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Use of coupling agents for increasing passivants and cohesion ability of consolidant on limestone

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ABSTRACT

Deterioration of monuments constructed of limestone could be potentially arrested by applying a combination of coupling agents with consolidants, which can prevent acid attack and mechanical weakening. Two different coupling agents including N-(2-aminoethyl)-3-aminopropyl methyl dimethoxysilane (AE-APMDMS) and diethyl phosphatoethyl triethoxysilane(DEPETES) were used to link calcite. Calcite was impregnated with these coupling agents and studied by FTIR, TG-DSC and contact angle measurement. According to these techniques, new bands, a two stage decomposition pattern appeared and a slight increase in surface hydrophobicity for AE-APMDMS and DEPETES that indicated interactions between the coupling agents and calcite. The Scotch Tape test and compressive strength test showed that the cohesion between consolidant and limestone powder improved, while the ability of consolidation decreased, which were resulted by coupling agents. Resist acid test on limestone powder coated with the coupling agents resulted in a decreased deterioration rate. Limestone treated with combined consolidant plus AE-APMDMS or DEPETES showed a significant decrease in capillarity water absorption.

1. Introduction

Historic stone structures such as monuments, sculptures and temples having immense aesthetic and cultural value are a vital economic resource for many parts of the world. In general, there are three types of weathering: chemical, physical and biological decay. In nature these three types often cannot be separated and are influenced each other. For architectural and sculptural stone, the principal mechanism of chemical weathering is acidic dissolution of the carbonate stone [1,2]. So far, the materials were used to preserve stone including epoxies, acrylics, silicones, alkoxysilanes and other organic polymers in order to reduce or delay weathering effects on sculptures and monuments [3–8]. These materials have been proven to work very well for some existent problems, for example, granular disintegration, while limestone conservation is still a challenge. This is due to the chemical composition and pore structure of the limestone. Recently, calcium hydroxide nanoparticles are considered as a good compatible consolidation materials to increase the durability of carbonate stones [9,10], however, they cannot resist acid rain.

Alkoxysilanes, such as tetraethoxysilane (TEOS) based coating, are commonly used for the protection of stone in China. The poor chemical affinity between calcite and the silica molecules formed after hydrolysis and condensation of alkoxysilanes [11,12]. Due to the gel brittleness, the tendency to crack during shrinkage and drying has been responsible for several studies with the objective of modifying and improving alkoxysilane performance [13–16]. Mosquera' group have obtained crack-free products by the addition of n-octylamine to TEOS [17,18]. They also prepared hydrophobic products by adding PDMS-OH to the starting sol [19–21]. Our group also prepared consolidant products by adding n-octylamine and PDMS-OH to TEOS [22]. The n-octylamine provides an efficient means of preventing cracking of the gel, as the result of two factors: (1) coarsening of the gel network, which reduces the capillary pressure; and (2) decreasing surface tension, which also reduces capillary pressure [17]. The organic component conferred toughness and flexibility on the product, and collaborated in preventing cracking of the gel; in addition, organic groups were integrated in the silica polymer giving it hydrophobic properties [18]. Demjén [23,24] found that aminofunctional silane coupling agents can adhere well to the $CaCO_3$ and also react with the polymer. The amount of coupling agents creating a monolayer coverage changed between 0.3% and 1.0 wt% calculated for the $CaCO_3$. Doehne et al. [12] proposed various coupling agents based on

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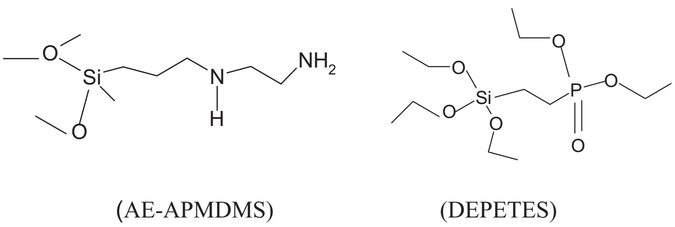


Fig. 1. AE-APMDMS and DEPETES.

silanes for improving the adhesion between SiO_2 gel and calcareous and clay-rich substrate. Beyond that, coupling agents plus Zr alkoxides consolidant were applied to calcite stone in order to increase adhesive ability between consolidant and limestone surface [25]. The silanol part of the aminosilane is condensed with the network of the SiO_2 gel, while the positively charged aminofunctional group at the other end of the molecule is connected to negatively charged positions on the calcite substrate surface.

Our strategy to protect limestone is a surface-specific treatment that is designed to retard any further chemical corrosion by rendering the limestone surface passivation towards acid rain. A mineral-specific passivant molecule energetically binds to the calcite surface, therefore, passivant can act as a coupling agent to link the consolidant and calcite. The coupling is achieved by a polymerizable "tail" on the passivant that enables sol–gel condensation reactions with the consolidant. The consolidant offers strength to the limestone by forming an inorganic framework within the pore system.

