INTERNATIONAL JOURNAL OF CONSERVATION SCIENCE

ISSN: 2067-533X Volume 6, Issue 1, January-March 2015: 35-44 www.ijcs.uaic.ro

HYDROPHILIC ORGANOSILICONE RUBBER: THE NEW ORGANIC-INORGANIC HYBRID CONSOLIDANT FOR ANCIENT EARTHEN ARCHITECTURES

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Abstract

Organic-inorganic hybrid material used as consolidant for earthen relics was synthesized by adding silica nano particles into polysiloxane with the presence of surfactant. This composite material is less hydrophobic than other polymer consolidant, which can avoid the preservation damage caused by the incompatibility between the hydrophobic consolidant and the hydrophilic soil. The tensile strength of the synthesized consolidant is close to other rubbers, which can relieve the stress between consolidant and soil within the expansion-shrinkage process when environmental conditions change. The product was applied on ancient Liangzhu city wall and its effectiveness was examined.

Keywords: *Earthen relics; Consolidant; Composite material; Organosilicone; Liangzhu*

Introduction

Earth is one of the most widely used construction materials in the ancient world, but the deterioration of earthen architectures is much faster than the equivalent constructed by stones and bricks. The major cause of the earth deterioration in moisture environment is rainwater erosion, often in combination with soluble salts, which leads to the granular disintegration and failure of structures [1]. Consolidants are often used to treat these pathologies. Typical consolidants for earthen relics can be grouped into two categories based on the chemical composition of the raw materials: inorganic consolidants (potassium silicates, calcium hydroxide, etc.), and organic consolidants (acrylic resins, vinyl acetate polymers, alkoxysilanes, epoxy resins, etc.). These materials can improve the compressive strength and water resistance property of earthen relics. However, both the inorganic and organic consolidants have some disadvantages in the preservation. For example, the water resistance property and penetrability

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of inorganic consolidants are not good enough to obtain satisfied consolidation results [2, 3]. Even worse, it is very common to observe colored crust on the relic surface after the use of inorganic consolidants so that the appearance of relics is altered [4]. As for the organic consolidants, their degradation can not be neglected [5-7] and their super hydrophobic nature can cause preservation damage to relics [8].

Therefore, the interest in the application of organic-inorganic hybrid composite materials in the conservation is growing [9, 10]. Much attention has been devoted to the addition of nano particles of oxides into silicone-based polymers [11-17]. Kapridaki et al found that TiO_2-SiO_2-polydimethylsiloxane(PDMS) nano composite material can form a homogeneous crack-free coating on marble surface and therefore play a protective role [18]. Facio et al provided a new and simple synthetic route to obtain a super hydrophobic coating by mixing PDMS, colloidal silica particles, TES40 (a mixture of monomeric and oligomeric ethoxysilanes) and surfactant. This nano composite can be applied on outdoor building substrate, penetrate into the porous structure and achieve required adhesion [19]. However, the currently available inorganic-organic hybrid materials are not designed to consolidate earthen relics. Their penetrability into soil is unknown and the super hydrophobic nature may cause damage [8]. Also, considering that the expansion-shrinkage process which soil may experience with the temperature and moisture change, the consolidant material with tensility is desired.

In this work, an innovative inorganic-organic hybrid material was synthesized by adding silica nano particles into polymerized siloxanes. This material can penetrate into soil and its tensile strength is close to silicone rubbers so that the stress between soil and the material can be relieved. It is also less hydrophobic than other polymer consolidants to avoid the preservation damage. The consolidation effect of this material in the conservation of earthen relics was evaluated.

