A NEW PREPARATION METHOD OF NANOLIME DISPERSION FOR THE CONSERVATION OF ARTWORKS

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Abstract

The application of nanolime dispersions for consolidating wall paintings constitutes a valid alternative to the lime traditional ones.

Particles size, polydispersion, and agglomeration depend on the preparation method. Tailoring the experimental condition of the synthesis, it is possible to produce nanodispersions for other specific artistic artworks such as stones, papers or woods.

In this work a new preparation method, the insolubilisation-precipitation, will be shown. It was used to obtain nanoparticles dispersed in a water-isopropanol mixture.

The stability of dispersion together with particle size and their morphology were found to be dependent on water to isopropanol ratio.

Keywords: Nanolime, Consolidation, Insolubilization

INTRODUCTION

In the last years, the scientific community was present at the continuous and intensive development of the nanotechnology. The application fields of the nanotechnology are unlimited: the conservation of Cultural Heritage (CH) is one of them [1]. The nanotechnologies can give a notable boost to the innovation of the methods and of the products used for the conservation of the CH making the intervention non harmful, more compatible and lasting. Dei, Baglioni, and co-workers [2-6] have given a big contribute in this field. The studies concerned the removal of polymeric materials from various substrate, the conservation of papers and woods, and the develop of inorganic consolidants for wall painting. They have presented several examples of calcium hydroxide nanoparticles with controllable stability, a crucial property for applications.

In particular, calcium (and magnesium) hydroxide nanoparticles applied to paper and wood deacidification [7-8] have provided clear evidences for the huge potential of nanotechnology in cultural heritage conservation. [9] Silver nanoparticles having antimicrobic properties [10,11], TiO_2 and ZnO nanoparticles having autocleaning properties

and acting as Uv-filters [12,13] have been applied on canvas.
One of the problems for the conservation of cellulosic materials such as papers, woods, canvas and photographs is the neutralization of the acidity which catalyzes reactions of degradations of the cellulose. The deacidification method for papers are the Wei t'O and the Bookkeeper ones, that use a solution of metylcarbonate of methoxmagnesium and a dispersion of magnesium oxide in a fluorinate organic solvent, respectively. The need to find new alternative methods is given by the fact that these products have a significant environmental impact and are harmful and dangerous to the user.
In the last years, the research in this field has been based on the development of calcium hydroxide and magnesium hydroxide nanoparticles and of methoximagnesium methylcarbonate [7,8,14,15]. All new materials have been tested and compared with traditional ones. Results showed that the nanomaterials have a high compatibility with the substrates and constitute an alkaline reservoir against the acidity. In particular, the nanoparticles have been tested on the Sweden Vasa ship [8,16] of XVII sec.
The conservation of wall painted requires a particular attention. The degradation of the wall painting principally depends on the water adsorption inside the porous walls which causes a swelling of the coating layer or the pigment pulverization.
The wall porosity and the continuous exchange with the atmospheric environment require that the conservation treatments are reversible, durable and compatible with the substrate.
Alcoholic dispersions of $Ca(OH)_2$ nanoparticles have been successfully applied on mural painting surfaces and on limestones as consolidant agents to stop the powdering and flaking processes that affect these types of works of art exposed to the natural weathering and to the anthropic action [17].
Their physicochemical compatibility with the inorganic nature of the mortar or limestones makes this kind of compounds a valid alternative to the organic polymers usually adopted in the consolidation during restoration works. In fact, the calcium hydroxide reacts with the carbonium dioxide of the air producing calcium carbonate, the same binder of the fresco technique and the fundamental constituent of carbonatic stones. The nanometric size of the particles ensures both their good penetration into the porous matrix, and the minimization of possible whitening effects. The carbonatation process leads to the formation of new calcium carbonate. Its action as binding medium for the powdered pigment is made easier.
The nanolime dispersions were recently applied in some important graffiti of the Steri's Prison, Palermo (Italy) [18,19]. A particular of the treated part of the graffiti is reported in Fig. 1.

