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Cellulose ethers and nanoconsolidants: preliminary observations on the suitability of the use of cellulose derivatives in the synthesis of nanolime particles

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***Abstract* – This communication reports the preliminary results of our ongoing research on the effect of addition of cellulose-derivatives, such as cellulose ethers, in the synthesis of calcium hydroxide ($Ca(OH)_2$) micro-sized particles. Particles of $Ca(OH)_2$ were synthesised without and with addition of different amounts hydroxypropyl methylcellulose (HPMC). The obtained particles were characterized with X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy (FTIR). Our preliminary results anticipate that syntheses with addition of HPMC originated the formation of smaller and more uniform in shape and size $Ca(OH)_2$ particles in comparison with the $Ca(OH)_2$ particles synthesized without addition of HPMC. This study contributes to the urgent need of innovative non-toxic sustainable materials, compatible with the original artworks, with long-term efficiency and easy for application.**

I. INTRODUCTION

Nanoconsolidants, in particular, nanoparticles alcohol dispersions of alkali earth metals hydroxides ($M(OH)_2$, where M = Ca (calcium), Mg (magnesium), Sr (strontium), have shown suitability for consolidation and conservation of different deteriorated substrates in Cultural Heritage, such as lime mortar, stone, paper, wood and earthen constructions [1,2]. Some of their beneficial characteristics are enhanced stability, good penetration capacity inside decayed substrates, high potential for long-term durability and efficiency [1]. The effectiveness of such dispersions particularly depends on the particles dimension, among other factors. Particles dimensions influences the lattice symmetry, surface free energy, electronic structure, carbonatation mechanism [2].

Various possibilities to functionalize nanoparticle surface provide such materials also selectivity and open possibilities for multiple applications. Each potential application depends on reactivity, size, shape, chemical and mechanical stability, surface properties, ability to not be affected by external factors. Consequently, preparative conditions of their synthesis should be adopted in order to tailor morphology as an attempt to avoid issues related to nanoparticles application for conservation / restoration purposes: for example, clusters formation, aesthetic changes (in colour and brightness) of the treated substrate, back migration, occlusion, and so on.

A common method for the synthesis of nanolime nanoparticles for consolidation of wall paintings consists of a homogeneous-phase reaction in water at temperatures of 60 ºC – 90 ºC, during which some of the reaction parameters (temperature, surfactant addition, molar ratio of reactants) are varied to give different morphological features. Obtained nanolime nanoparticles exhibit different morphologies and inhomogeneous distribution of particle sizes within the range of 50-300 nm [3] and often they are unfavourably agglomerated in clusters of particles [3]. Less agglomerated smaller particles/nanoparticles may eventually be obtained by adding a surfactant to the reaction with a reduced preparation time [6]. Besides agglomeration, the importance of addition of a surfactant or templating agent is determined by its capacity to influence the nanoparticles' surface area, steric stabilization, particle size, shape and orientation [7], but often it is toxic. Newly explored synthesis of nanolime nanoparticles with ion exchange between the respective metal salt and anionic-exchange resin at room temperature [8,9] appears to be an advantageous preparation method compared to chemical precipitation [2,10]. Yet issues

related to agglomerated in clusters particles and to carbonatation mechanism, among others, can lead to undesired white haze formation, for instance, when nanolime is applied for wall paintings consolidation [11-14]. Possible changes in the aesthetic appearance after treatment remains one of the main concerns of conservation scientists [11,13,15].

Cellulose ethers have film formation capacity and may influence water transport and porous structure of, e.g., cement-based materials [16]. They could open up a possibility to prepare concentrated nanoparticles dispersions at room temperature by forming intermediary complexes of raised solubility of calcium [17].

This research intends to demonstrate that the use of cellulose derivatives in the synthesis of nano- or micro-sized consolidants particles could be beneficial towards room or near-room temperature and favourable morphology (size, shape, tendency to form particles clusters). We anticipate the possibility that such use could be beneficial in terms of effectiveness, e.g., in the carbonatation process and in avoiding the possible aesthetical changes when applied to substrates. The use of cellulose derivatives would replace the use of toxic surfactants and allow syntheses at room and near-room temperatures.

In this communication we discuss our preliminary results of our ongoing research, in particular, we report the synthesis of $Ca(OH)_2$ particles with different amounts of hydroxypropyl methylcellulose (HPMC). The study contributes to the urgent need of innovative non-toxic sustainable materials, compatible with the original art works, with long-term efficiency and easy for application as consolidants. With this research we aim to give a contribution to the UN's Sustainable Development Goal (SDG) 11, target 4, to strengthen efforts to protect and safeguard the world's cultural heritage.