Experimental

Materials

Octamethyl cyclotetrasiloxane (D4), sodium dodecylbenzene sulfonate (SDBS), polyvinyl alcohol (PVA 1788), silica solution, silane coupling agent KH-550 (γ-Aminopropyl triethoxysilane) and emulsifier OP-10 were used to synthesize the organosilicone rubber. The soil samples used in the experiment were taken from ancient Liangzhu City Wall relics (3000 B.C.) in Hangzhou, China. The model test blocks of earth were made according to the method described below: smash and sieve the soil sample with 10 mesh number griddle, then evenly blend the soil with water; add the mixture into the cylinder-shape mould with the diameter of 38mm and height of 41mm; compress the sample with hammer for 50 times until the compact block was obtained. The test blocks were stored under 20°C and 70% humidity for 7 days prior to use.

Synthesis of the hydrophilic organosilicone rubber

Add the emulsifier OP-10 and water into D4 and stir for 10min, and then add the solution into the beaker containing PVA 1788 and SDBS under 90°C keep stirring for 60min to complete the polymerization reaction. Finally, add silica solution and KH-550 to obtain the organosilicone rubber emulsion. Fourier transformer infrared spectra (FTIR) were recorded in the dry film of synthesized organosilicone rubber using Nicolet iS10 FT-IR from Thermo Fisher Scientific.

Conservation of the model earthen test blocks

The conservation material was applied in two different ways to test its consolidation effect. One way is to add the material into the soil when preparing the earthen test blocks so that the material could be mixed thoroughly with the soil. This method is helpful for the comparison of consolidation effect of different concentrations of conservation material because of the homogenous nature of earthen test blocks. In the other way, the consolidant was sprayed onto the test block's surface to penetrate into the block. This is the usual method to apply conservation materials onto the earthen relics.

The assessment of the conservation efficiency

The conservation efficiency was estimated by compressive strength test, water resistance test and surface hardness measurement. The compressive strength was determined by a hydraulic universal testing machine (YC-125B, Shanghai, China). In the water resistance test, the earthen test blocks were immersed in water and the time when the block collapsed was recorded. The longer the time, the better the water resistance is. The surface hardness was measured using Shore's hardness tester (LX-D, Beijing, China). The morphologies of the block samples were observed by scanning electronic microscopy (SEM, FEI SIRION-100).

Results and Discussion

The synthesized organosilicone rubber

The chemical bonds in the dry film of the organosilicone rubber were analyzed by FTIR. The spectra are presented in Fig. 1. The pronounced band appearing at 3440cm^{-1} and the sharp band at 1600cm^{-1}, which corresponded to the stretching and bending adsorption of O-H group, indicated hydrophilic property of the material under study. The band centered at 1092cm^{-1}, along with the band at 800cm^{-1}, which were assigned to the vibration adsorption of Si-O-Si groups, gave the fact that the material was mainly composed of a silica network. The band between 2800cm^{-1} and 3000cm^{-1} was attributed to alkyl groups, giving hydrophobic property of the material.

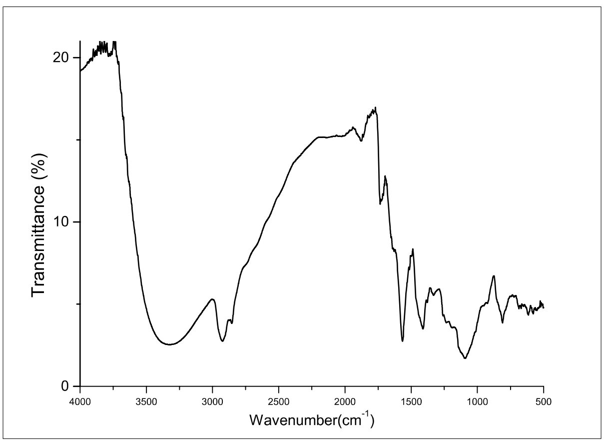

Fig. 1. FTIR spectra of the synthesized organosilicone rubber

To investigate the hydrophobic/hydrophilic feature of the synthesized organosilicone rubber, the contact angle measurement was carried out. Four different conservation materials were coated onto the surfaces of earthen test blocks and their contact angles were measured using JC200A tension meter (Shanghai Zhongchen Instrument). The results are shown in Table 1.

