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Original article

Evaluation of vibrational spectroscopic techniques for consolidants' penetration depth determination

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ABSTRACT

The penetration depth of consolidants applied to cultural heritage objects plays a crucial role in a successful conservation and protection of them. In the frame of HEROMAT FP7 project new consolidants for carbonate and silicate based materials were developed. Among many other investigated properties, the penetration depth was defined by Raman and FTIR spectroscopies, for which their ability was also evaluated. Due to the formation of calcium carbonate in the consolidation process of carbonate forming consolidants, the addition of sodium nitroprusside indicator supported Raman differentiation of treated and non-treated areas in the calcium carbonate based substrate. Furthermore, the combination of the indicator reaction and Raman results gave much more precise penetration depth estimation than the visual assessment alone. For following the penetration depth of modified TEOS based consolidants for silicate based substrates, FTIR spectroscopy turned out to be very successful without any indicator application or pre-treatment of samples. Furthermore, the penetration depth related to different application methods, such as brush, cellulose pulp, airless spray and roller, was also studied. The deepest penetration was achieved by 8 h of application of consolidants in cellulose pulp, while in comparing one application by roller, airless spray and brush within the same substrate, the deepest penetration can be achieved by brush.

1. Introduction

Since the middle of the last century different synthetic polymers have been used for consolidation of limestone surfaces. Due to their aesthetical alteration, change in the polymers solubility and degradation, which could alter the physico-chemical properties, such as creaking, flaking and glossy effect, their potential application is hindered. In this respect, the use of "compatible" materials is preferable since this way durability and long-term stability is granted [1,2]. In the last decade much of the research has been made in the field of synthesis of macro- and nano-particles of $Ca(OH)_2$ in different alcohols [1]. Dispersions of $Ca(OH)_2$ nanoparticles have been proven to be effective for consolidant treatment due to their small dimensions and ease of the penetration as well as increased reactivity towards CO_2 [2,3]. However, there still exist important obstacles for their use such as the variable particle size, incomplete carbonization (due to the need of atmospheric CO_2) and the low concentrations (5–25 g/L) [1,3]. In fact, a consequence of the low concentration and volatility of solvents used in consolidants is that multiple applications are needed [1,2].

For effective consolidation of deeper layers of degraded substrates, use of soluble starting materials is desirable. However, since the solubility of calcium carbonate is low, the preparation of such a material is very difficult [4]. In the scope of HEROMAT FP7 project a new solution of calcium acetoacetate for consolidating carbonate based substrates was developed [5]. Since the consolidant is a solution, it can penetrate deeper into the material, where re-cohesion between particles can be established. Additionally, due to higher concentrations (from 5–100 g/L) the number of consolidant applications can be strongly reduced.

On the other hand, for consolidation of silicate substrates consolidants based on alkoxylanes or tetraethoxy silane (TEOS) are used [6,7]. They can have a poor affinity to materials with large pores, for example such as found in some sandstones. Namely, during the hardening phase or under mechanical stress thick and brittle

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silica-gel structures of consolidants fill the pores with silica-gel resulting in a material that is less permeable to the water vapour [8,9]. For the silicate based substrates modified formulations of commercial product based on silicate ester was developed in the scope of HEROMAT FP7 project. Due to its balanced combination of polysilicate, dioxalane, mixture of C11-C13 alkanes (liquid paraffin) and diethylethanolamine, the consolidant has a low dry mass and therefore does not reduce the porosity of consolidated material. Furthermore, it has a good retained water vapor permeability, efficient and uniform consolidation through the profile of the substrate without skin forming.

