, presented with formula C5, and C6, respectively), the consolidation of the mortars is not effective, the hydrolysis and condensation of TEOS to create silica bridging system were not obtained. The consolidation occurs at 3% and increases with the increase of TTIP up to 5% and to be constant at 6%. The hydrolysis TTIP has a higher hydrolysis rate than TEOS. By mixing TTIP and TEOS, the hydrolysis rate is between TEOS and TTIP ones. Consolidation occurs when hydrolysis and condensation of the mixture are able to bond inter-particles effectively. This inter-particle bonding increases the cohesion between particles and leads to strengthening the material presented with modulus elasticity.

Water is an essential agent in the consolidation process with a TEOS-based consolidant that involves hydrolysis. In consolidation with TEOS-based consolidant using an acid catalyst, few portions of water are added to hydrolyze TEOS to form a silica oligomer. The quantity of water and acid catalysts used for partial hydrolysis is also an important factor in this consolidant formula. The higher presence of water in the consolidant shortens the shelf life of the solution leading to difficulties in application [29].

The hydrolysis reaction rate of TEOS depends on the amount of water in the system. Therefore, the specific and low concentration of water is needed for the next simultaneous step with the condensation reaction of silica. On the other hand, the high water content will accelerate the reaction before contact with the stone and disturb the consolidation process. The consolidation effectiveness of the andesite block sample represents the condition of field implementation. The result of the consolidation effect of different consolidation formula is shown in Table 5.

Compressive strength is an appropriate parameter to understand the effectiveness of the consolidation. An effective consolidant can increase the compression strength of the deteriorated andesite. According to

Table 4. Ultrasound velocity and Young Modulus of mortars produced from consolidation with various concentrations of TTIP in consolidant

	Consolidant sample code					
	C5	C6	C7	C8	C9	C10
Ultrasound velocity (km/s)	*	*	0.868	1.067	1.555	1.565
Raw density (g/cm^3)	*	*	1.52	1.56	1.68	1.674
Young Modulus (N/m^2)	*	*	0.939	1.645	3.786	3.715

* Unmeasurable due to very low consolidation performance, the samples were very fragile

Table 5. Compressive strength of andesite rock sample consolidated using consolidants with different TTIP concentration

	Untreated andesite	Consolidant sample code					
		C5	C6	C7	C8	C9	C10
Compressive strength (kgf/mm^2)	0.368	0.38	0.402	0.474	0.519	0.58	0.589
% Strength increase *		3.26	9.24	28.80	41.03	57.61	60.05

* Based on the comparison with untreated deteriorated andesite from the same block

Clifton [30], effective consolidant increases the compressive strength at a minimum of 10%. This result shows the high increase of andesite compressive strength at more than 3% of the consolidant formula. This result is consistent with the result of the andesite mortar test.

In this study, the effect of water content in the matrix on the consolidation was also evaluated. Table 6 shows mortar performance resulted from consolidation in the various contents of water. The result shows that the consolidation does not work in the presence of water more than 0.75%. The dry matrix is the best condition for the consolidation, and 0.5% of water content is still acceptable for the consolidation.

This result is very important to understand the sensitivity of the formula to the water content. Andesite is commonly used as the heritage materials in Southeast Asian countries, such as Indonesia, Malaysia, and Thailand, located in tropical areas with relatively high humidity. The heritage materials are typically found in the open area. Therefore, the conservation of rock heritages containing water is still a challenge. All of the TEOS-based consolidants are sensitive to water. This study reveals that the water content limits in the matrix to be conserved and the selection of consolidants used in wet matrixes are important.

Effect of silica particle addition

The influence of silica particle modifier on the mortar parameters by measuring the ultrasound velocity and Young modulus was evaluated, and the result is expressed in Table 7. The data shown in the table corresponds to the qualitative observation of the gel shrinkage, as presented in Fig. 2. Ultrasound velocity and Young modulus of the sample increase in accordance with the percentage of added silica particles. The significant increase in the addition of 1 and 2% is observed, and the addition of more than 2% of the values tends to be constant. Therefore, the optimum addition of the silica particles was at 2%, and higher addition may lead to change the color in the application [6].