Table 1. The contact angles of different conservation materials

Conservation material	Organosilicone rubber	Aqueous consolidant	Oily consolidant	Tetraethoxysilane (TEOS)
Contact Angle	78.3°	86.5°	88.7°	30.8°

The contact angle of TEOS was the lowest, indicating its hydrophilic feature; while the contact angle of organosilicone rubber was lower than aqueous and oily consolidants, which means organosilicone rubber is not strongly hydrophobic.

The tensile test showed that the synthesized organosilicone rubber had tensile strength to some degree. In this test, the organosilicone rubber emulsion, aqueous and oily consolidants were brushed onto the surfaces of glass slides respectively, and then they were kept in oven until they were dry. The glass slides were broken by knife and the consolidant thin films were left. The aqueous and oily consolidants films were not tensile since they were easy to break. The tensile strength of the organosilicone rubber can be obtained by measuring the force that was needed to break the rubber thin film, according to The National Standard of Chemical Industry [20]. The tensile strength of synthesized organosilicone rubber was about 2.0MPa, which is close to the tensile strength of the common commercial rubber products. For example, the tensile strength of fluorinated silicone rubber is about 8.7-12.1MPa, the tensile strength of common solid silicon rubber is about 4.0-12.5MPa. The advantage of the tensile property of consolidants is that, when the cultural relic object is experiencing expansion-shrinkage cycles, the consolidants can expand and shrink with the relic objet, so that the stress between the different materials can be relieved.

The influence of KH-550

The addition of KH-550, a silane coupling agent, can accelerate the solidification of organosilicone rubber emulsion. In this process, when silane is subjected to hydrolysis, a reactive silanol group is formed and can condense with other silanol groups to form silxane linkages. In this section, the effect of the concentration of KH-550 on the consolidation is discussed.

The consolidant emulsions with four different solid concentrations of 1%, 2%, 3% and 4% were prepared using three different KH-550 concentrations (i.e., 2.1%, 2.8% and 3.5%). These emulsions were added in the simulated earthen test blocks and their 7-day compressive strengths were measured (Fig. 2). It can be seen that the concentration of KH-550 has obvious influence on the compressive strength. The best strength result was obtained when KH-550 concentration was 2.8%. On the other hand, when the solid concentration of consolidant was 3%, the consolidation efficiency was better.

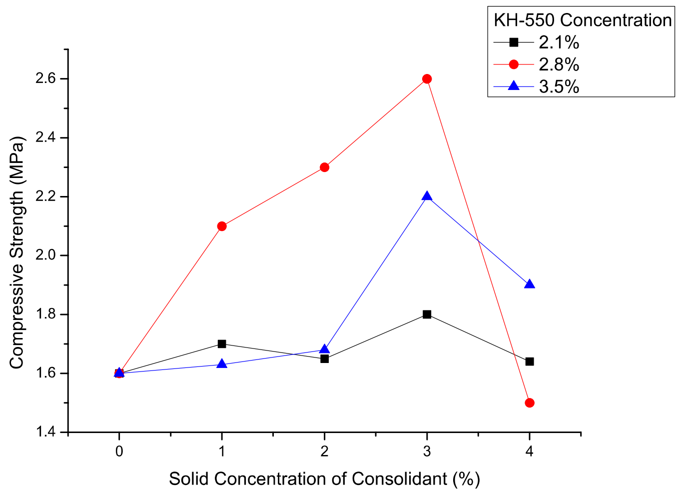

Fig. 2. Compressive strength values of the test blocks when treated with different concentrations of synthesized organosilicone rubber using mixing method.

The conservation efficiency

The water resistance test was performed to evaluate the conservation efficiency of the consolidant. The soils were mixed with consolidant emulsions with different solid and KH-550 concentrations to make simulated earthen test blocks. These blocks were then kept in water to observe the time when they collapsed.

Table 2 shows that when KH-550 concentrations were 2.8% or 3.5%, the water resistance property of the samples was better and when the solid concentration was 3%, the water resistance property was better.