Chemical and/or physical response of the substrate (*i.e.* calcareous and silicate materials) varies strongly due to their heterogeneous properties (*e.g.* different porosity, distribution of components). Therefore, to validate the conservation treatment of the materials composing cultural heritage objects, a careful selection of the application method of the consolidant and the analytical technique for monitoring and assessing the performance of the consolidation should be made. The non-destructive methods, in which a sample is left intact, such as Environmental Scanning Electron Microscopy (ESEM-EDS), spectrophotometry, ultrasound velocity, Nuclear Magnetic Resonance (imaging and relaxometry) and Optical Surface Roughness analysis could offer a platform to determine not only the chemical characteristics, but also the morphological, physical and the hydric properties of the materials before and after consolidation [10]. One of the parameters besides the compatibility, durability, effect on appearance [11] *etc.*, which should be taken under consideration, when evaluating new consolidant formulations is also the depth of consolidant penetration. Regarding compatibility of the consolidant with the material being consolidated, the *in situ* carbonation using the solutions of calcium hydroxide is gaining much attention, as has been previously mentioned. Despite the fact that the formed carbonate could exist in different grain size and different crystal-aggregate texture [11], it is difficult to differentiate them from the original one constituting the cultural heritage object. With the assumption that the magnesium hydroxide particles have the same capability as the calcium hydroxide for the penetration, Dei and Salvadori [12] showed that by using the magnesium hydroxide as the marker, SEM-EDX analysis and superficial area analysis (BET) could be used for following the depth of penetration of the consolidant in addition to water absorption capillarity measurements for evaluation of water-interaction properties. Pinto and Rodriguez [13] quantified the consolidation effect and the role of treatment procedures (*i.e.* by capillary absorption, by immersion and by brushing) for on-site building stones (monuments) in complementation to laboratory studies of different carbonate samples with different intrinsic properties by weighing, micro drilling resistance (DRMS), ultrasonic velocity and flexural strength. In accordance, also the penetration depth could be consequentially correlated with those results. Moreover, Pinto and Rodriguez [14] showed, that DRMS methodology is one of the most promising for the assessment of the consolidation rate in the soft stones, while the depth of the strengthening action could be further successfully determined by other techniques such as by the collection of longitudinal ultrasound velocity profiles. For evaluation of penetration depth of the polymer consolidant within porous stone substrates, several direct analytical methods such as staining test using for example iodine vapor [15] or fluorescent dyes for visualizing the location of the consolidant, Fourier transform infrared spectroscopy (FTIR), SEM-EDX and XPS, and also indirect, which includes measurements of contact angle, bending strength, modulus of elasticity *etc.* could result in gaining valuable information of the interaction between the consolidant and the substrate[16]. μRaman mapping proved to be an effective tool for assessing the penetration depth of consolidant products based on oxalate formation. Consolidation with ammonium oxalate (oxammite) in different plasters made of lime and carbonate aggregate was studied by Conti et al. [17]. It was shown that during consolidation process, oxammite induces the transformation of calcium carbonate to calcium oxalate (whewellite), which gives a better resistance to decay phenomena. Strong and characteristic bands at 1462 cm^{-1} (whewellite) and at 1085 cm^{-1} (calcite) have been considered for following the penetration depth by μRaman mapping. Furthermore, neutron radiography and tomography allow the visualization of polymerized as well as non-polymerized conservation materials inside the porous materials. With these methods Cnudde et al. [18], Dierick et al. [19] and Masschaele et al. [20] successfully defined the impregnation depth of silicate-based materials inside the natural building stones and resulting effects on the uptake water. Alternative technique for the investigation of depth profile, which also allows the visualization of the presence and distribution of different hydrophobic product in stone material, is magnetic resonance imaging (MRI) [10,21]. The structure of natural building stones as well as the visualization of consolidants and/or water repellents within the stones could be investigated using non-destructive X-ray radiography computed with micro-tomography [22]. As the resolution of micro-tomography depends on the amount of treatment materials inside the investigated sample, the addition of contrast agent (*e.g.* 3-bromopropyltrimethoxysilane) is often needed [22]. Another non-destructive method for observation of penetration depth is the tabletop high-resolution X-ray radiography, which became useful after the integration of pixel detectors of Medipix type. This technique has proved to be an optimal tool for observation of penetration depth of organosilicon consolidants in the Opuka stone [23].

When using Raman and FTIR spectroscopy, which are usually available in conservation laboratories, the difficulties may arise due to the overlapping of modes of consolidants and the matrix. For that reason our study was focused on exploring the abilities of vibrational spectroscopic techniques for penetration depth evaluation, where the same composition is formed in the consolidation process as it is present in the matrix of the material that is consolidated.

2. Research aims

In this work, in the framework of HEROMAT FP7 project, spectroscopic techniques, Raman and FTIR, were evaluated for following the penetration depth of developed carbonate and silicate forming consolidants for carbonate and silicate substrates, respectively. This, however, was specifically challenging since the same composition is formed in the consolidation process as it is present in the matrix of the material that is consolidated that can result in overlapping of specific vibrational modes. To overcome the difficulties, in the case of carbonate consolidants an indicator sodium nitroprusside is proposed, while in the case of the silicate consolidant, the new formulation itself, consisting also paraffin, offers the solution. Furthermore, different application methods, usually applied in restoration or in buildings refurbishment were tested. The work was done on prepared model substrates that mimic the composition of outside materials at Dornava Manor, one of the selected test sites of the HEROMAT project, in order to provide results relevant for later on-site application of, within the project, developed consolidants.

3. Experimental

3.1. Consolidants

For carbonate substrates new consolidant formulations, thoroughly described in the patent PCT/SI2014/000028 [5] and based on soluble calcium compound calcium acetoacetate $Ca(OAcAc)_2$ were

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