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A novel TiO_2–SiO_2 nanocomposite converts a very friable stone into a self-cleaning building material

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ABSTRACT

A TiO_2–SiO_2 nanocomposite material was formed inside the pore structure of a very friable carbonate stone by simple spraying of a sol containing silica oligomers, titania particles and a non-ionic surfactant (*n*-octylamine). The resulting nanomaterial provides an effective adhesive and crack-free surface layer to the stone, and gives it self-cleaning properties. In addition, it efficiently penetrates into the pores of the stone, significantly improving its mechanical resistance, and is thus capable of converting an extremely friable stone into a building material with self-cleaning properties. Another important advantage of the nanocomposite is that it substantially improves protection against salt crystallization degradation mechanisms. In the trial described, the untreated stone is reduced to a completely powdered material after 3 cycles of $NaSO_4$ crystallization degradation, whereas stone treated with this novel product remains practically unaltered after 30 cycles. For comparison purposes, two commercial products (with consolidant and photocatalytic properties) were also tested, and both alternative materials produced coatings that crack and provide less mechanical resistance to the stone than this product. These results also confirm the valuable role played by *n*-octylamine in reducing the capillary pressure responsible for consolidant cracking, and in promoting silica polymerization inside the pores of the non-reactive pure carbonate stone.

1. Introduction

Natural stone of diverse types is employed as construction material around the world, for reasons of esthetic appeal and elegance but mainly for its durability. Demand for natural stone is, therefore, usually limited to the more durable varieties, such as granites, marbles and some sandstones. Another type of stone, pure carbonates, presents an exceptionally bright white color, which is much appreciated by consumers as a building material for floors, walls and external facades. However, this natural rock has low mechanical resistance and is easily stained, thus inhibiting it commercial application. Therefore, the development of a treatment product specifically intended to enhance the robustness and durability of carbonate stone, and with self-cleaning properties, should be of considerable interest for architecture and construction.

Since the early discovery of the self-cleaning properties of titanium dioxide [1], it has been considered to be the most efficient, stable and cheap photocatalytic material available [2,3]. In recent years, the application TiO_2 to very widely different substrates, such as textiles [4–7], plastics [8–12] and glasses [13–16], has been widely reported. However, its application to various types of stone has been much more limited [17–21]. It is commonly employed as an aqueous dispersion of titania particles [17,19,20]. The results obtained for these products on stone are not wholly satisfactory, for two reasons: (1) a cracked coating is formed on stone [17], and (2) the titania is easily removed from the stone surface [18].

Nowadays, most commercial products applied for the protection of stonework and other building materials contain alkoxysilane monomers or oligomers [22]. These species polymerize, in situ, inside the pore structure of the stone, by a classical sol–gel process; this improves properties of the product such as its mechanical resistance or its hydrophobic behavior. Two main reactions take place during sol–gel transition: (1) hydrolysis of alkoxy groups to create silanols; (2) polymerization by condensation of silanol groups from the products. In addition, condensation also occurs between silanol groups from the products and those present in the siliceous mineral surface of the stone. The advantages of these products, widely reported in the literature, are: (1) the low viscosity of the monomer or oligomer facilities penetration deeper into the pore structure of the stone; (2) environmental moisture is sufficient to produce the hydrolysis process; and (3) stable siloxane polymers are created, of a composition similar to the siliceous minerals of the stone.

However, a well-known drawback of these products, which is characteristic of all the sol–gel materials, is their tendency to crack

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during their drying process [23]. It is obvious that a cracked substance cannot protect the treated stone very effectively. In earlier work, our research group has developed surfactant-synthesized nanomaterials specifically designed for protecting and restoring various types of stone and other building materials [24–29]. The inclusion of the surfactant provides an efficient means of preventing cracking of the gel by reducing the capillary pressure; this effect is the result of two factors: (1) a coarsening of the gel network; and (2) decreased solvent surface tension. Adopting to this strategy, we have prepared consolidants [24–28], hydrophobic products [25–28] and stain-resistant materials [28]. In a recent paper [29], we describe the addition of titanium dioxide particles to a silica oligomer, in the presence of the surfactant, in order to produce a self-cleaning product for stonework and other building materials.

In this paper, we report the application of a sol containing titania particles and silica oligomer, to an extremely low-compaction and friable dolostone with an exceptionally bright white color. This dolostone is very prone to severe disaggregation, and can easily break into several pieces on routine manipulation. Consequently, this esthetically attractive stone is totally unusable as a building material. The aim of the work described is to convert the dolostone into a self-cleaning building material with adequate mechanical resistance. If achieved, this would make the dolostone a significant new product in the market for building stone. Specifically, the present study is focused on evaluating the effectiveness on the dolostone under study for: (1) providing self-cleaning properties; (2) improving mechanical resistance; and (3) adherence to the substrate. We also investigate the durability of the stones treated, by applying a standard crystallization test. The effectiveness shown by this nanocomposite product as a consolidant and self-cleaning product has also been compared, in additional tests, with a commercial photocatalytic product and a commercial consolidant which were also evaluated on the same dolostone.