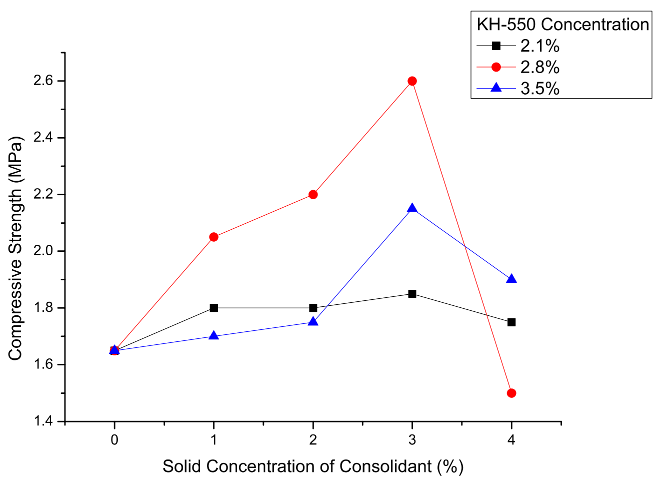

Fig. 3. Compressive strength values of the test blocks when treated with different concentrations of synthesized organosilicone rubber using spraying method.

Table 2. Water resistance test results of the synthesized consolidant with different KH-550 and solid concentrations

Time in water	KH-550 concentration											
	2.1%				2.8%				3.5%			
	Solid Concentration				Solid Concentration				Solid Concentration			
	1%	2%	3%	4%	1%	2%	3%	4%	1%	2%	3%	4%
1 min	began to collapse	began to collapse	began to collapse									
5 min	completely collapsed	completely collapsed	completely collapsed	crack	crack	crack			began to collapse	began to collapse		
10 min				began to collapse	completely collapsed	completely collapsed	crack	crack	completely collapsed	completely collapsed	crack	crack
20 min				completely collapsed			began to collapse	completely collapsed			began to collapse	began to collapse
1 hr							completely collapsed				completely collapsed	completely collapsed

When the consolidant emulsion was sprayed onto the sample block's surface, the 7-day compressive strength was measured. Fig. 3 shows that the best overall conservation efficiency was obtained when KH-550 concentration was 2.8%. On the other hand, when the solid concentration was more than 3%, the consolidation effect was not evident; even worse, thin film of consolidant was formed on the sample's surface. The thin film will not only alter the appearance of the block surface, but also prevent the penetration of the consolidant. Therefore, 2% should be the appropriate concentration in the practice of earthen relic conservation.

Figure 4 shows the SEM images of the earthen sample block before and after the treatment of consolidant. After treatment, gaps and cavities among the soil were filled so that the block was more compact. It is consistent with the compressive strength measurement.

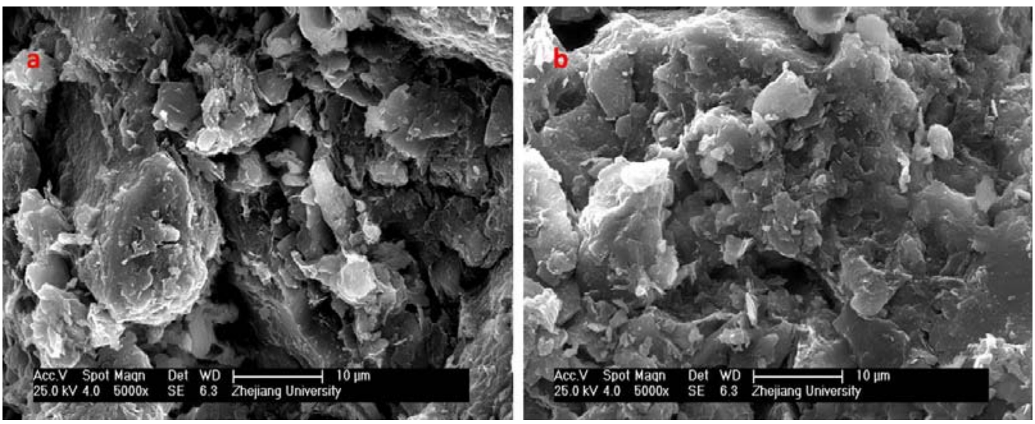

Fig. 4. SEM images of the test blocks. (a) Untreated and (b) treated with synthesized organosilicone rubber.

