Nanocomposite coatings for the protection of marble against salt weathering

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Abstract

Moisture presence, salt precipitation and crystallization are main deterioration problems of the building materials of historic monuments. The presence of moisture in a material is due to rising and falling damp. The total moisture content and the contributions to salt damage of these forms of damp in a specific material will depend on the amount and nature of the salts in the soils beneath, on the humidity and temperature. For salt attack to occur the presence of a combination of conditions is needed, which are a permeable material, moisture, soluble salts and evaporation circumstances. The presence of salts changes the liquid transport properties of marbles, influencing also their structure and surface stability. Many commercial stone consolidation and some water repellent products contain tetraethoxysilane (TEOS). A drawback of these materials is their tendency to form gels susceptible to cracking. Nanomaterials resulting from the addition of TiO_2 nanoparticles to TEOS based commercial products, Rhodorsil RC-70 and RC-90, were synthesized. The protective properties of the nanomaterials on a dolomite marble substrate against salts weathering were examined by water capillary absorption tests and accelerated aging tests. The consolidating and hydrophobic properties of the treatments were found to depend on the type of the nanomaterial and the type of salt. The type of the polymeric material and the presence of the nanoparticles affect in different ways the examined properties. Capillary rise is correlated with the rate of evaporation, the crystallization of salts and the growth of salt crystals within the pores of the marble. The aging behaviour of the treatment was found to depend on the type of the polymeric material and the presence of the nanoparticles.

Keywords: consolidant, nanomaterial, salt crystallization, dolomite marble, titanium oxide

Experimental

Five series of specimens of dolomite marble were prepared. Bare marble and marble treated with four types of consolidants, Rhodorsil RC-70, Rhodorsil RC-90, Rhodorsil RC-70 with 3% TiO_2 nanoparticles and Rhodorsil RC-90 with 3% TiO_2 nanoparticles. The capillary tests were carried out, for a period of seven days, in three different saturated solutions of sodium chloride, sodium sulphate and mixture of these salts. The behaviour of the treatments, the moisture presence and distribution, the form and the amount of the salts crystallized on the surface as well as the height of the capillary rise were investigated. The investigation was performed by gravimetric, optical microscopy, X-R Diffraction, X-R Fluorescence methods. The accelerated aging tests were carried out, for a period of three months, in 40^{o}C temperature, 90% relative humidity, UV light conditions. Analysis by FTIR was performed and contact angle and colour alteration measurements were carried out.

Results and discussion

The gravimetric results of the capillary tests are shown in Table 1. The water absorption and salts crystallization is greater in the case of sodium chloride. All treatments show a decreased water absorption. The addition of TiO_2 further decreases the water absorption, and this more extensively for Rhodorsil RC-90 compared to the RC-70 product, probably due to the presence of methyl-phenyl resin in the first one. Similar results were observed in the optical examination (Fig. 1) concerning the height of the capillary rise and salts crystallization on the surface of the specimen.

Table 1: Results of capillary tests, absorption, w % increase

	Marble	Rhodorsil RC-70	Rhodorsil RC-90	Rhodorsil RC-70 + TiO_2	Rhodorsil RC-90 + TiO_2
NaCl	2.97	2.10	0.61	1.53	0.41
Na_2SO_4	0.86	0.58	0.28	0.42	0.17
Mixture	1.55	0.75	0.48	0.62	0.31

The results of the optical examination of the specimens after the capillary tests are shown in Figure 1. XRD analysis was carried out on the powder of the salts crystallized on the surfaces of the various series of the specimens, after their removal from the surface. The results showed that in the case of untreated marble the salts consist of sodium chloride and calcium and magnesium chlorides, sodium sulphate and calcium and magnesium sulphates or mixtures of these, according to the solution exposed. In all cases of treated marbles the calcium and magnesium salts exist, but their presence is significantly lower, indicating the protective properties of the products against the dissolution and transportation effects of salts. XRF analysis was carried out on the surfaces of the specimens after the removal of the salt layers. The results indicated the presence of sodium or sulphur ions that remained on the surface of the marble and also the existence of titanium in the case of a treatment to which TiO_2 was added.