Different preparation methods have been proposed by the Nanomaterial Group at the CSGI Consortium of the University of Florence in order to obtain a product avoiding chromatic alterations of surfaces, increasing the penetration depth and obtaining a complete conversion of lime into calcium carbonate.
Although some work on nanolime syntheses and on its application in workshops have

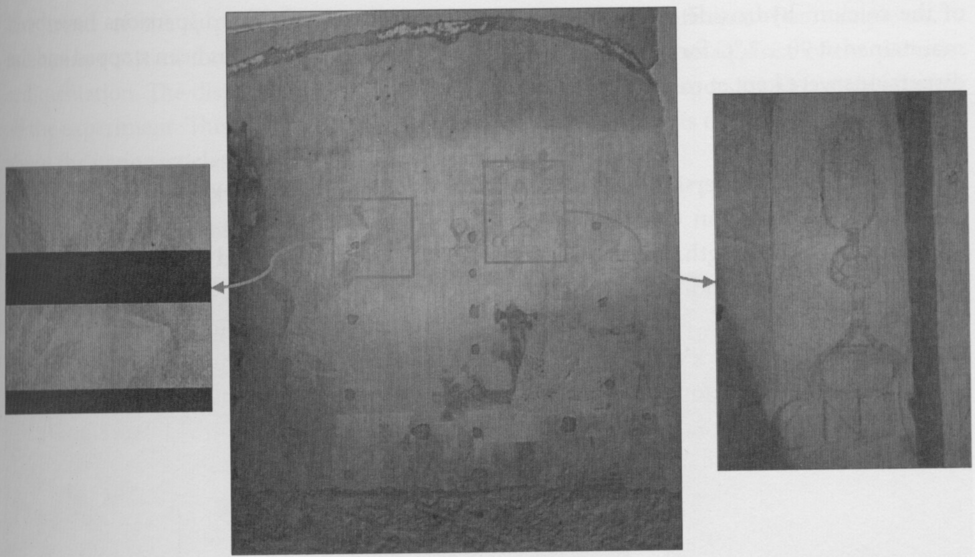

Fig. 1: Particular of the graffiti treated with the nanolime dispersion [18]; at left the Chris's hand, at right the base of mostrance.

been reported, the understanding of the mechanisms which influence the stability of dispersion is one of the most important requirements to assess the methodology and to understand all the possible effects associated to the applications.

The aim of the present work was the synthesis of the calcium hydroxides nanoparticles using the insolubilization-precipitation method. The synthesis was performed at different percentage of iso-propyl alcohol in water.

The stability of the nanolime dispersions was checked using an Uv-vis spectrophotometer, while the shape and the size of the nanoparticles were investigated using the Trasmission Electron Microscopy.

EXPERIMENTAL PART

Materials

Calcium hydroxides (Sigma-Aldrich CAS 1305-62-0 ≥ 95%); 2-propanol anhydrous (Sigma-Aldrich CAS 67-63-0; 99.5 %); deionized water (Millipore, Ω = 18,1 M Ω).

Method

Three aqueous solution of $Ca(OH)_2$ at the solubility limit have been prepared [20]. The solutions have been maintained at 90°C in nitrogen atmosphere. The 2-propanol has been added in the solutions in order to obtain the alcohol concentration equal to 20, 50, 90 vol.%, respectively. The dispersions have been called A, B and C, respectively. The precipitation of the calcium hydroxide nanoparticles immediately occurred. The dispersions have been maintained at 90 ± 2 °C for 30 min under stirring. Then, the stirring has been stopped and the dispersions were kept at room temperature.

Instrumentations

The stability of the dispersions was investigated at l = 600 nm by UV–vis spectroscopy, using a double beam Beckman Coulter DU800 spectrophotometer with a resolution of 1.0 nm. The operative wavelength, coincident with the one previously used [14], was chosen by checking that in this condition samples does not show any absorption band.