In situ conservation of the city wall of Liangzhu

The organosilicone rubber emulsion with the solid concentration of 2% was used to consolidate the earthen wall of ancient Liangzhu City with about 5000 years history, located in the south region of Yangtze River Triangle. Before the consolidation, we drilled 8 holes on the experimental wall area with the length of about 8 cm. The emulsion was injected into the holes by perfusion tubes (see Fig. 5).

Fig. 5. Pictures of ancient Liangzhu city wall consolidation work: a - north city wall relic of Liangzhu, where the consolidation work was performed; b - Injecting the consolidant using perfusion tubes; c - the consolidation area one month after the treatment.

Stop injection until the emulsion can not penetrate into the soil. Then fill the holes with the mixture of soil and consolidant. Finally, spray the consolidant onto the wall surface using sprayer. One month later, the examination of the consolidation results revealed that the consolidant didn't alter the appearance of the wall. Seven days after the treatment, surface hardness values of 8 spots around the holes were recorded (see Fig. 6). The increase of surface hardness indicates that the consolidant can reinforce the earthen wall. In the future work, the consolidation effect of organosilicone rubber on the earthen wall of Liangzhu city will be monitored and assessed regularly.

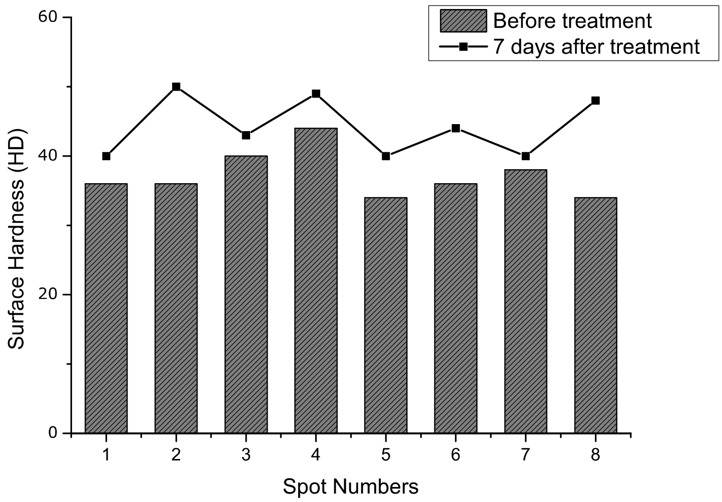

Fig. 6. Surface hardness measurement results in ancient Liangzhu city.

Conclusions

We synthesized an innovative consolidant material for the conservation of earthen relics. This inorganic-organic hybrid material can be achieved by mixing silica nanoparticles and polysiloxane with surfactant. The compressive strength of the soil block was increased by about 30%-40% after the use of our new consolidant with good penetrability. We found that 2% should be the appropriate consolidant concentration in the field conservation of earthen relics. A consolidant with higher concentration could form a thin film on the relic surface, not only altering the appearance of the object but also preventing the penetration of consolidant emulsion. The tensile strength of the material is fairly close to that of organosilicone rubber, which means it can expand or shrink with the soil when temperature and moisture conditions change. It is believed that the tensile property can relieve the stress between the consolidant and soil and then reduce the risk of crack or detachment. The field work in ancient Liangzhu city wall relic demonstrated the effectiveness of our new material which also preserves the aesthetic appearance of the relics.

Acknowledgements

The National Basic Research Program of China (Grant Number 2012CB720902), the National Science and Technology Support Program of China (Grant Number 2013BAK08B11) and Conservation Science and Technology Project of Zhejiang Provincial Administration of Cultural Heritage are greatly acknowledged for their financial support.

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Received: August, 21, 2014
Accepted: January, 31, 2015