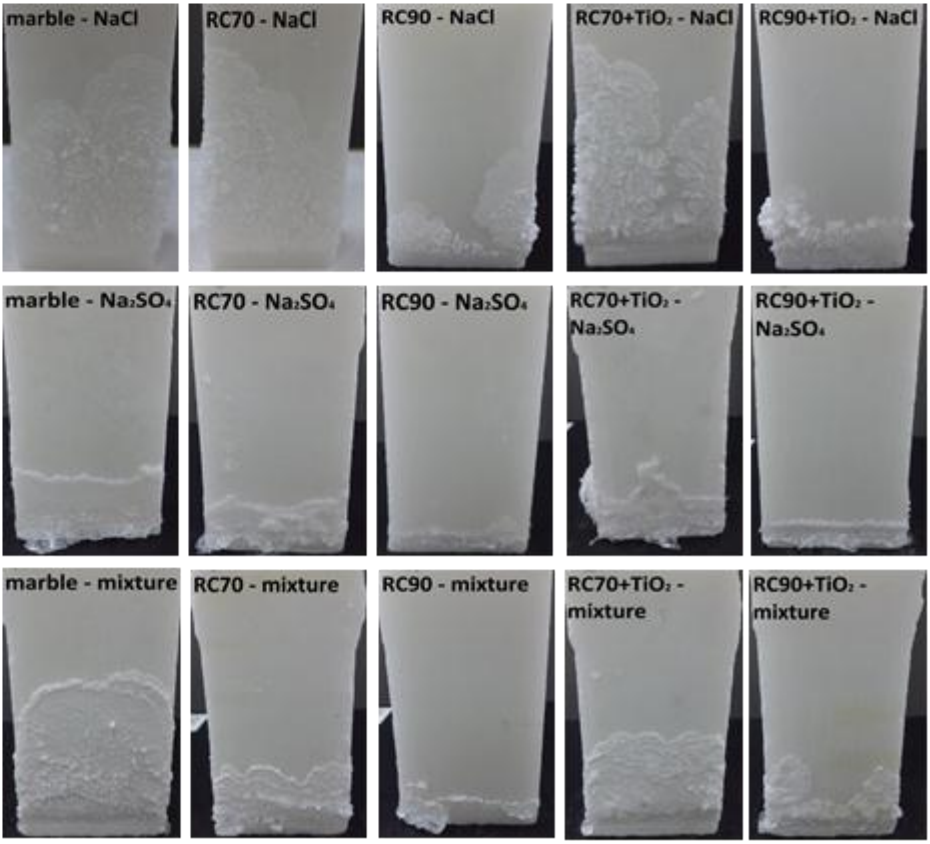

Figure 1: Capillary test, optical examination of bare and treated specimens after 7 days exposure in various salt solutions

Contact angle and colour alteration measurements, as well as FTIR analysis were carried out, before and after exposing in aging conditions. The results are shown in Table 2 and Figure 2.

Table 2: Contact angle and colour alteration results before (initial) and after (final) aging

	Marble	Rhodorsil RC-70	Rhodorsil RC-90	Rhodorsil RC-70 + TiO_2	Rhodorsil RC-90 + TiO_2
Contact angle initial, degree	71	92	95	93	101
Contact angle final, degree	82	98	104	103	108
Colour variation initial, ΔE*	-	4.1	5.2	2.0	4.8
Colour variation final, ΔE*	-	2.1	4.8	1.5	3.4

The results of the contact angle showed that the polymerised products all behaved water repellent, and this more intensively in case nanoparticles were added. After aging, the contact angle values increased slightly. This behaviour should be correlated to changes on surface microstructure and roughness during aging but further work is needed to confirm this supposition.

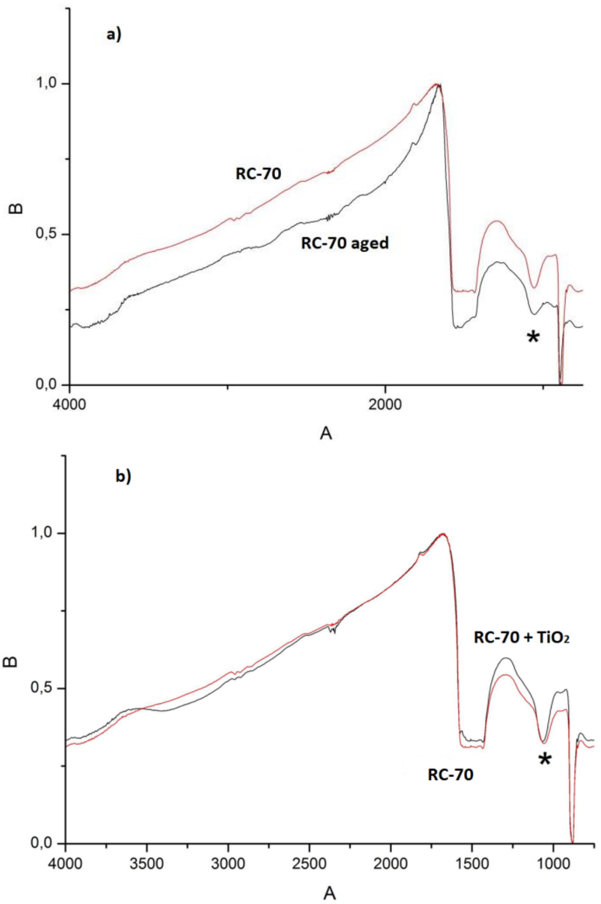

Figure 2: FTIR diagrams, a) before and after exposing in aging conditions, b) polymer and nanopolymer layer

In both FT-IR spectra of the samples treated with RC-70 (figure 2a), the (*) peak corresponds to the polymerised RC-70 product, which is wider and weaker for the sample after aging. From the results obtained for samples treated with RC-70 + TiO_2 (fig. 2b), it can be noticed that the addition of titanium oxide results in the formation of a better layer on the marble surface, as indicated from the closer and stronger form of the peak. Similar results were obtained for the samples treated with the RC-90 product.

Conclusions

The consolidating and hydrophobic properties of the tested products depend on the type of the nanomaterial and the type of the salt. The type of product and the presence of nanoparticles affect in different ways the examined properties as well as the aging behaviour.

All products used protect marble against salts weathering by decreasing the water absorption, salt crystallization and transportation effects. The addition of titanium oxide nanoparticles increases these protective properties.

The tested products had hydrophobic properties that further increase with the addition of the nanoparticles.

The application of a product having methyl and phenyl groupings and the addition of nanoparticles lead to the formation of a kind of modified resin with better surface and structure properties, enabling to increase its protective properties against salts weathering.