Construction and Building Materials 122 (2016) 90–94

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

# Synthesis of TEOS/PDMS-OH/CTAB composite coating material as a new stone consolidant formulation

Yurong Liu *, Jia Liu

*Chongqing Key Laboratory of Micro/Nano Materials Engineering and Technology, Research Institute for New Materials Technology, Chongqing University of Arts and Science, Chongqing 402160, PR China*

## HIGHLIGHTS

- TEOS/PDMS/CTAB composite coatings have been fabricated.
- TEOS/PDMS/CTAB composites create a hydrophobic, crack-free coating.
- The composite coatings have been used for sandstone conservation.

## ARTICLE INFO

*Article history:*
Received 28 March 2016
Received in revised form 3 June 2016
Accepted 14 June 2016

*Keywords:*
Stone consolidant
Coating materials
Crack-free
Hydrophobic

## ABSTRACT

A new stone consolidant formulation based on tetraethoxysilane (TEOS) and additives such as hydroxyl-terminated polydimethylsiloxane (PDMS-OH) and cetyl trimethyl ammonium bromide (CTAB) has been developed denoted as TEOS/PDMS-OH/CTAB composite coating material. The hydrophobic property, surface morphology, and abilities to resist acid corrosion and salt crystallization weathering have been measured to evaluate the stone protection performance of as-prepared TEOS/PDMS-OH/CTAB composite coating materials. The results demonstrate that the addition of PDMS-OH contributes to improve the hydrophobic properties of sandstones. The addition of CTAB to the siloxane composition results in the formation of superficial protrusions with a micro- and nanoscopic structure and overall alteration of surface morphology and roughness, thus preventing the cracking during the drying process. In addition, after treatment by TEOS/PDMS-OH/CTAB composite coating materials, the sandstone has improved the abilities to resist acid and salt crystallization weathering significantly. These advantages make TEOS/PDMS-OH/CTAB composite coating materials exhibit good comprehensive performance in terms of stone heritage protection.



## 1. Introduction

During the past few decades, many valuable historic stone sculptures located outdoors are subjected to various degrees of degradation because of a combination of several factors, such as acid rain, soluble salts and biodegradation of stone materials [1]. In order to protect the historic stone sculptures and decrease the risk of being irreparably lost as a result of degradation, it is very urgent and necessary to develop new protective coating materials for application as consolidants or hydrophobic agents on stone [2–6]. The purpose of consolidants is to strengthen weakened stone and slow down the rate of degradation by binding loosened grains and crystals [7,8]. The use of hydrophobic agents is aimed at preventing or reducing the penetration of water into the stone network, thereby minimizing the rate of degradation.

Among numerous stone protection materials, consolidants based on tetraethoxysilane (TEOS) are commonly used for consolidating weathered stones [9]. Their advantages are the low viscosity and the ability to form silicon–oxygen–silicon (Si–O–Si) bonds [10]. Low viscosity allows TEOS and its oligomers to transport easily inside the stone, wetting the stone surface well and penetrating into a certain depth [11]. The Si–O–Si bond is also the major chemical bonding form in many stones, which contributes to the compatibility between consolidant and the protected stones. Therefore, TEOS-based consolidant can function as a binder in the stone, leading to significant enhancement of cohesion and adhesion among the stone grains [12].

However, one serious drawback of TEOS-based consolidants is their tendency to develop cracks inside the stone due to the stress generated from significant mass and volume losses and increasing

* Corresponding author.
*E-mail address:* liuyr1978@163.com (Y. Liu).

http://dx.doi.org/10.1016/j.conbuildmat.2016.06.069
0950-0618/

capillary forces during the aging and drying process [13–15]. Recently, several experiments have been carried out to suppress the generation of cracking. Particular attention has been given to nanocomposites, which are obtained by introducing various inorganic nanoparticles ($SiO_2$, $TiO_2$, etc.) into siloxane polymers [16–18], thus the cracking of gel network can be avoided by the addition of nanoparticles [19–23]. However, nanoparticles are reported to act as a barrier to water vapor movement if they are not dispersed evenly [24]. Another approach is adding a surfactant to the starting sol to coarse gel network and decrease the surface tension, thus preventing the cracking during the drying process [25,26]. Despite the advantages of surfactant, there is a limited number of laboratory tests and reports about fabrication and practical application of stone consolidants with the addition of surfactants.

The present work present a new stone consolidant formulation (TEOS/PDMS-OH/CTAB composite coating material) based on TEOS and additives such as hydroxyl-terminated polydimethylsiloxane (PDMS-OH) and cetyl trimethyl ammonium bromide (CTAB). PDMS-OH is added in order to reduce the coating surface energy and consequently to give hydrophobic properties to the materials. The incorporation of CTAB provides an efficient means of preventing the gel cracking during the drying process. The hydrophobic properties, surface morphology, acid rain attack and salt crystallization weathering tests have been performed to evaluate its effectiveness as a consolidant on sandstones of Chongqing Dazu stone sculptures in China. Fig. 1 is an example of Dazu stone sculptures affected by acid rain, soluble salts and biodegradation of stone materials.

## 2. Materials and methods

### 2.1. Materials

TEOS and CTAB were obtained from Chengdu Kelong Chemical Reagent Corporation. Hydroxyl-terminated PDMS (PDMS-OH) with a molecular mass 500–700 and a percentage of OH ranging from 6 to 8 wt% was supplied by Chenguang Research Institute of Chemical Industry.