Another well-known and serious drawback of existing commercial siloxane products [22–30] is their very limited effectiveness as a consolidant of pure carbonate stones not containing siliceous minerals; there are two reasons for this deficiency: (1) carbonates slows the sol–gel transition [31]; and (2) carbonate salts do not have active—OH groups on their surface which could react with alkoxysilanes included in the products [32]. Hence chemical bonds between the stone and the consolidant product are not created. However, the significant increase in mechanical resistance observed in the dolostone under study after application of the nanocomposite synthesized in our laboratory demonstrates the useful contribution made by *n*-octylamine in the interaction between a non-siliceous stone and this siloxane product, which is also discussed in the present paper.

2. Experimental

The titania–silica nanocomposite was prepared from a starting sol containing TES40 WN (Wacker Chemie AG, GmbH), P25 particles (Evonik AEROXIDE® TiO_2 P25) and *n*-octylamine (Aldrich). According to the technical data sheet, TES 40 WN (hereafter TES40) is a mixture of monomeric and oligomeric ethoxysilanes. The average chain length is approximately 5 Si—O units. P25 has an average primary particle size of 21 nm and a specific surface area (BET) of $50 \pm 15\,m^2\,g^{-1}$. The Sol was prepared by mixing TES40 with P25 particles in the presence of *n*-octylamine under ultrasonic agitation ($125\,W\,cm^{-3}$) for 10 min. The proportion of *n*-octylamine and P25 to TES40 was 0.36% v/v and 2% w/v, respectively. The formulation has been designated as UCATiO2 via the procedure devised at the University of Cadiz (the number indicates the % w/v of P25 included in the material).

After synthesis, the product was applied to the dolostone samples under study. For comparison, a popular commercial consolidant, Tegovakon V100 (hereafter TV100), supplied by Evonik, has also been applied. TV100 is a solvent-free one-component consolidant consisting of partially pre-polymerized TEOS and dioctyltin dilaurate (DOTL) catalyst. A commercial photocatalytic coating, E503 supplied by Nanocer, was also applied. According to the material data sheet, E503 is a TiO_2-containing water-based sol with 7500–10,000 ppm of the oxide. Prior to their application to the stone, the rheological properties of the products were studied, using a concentric cylinder viscosimeter (model DV-II+ with UL/Y adapter) from Brookfield. Experiments were performed at a constant temperature of 25 °C maintained by recirculated water from a thermostatic bath. A shear stress versus shear rate flow curve was generated.The stone selected is a very friable dolostone composed of magnesium carbonate (99%). It presents evident disaggregation problems due to its geological formation and/or natural aging processes. This stone was selected particularly because of its high degree of whiteness, which makes it a suitable candidate for self-cleaning treatment application. For all the experiments carried out, the stone samples were cut in the form of $5 \times 5 \times 2$ cm slabs. The sols under study were applied by spraying onto the upper surface of the samples, in 5 periods of 5 s, during a total time of 25 s. The stone samples were then dried under laboratory conditions until reaching constant weight. Uptake of products and their corresponding dry matter by the stone samples was calculated. The samples corresponding to untreated stone and their treated counterparts were characterized by the procedures described below, after constant weight was reached. All the results reported correspond to average values obtained from three stone samples.

A JEOL Quanta 200 scanning electron microscope (SEM) was used to visualize changes in the morphology of the stones after coating. Surface fragments of treated stone specimens and their untreated counterpart were visualized.

The chemical bonds in the treated samples under study were analyzed by Fourier transform infrared spectrophotometry (FTIR). The spectra were recorded in powder using a FTIR-8400S from Shimadzu ($4\,cm^{-1}$ resolution) in the region from 4000 to $650\,cm^{-1}$. Experiments were carried out in attenuated total reflection mode (ATR). FTIR spectra of powdered fragments of untreated and treated samples were obtained.

The adherence of the coating to the stone surface was evaluated by performing a peeling test using Scotch® Magic™ tape (3M). The test was carried out according to previously reported methods [29,33,34]. The changes in stone surface morphology were visualized by SEM working in low-vacuum mode, and energy-dispersive X-ray spectroscopy (EDX) spectra were recorded in order to elucidate the variations in surface composition after the test.

The improvement in mechanical properties in treated stone was evaluated means of the Standard procedure Vickers hardness test, using a Universal Centaur RB-2/200 hardness tester. The loading was 30 kg during 30 s, with a preload time of 15 s. 10 measurements were made for each stone specimen. Vickers hardness (VH) was calculated according the following equation:

$$VH = \frac{1.8544 \cdot W}{d^2} \quad (1)$$

where W is the load over the surface area of the indentation; d is the indentation diagonal.

The improvement in mechanical properties was also measured using the drilling resistance measuring system (DRMS), by SINT Technology. Drill bits of 4.8 mm diameter were employed with a rotation speed of 600 rpm and penetration rate of 5 mm/min. For each specimen, 10 holes were carried out.