Table 6. Ultrasound velocity and Young modulus of mortars made of andesite rock powder with different water content

Parameters	Water content in the mortar (%)				
	0	0.25	0.5	0.75	1
Ultrasound velocity (km/s)	1.565	1.426	1.44	*	*
Raw density (g/cm^3)	1.74	1.78	1.66	*	*
Young Modulus (N/m^2)	3.715	3.253	3.182	*	*

* Unmeasurable due to very low consolidation result, the samples were very fragile

Table 7. Ultrasound velocity and Young modulus of mortars made from a different percentage of silica particle modifiers in the consolidant

	Silica particle addition (%)				
	0	1	2	3	4
Ultrasound velocity (km/s)	1.486	1.517	1.574	1.613	1.609
Raw density (g/cm^3)	1.61	1.59	1.76	1.76	1.76
Young Modulus (N/m^2)	3.407	3.56	4.156	4.327	4.015

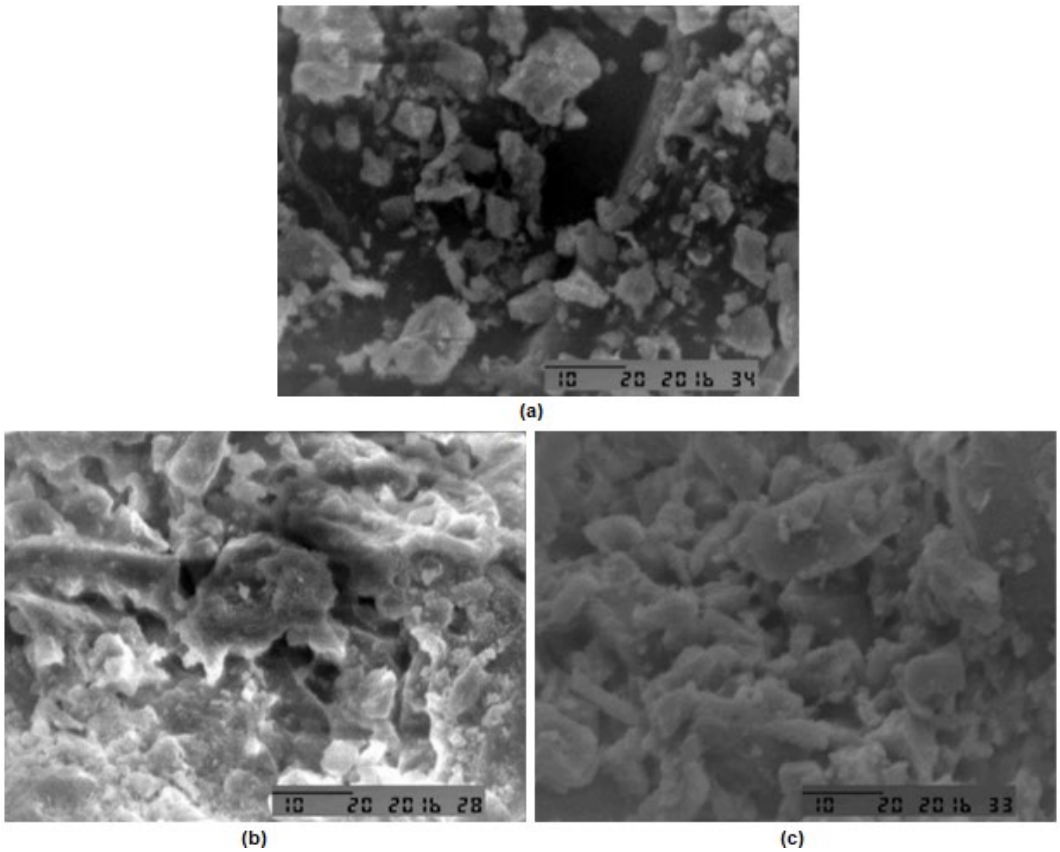

Fig 6. The SEM analysis (2.000× magnification) of (a) andesite powder before consolidation, (b) andesite mortar with silica-titania composite consolidant, and (c) andesite mortar using silica-titania consolidant modified with silica particles

Fig. 6 shows the SEM image of the mortar samples compared to the andesite powder before consolidation. This SEM result indicates the role of the consolidant as a binder between andesite particles. Andesite powders before consolidation appear separate from one another, while the particles in the mortar after consolidation becomes solid and connects each other. There is no significant difference in the appearance between mortar with and without silica particle addition. It occurs probably due to the similar appearance of andesite powder and silica particles.

■ CONCLUSION

The performance of the TEOS-based consolidant was successfully improved by the addition of TTIP and silica particles for andesite rock consolidation. The optimum consolidant composition of TTIP 5%, TEOS 55%, and ethanol 40% significantly increased the compressive strength up to 57.61% (0.58 kgf/mm^2) of the consolidated andesite rock, which is comparable to that of the fresh one. The water content in the rock matrix reduced the consolidation performance using TEOS-based consolidant, and 0.5% was the maximum water content allowed to maintain the consolidated rock performance. The addition of silica particles 2% to the TEOS consolidant decreased the gel shrinkage and increased the hardness of the consolidated mortar.

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