II. EXPERIMENTAL

A. Synthesis

Synthesis of $Ca(OH)_2$ without addition of HPMC (Fig. 1a): $Ca(OH)_2$ was synthesized by precipitation method of equal volumes (150 mL) of aqueous solutions of 0.4 M calcium chloride ($CaCl_2$, 99.9% pure, Sigma-Aldrich) and 0.8 M sodium hydroxide (NaOH, 99.9% pure, Sigma-Aldrich) at room temperature. The reaction took place over one hour. The resulting white powder was filtered off by vacuum filtration and washed several times with water and dried overnight at *ca.* 70 ºC.

Synthesis of $Ca(OH)_2$ with addition of HPMC (Fig. 1b): Two kinds of solutions in ultrapure water (50 mL) with different amounts of HPMC (10 mg and 20 mg) were prepared at *ca.* 50 ºC under vigorous magnetic stirring. HPMC was added slowly to heated water (35 mL) and the suspension was cooled to room temperature for 30 mins until full dissolution, when the rest 15 mL of water were added. The solution of HPMC was added dropwise under stirring to 150 mL of aqueous solution of 0.4 M $CaCl_2$ (99.9% pure, Sigma-Aldrich) and finally the same volume of NaOH aqueous solution (0.8 M, NaOH, 99.9% pure, Sigma-Aldrich) was added to the initial mixture. Reaction took place over one hour. The resulting white powder was filtered off and washed several times with water and dried overnight at *ca.* 70 ºC.

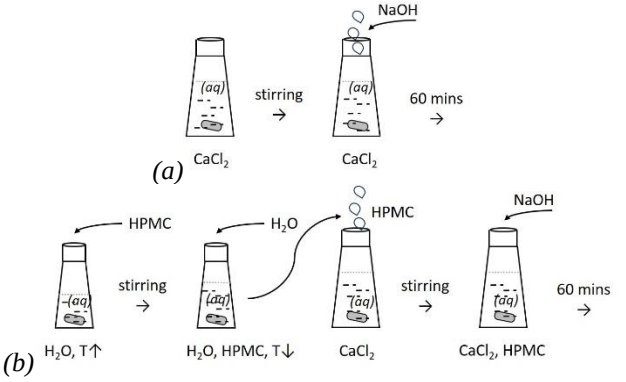


Fig. 1. Schematic representation of the syntheses of $Ca(OH)_2$. (a) without addition of HPMC; (b) with addition of HPMC.

B. Instrumentation

The synthesized calcium hydroxide ($Ca(OH)_2$) particles were characterized by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Fourier-transform infrared spectroscopy (FTIR).

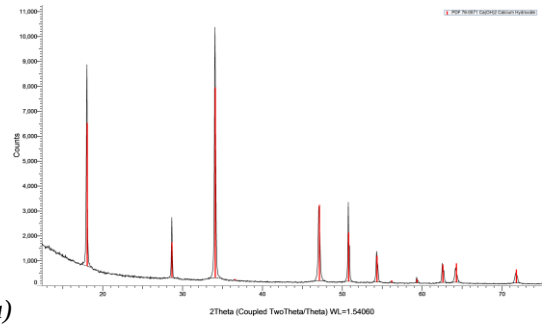
The identification of crystalline phases of the dried particles samples was done with a BRUKER AXS D8 Discovery XRD with monochromatized Cu Kα radiation k = 1.5406 Å operating at 40 kV and 40 mA in the 2θ range 3–75° with a step size of 0.05° (2θ) and 1 s per step (increment: 0.05°, time 1000 s, steps = 1438). The mineral phases were identified with DIFRAC.SUITE.EVA software (Powder Diffraction Files of the International Center for Diffraction Data-2).

SEM analysis was performed on a variable pressure scanning electron microscope HITACHI S-3700N coupled with an energy dispersive X-ray spectrometer BRUKER XFlash 5010 SDD EDS. For the SEM analysis, $Ca(OH)_2$ particles were dispersed in 2-propanol (as diluted nanolime dispersion). One drop of dispersion was deposited over a glass plate and after the solvent evaporation it was coated with a metallic conductive layer of gold/palladium with Quantum Q5150RES/sputter

coater SC 7620 Polaron. The images were recorded under SE mode and at 10.0 keV.

FTIR spectroscopy of KBr pellets (FTIR grade) was recorded on a BRUKER Hyperion 3000 spectrophotometer with OPUS 7.2 software in the range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1}. The obtained spectra were converted to absorbance.