Two classes of silylated coupling passivants were tested based on the binding functional groups and the charge present on them: N-(2-aminoethyl)-3-aminopropyl methyl dimethoxysilane (AE-APMDMS), diethyl phosphatoethyl triethoxysilane(DEPETES) (Fig. 1). In this case, the purpose of using the coupling agents was to bond the functional groups (amino, phosphate) to the calcite surface. For the consolidant, alkoxysilane solutions were prepared according to our past research [22].

Schematic diagram of the aim of the investigation is presented in Scheme 1.

2. Materials and methods

2.1. Reagents

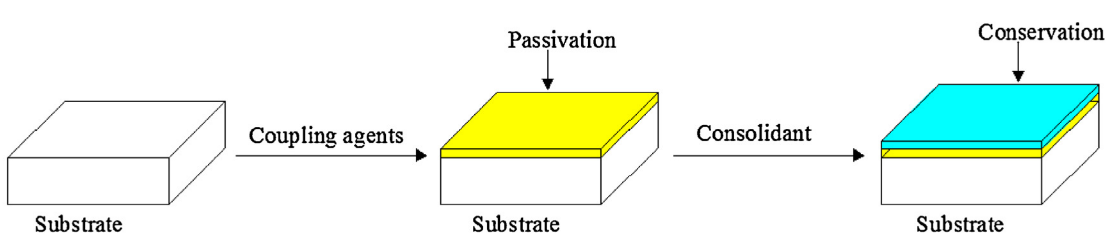
TEOS and calcite ($CaCO_3$) powder were analytical grade reagents obtained from Sinopharm Chemical Reagent Corporation. PDMS-OH, Mn = 550 was obtained from Sigma–Aldrich Co. Inc. The surfactant was n-octylamine (aladdin) as polycondensation catalyst. Coupling agent AE-APMDMS was obtained from Fluorochem Chemical Industry Co. Ltd. DEPETES was obtained from Tokyo Chemical Industry Co. Ltd. The samples of limestone were obtained from Nanjing Dou village. Mineralogical analysis and XRD showed that composition of the stone is composed of calcite (approximately 97%), with trace amounts of quartz, alumina, and iron oxides. The limestone was cut [5 cm × 5 cm × 1 cm] and polished using a graded silicon carbide paper, in order to give uniform surfaces and to reduce cutting imperfections. Then they were washed with water to remove the dust deposit and stored in desiccators at 25 °C and 50% RH for 48 h prior to coating application. In addition, a part of limestone was crushed and screened to a No. 80 screen [26].

2.2. Passivation and consolidation of $CaCO_3$ powder

For single coatings, coupling agent solution was prepared by dilution in ethanol. Five grams of limestone powder and calcite powder was added to 20 mL coupling agent solution while stirring, respectively. The solution was ultrasonically treated for 2 min to promote complete wetting of the powder and minimize agglomeration. The coupling agent/powder solution was stirred at room temperature for at least 30 min and vacuum filtered through a l μm Teflon filter. The filter cake was gently broken up and allowed to dry at 50 °C. For multiple coatings, the dried limestone powder was resuspended in the coupling agent solution and consolidant. Following filtration through a 1 μm Teflon filter, the limestone powder was dried under ambient conditions. A sol–gel derived from consolidant was chosen from a family of silica sols based on our previous studies [22]. The consolidant was prepared by mixing TEOS and ethanol. Next, water was added under high-power ultrasonic agitation, and PDMS-OH was added drop by drop under the same agitation. The total time of ultrasonic agitation was 10 min. Finally, n-octylamine was added to the mixture under vigorous stirring. The mole ratios of mixture were $1TEOS/16ETOH/10H_2O/0.04PDMS\text{-}OH/0.004n\text{-}octylamine$. The 10 g passivated and unpassivated limestone powder were cast in one mould of 3.2 cm in diameter under the pressure of 20 MPa, respectively. All samples were treated with self-made product and stored in desiccators for three months. Compressive strength test was carried out on the overlying protected samples by means of an Instron-5500R universal testing instrument operating with a crosshead speed of 0.5 mm min^{-1}, the value of each sample was decided by the numbers of sample into the total value of the test results.

2.3. Peeling performance tests

The adherence of the consolidant to the powder samples surface was evaluated by performing a peeling test using Scotch magic Tape (translucent Scotch 810). The test was carried out according to previously reported methods [27]. 3 M transparent Scotch Tape was cut into pieces not less than 2 cm in length and with a contact surface area about 4 cm^2. The weight of the piece of Scotch Tape was calculated as an average of 10 pieces. During the tests, the passivated and unpassivated limestone samples were tested, and after 3 min it was peeled off using steel pincers. Peeling was done with a rapid and constant action.



Scheme 1. Schematic diagram of the aim of the investigation.