### 2.2. Preparation of TEOS/PDMS-OH/CTAB composite coating materials

The TEOS/PDMS-OH/CTAB composite coating materials were prepared through acid-catalyzed TEOS hydrolysis in the presence of CTAB surfactant and PDMS-OH. First, the silica sol was prepared by refluxing TEOS, ethanol, water, and hydrochloric acid at 60 °C for 1 h in the presence of CTAB surfactant. Next, PDMS-OH was added to the mixture under vigorous stirring for another 1 h. The mole ratio of TEOS/$H_2O$/ethanol/PDMS-OH/CTAB was 1:4:4:0.03:0.005. Then, the 5 wt% TEOS/PDMS-OH/CTAB composite coating materials were obtained after adding a certain amount of ethanol to the above solution.

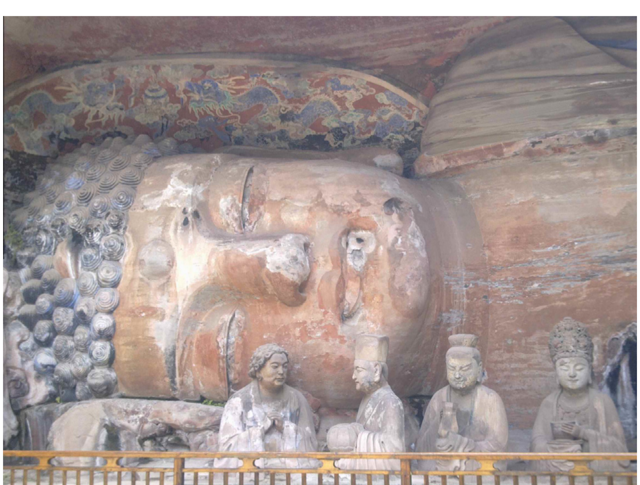

**Fig. 1.** Dazu stone sculptures affected by acid rain, soluble salts and biodegradation stone materials.

### 2.3. Consolidation of stone samples

The sandstone samples from Chongqing Dazu sculptures was composed of quartz ($SiO_2$) and calcium feldspar ($CaAl_2Si_2O_8{\cdot}4H_2O$). The sandstone block with dimensions $3 \times 3 \times 1$ $cm^3$ was scraped off with a grinding machine in order to give uniform surfaces and reduce cutting imperfections. The sandstone samples were rinsed with deionized water and dried in an oven at 110 °C for 4 h. Then the dried sandstone samples were soaked in consolidant solutions (TEOS/PDMS-OH/CTAB composite coating materials) for 24 h and dried under laboratory conditions until the sol–gel process finished.

### 2.4. Methods of characterization

The chemical bonds of composite coating materials were analyzed by Fourier transform infrared spectrophotometry (FTIR). The spectra were recorded in KBr pellets using a Varian Cary 670 FTIR spectrometer in the region from 4000 to 400 $cm^{-1}$. The static contact angle ($\theta$) of the stone surfaces was measured using a JC2000C1 contact angle meter (Shanghai Zhongchen Digital Technic Apparatus Co., Ltd, China). The reported contact angle value were the average of five measurements. Scanning electron microscopy (SEM) was used to visualize the surface morphology of the stone, using a Hitachi Fields S-4800 SEM instrument.

### 2.5. Acid rain weathering tests

Acid rain weathering tests were conducted to study the acid resistance of sandstone samples. The samples were immersed in $H_2SO_4$ solution (pH = 3) for 50 h followed by absorption of excess water onto filter paper, and then the stone samples were dried at room temperature for 11 days. The water contact angle of stone samples measured after acid rain weathering was taken as a measure of the damage.

### 2.6. Salt crystallization weathering tests

Salt crystallization weathering tests consisted of eight cycles. In each cycle, stone samples were soaked in a 10 wt% sodium sulfate ($Na_2SO_4$) solution for 24 h, followed by drying at room temperature and freezing at −18 °C for 4 h, and subsequent drying at 65 °C in an oven for another 4 h. The water contact angle of stone samples measured at the end of each cycle was taken as a measure of the damage.

## 3. Results and discussion

FTIR spectrum of TEOS/PDMS-OH/CTAB composite coating materials is shown in Fig. 2. Specifically, the bands located at 800 and 1090 $cm^{-1}$ are attributed to the absorption of Si-O-Si bond, indicating that composite coating materials are mainly composed of a Si-O-Si network [27]. The peak at 1270 $cm^{-1}$ is attributed to the Si–$(CH_3)_2$ bond [28]. The broad band centers at 3450 $cm^{-1}$ and the sharp band at 1637 $cm^{-1}$ are assigned to the OH stretching

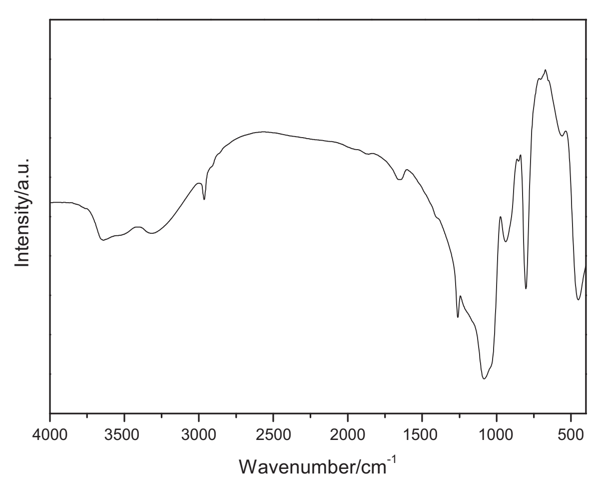


**Fig. 2.** FTIR spectrum of TEOS/PDMS-OH/CTAB hybrid materials.