III. PRELIMINARY RESULTS AND DISCUSSION



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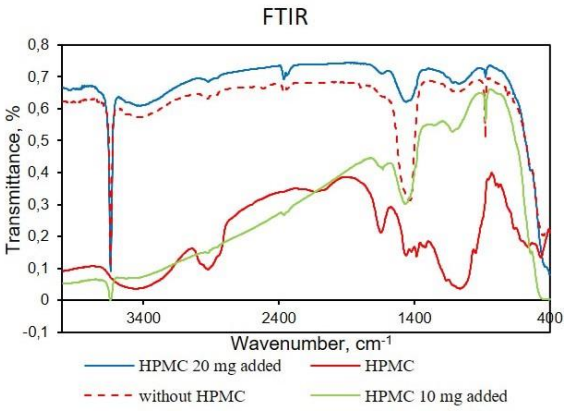

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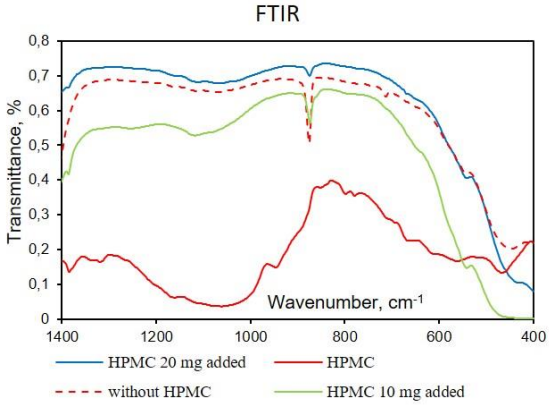
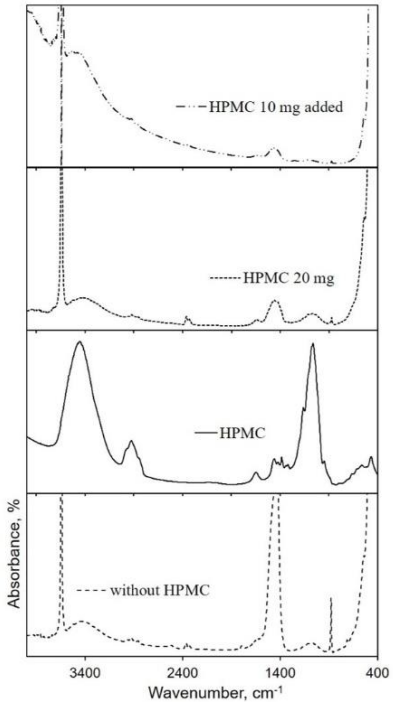


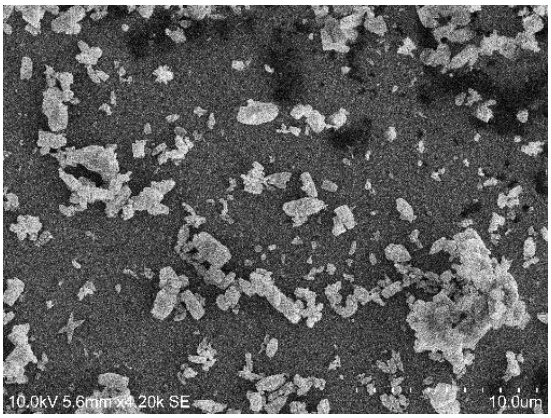
c)



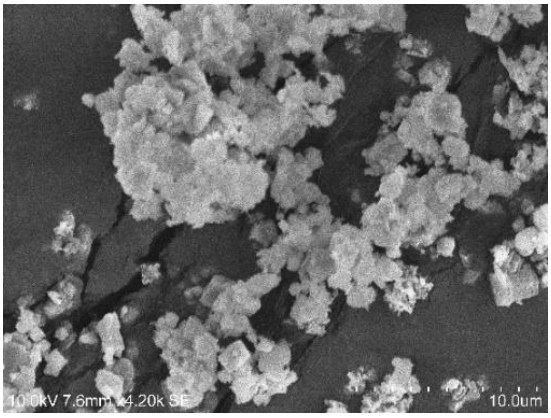
(d)

Fig. 2. Characterization of LAB nanoparticles: (a) XRD pattern of sample prepared with addition of HPMC (20 mg); (b) FTIR spectra (transmittance); (c) FTIR spectra (transmittance), wavenumbers region 400 cm^{-1}-1000 cm^{-1}; (d) FTIR spectra (absorbance).

Pure-phase particles of $Ca(OH)_2$ were prepared by precipitation method at room temperature in agreement with the XRD pattern that was obtained (Fig. 2a). The FTIR spectra confirm that the three syntheses resulted in the preparation of $Ca(OH)_2$ and that there is no presence of HPMC (Fig. 2b,c). The presence of the bands at wavelengths 3640 cm^{-1} (s), 3420 cm^{-1} (w), and 1610 cm^{-1}, 1787 cm^{-1} (w, synthesis without HPMC), 1653 cm^{-1} (w, synthesis HPMC 20 g), 1624 (w, synthesis HPMC 10 g), correspond to the stretching of O−H and H−O−H [18]. The bands at 875 cm^{-1} and the broad band at 1442 cm^{-1} (s, synthesis without HPMC), 1441 cm^{-1} (m, synthesis HPMC 20 g), 1447 (m, synthesis HPMC 10 g) are assigned to *v2* asymmetric CO_3 deformation and *v3* asymmetric CO_3 stretching [18 and references therein]. Their presence suggests a possible formation of $CaCO_3$ during the drying and storage. The FTIR spectra (transmittance mode) of the three synthesised $Ca(OH)_2$ (one syntheses without HPMC and two - with HPMC) share similar features and the characteristic bands of HPMC do not appear (Fig. 2b,c) although the overlap of some bands at wavenumbers, such as between 1000 cm^{-1} and 1700 cm^{-1}. Converted absorbance spectra (Fig. 2d) did not provide enough evidence for presence of the characteristic C−H absorptions (from the HPMC) in the products.



(a)



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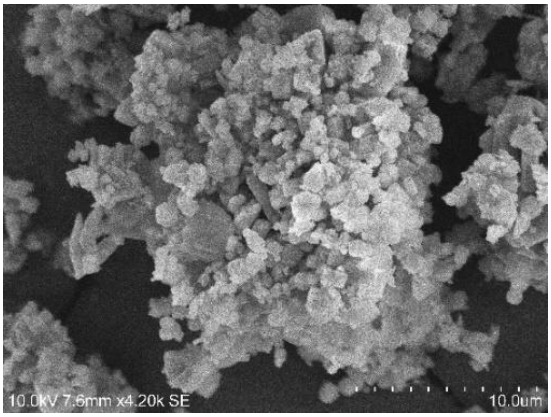

(c)

Fig. 3. SEM image of $Ca(OH)_2$ synthesized overnight at room temperature without and with addition of hydroxypropyl methyl cellulose: (a) without HPMC; (b) 10 mg; (c) 20 mg.

The SEM images of the three reaction products are shown in Fig. 3. The addition of HPMC has triggered the preparation of particles with more defined hexagonal particles shape, that are common for $Ca(OH)_2$ nanoparticles [3,7] (Fig. 3b,c). The most uniform are the particles prepared with the addition of 20 mg of HPMC (Fig. 3c). The addition of HPMC also allowed the preparation of particles of smaller dimensions (average diameter of *ca.* 1µm) compared to the particles that were synthesised without addition of HPMC (Fig. 3a). All kind of particles appear agglomerated in clusters, therefore more synthesis factors should be studied in order to tailor less agglomerated particles (e.g., HPMC concentrations, temperature and synthesis duration).

IV. CONCLUSION AND FUTURE CONSIDERATIONS

Our preliminary data of the addition of HPMC to the synthesis of $Ca(OH)_2$ particles at room temperature was favourable for the preparation of pure-phase particles with particular size and shape features.

The most promising sample of pure-phased $Ca(OH)_2$ particles has been prepared with the addition of the highest amount of HPMC.

Although the fact that these particles have exhibited the somewhat narrowest diameters and most uniform shapes, they still tend to agglomerate. The preliminary results obtained suggest that more future detailed studies should be carried out in order to determine the most favourable amount of HPMC (and other cellulose derivatives) to be added in the synthesis of the of $Ca(OH)_2$ and the optimal reaction duration that will allow to anticipate a systematic relation between "template" additive and morphology. Furthermore, more particles characterization should be carried out in order to analyse possible calcite formation before the particles application. Lime mortar mock-ups with lack of cohesion, replicas of wall paintings, will be treated with alcohol dispersions of particles with the most promising particles in order to assess whether the application of the prepared particles alcohol dispersions cause any changes in the aesthetic appearance of the treated substrate.

V. ACKNOWLEDGEMENTS

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