Trasmission Electron Microscopy (TEM) analyses were carried out using a JEM-2100 (JEOL, Japan) operating at 200 kV accelerating voltage, equipped with an energy dispersive X-ray spectrometer (EDS, Oxford, UK) suitable for element identification. A small drop of the dispersion was deposited on a 300 mesh carbon-coated copper grid, which was introduced into the TEM chamber analysis after complete solvent evaporation.

RESULTS AND DISCUSSIONS

The stability of the dispersions, whose appearance is shown in the inset of Fig. 4, was followed for 5 hours.

The higher turbidity of the dispersion B, confirmed by the absolute absorbance values at 600 nm ($Abs_A = 0.25$, $Abs_B = 0.60$, $Abs_C = 0.05$) can be ascribed to both the bigger particles size and the higher concentration.

The absorbance values have been corrected for the solvent contributes. The ξ parameter equal to $(A_t - A_{5h})/A_t$ and normalized to 1 has been calculated [14] and reported in Fig. 2.

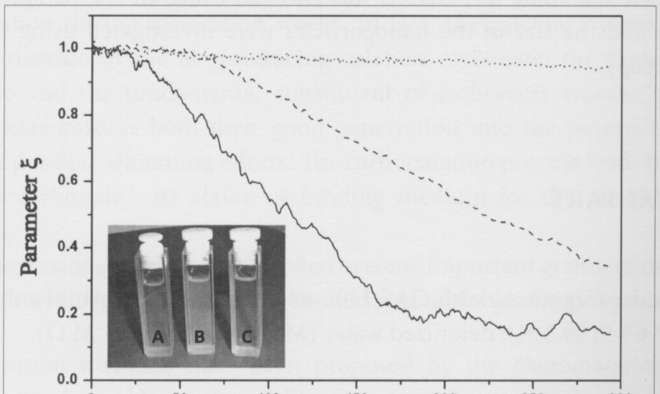

Fig. 2: ξ parameter as function of the time of the three dispersion. A) continuus line; B) dashed line; C) points. In the inset the 3 dispersions: A at left, B in the center, C at right.

The trend of the ξ parameter of the three dispersions is different. For sample A, it maintains constant for 20 min. Then, the ξ value decrease as a consequence of the particles sedimentation. The dispersion B is stable for 60 min, while the dispersion C is stable during all the experiment. This last finding is in agreement with the results obtained by Giorgi et al. about the nanoparticles dispersed in water and in 2- propanol [14].

In order to understand the reasons of the different kinetic stability, TEM measurements were performed to investigate the size and morphology of particles.

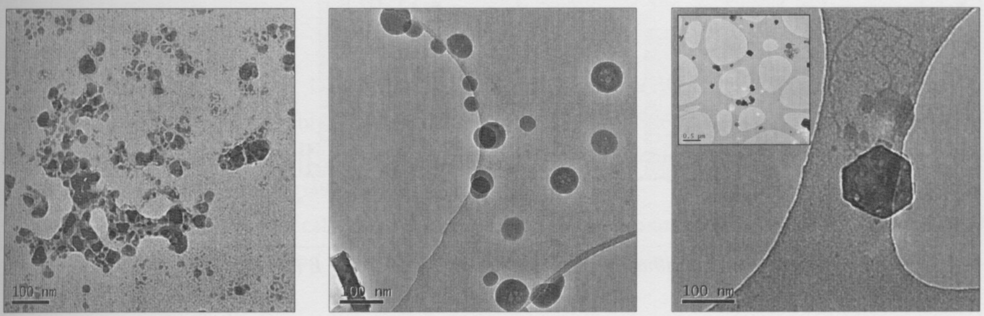

Fig. 3: TEM micrographs (magnification 25000x) of sample A at left, sample B in the centre and sample C at right. The Inset shows a micrograph at 5000x magnification.

Comparing the three samples, passing from the system at 20% vol. of alcohol to one at 90%, the size of nanoparticles increases, the shape becomes more regular and particles are less polydisperse in size.

Moreover EDS and SAED analysis were carried out on the samples to verify the composition of the particles observed. As an example we report the results for sample C. The analysis confirm that the nanoparticles consist of $Ca(OH)_2$.

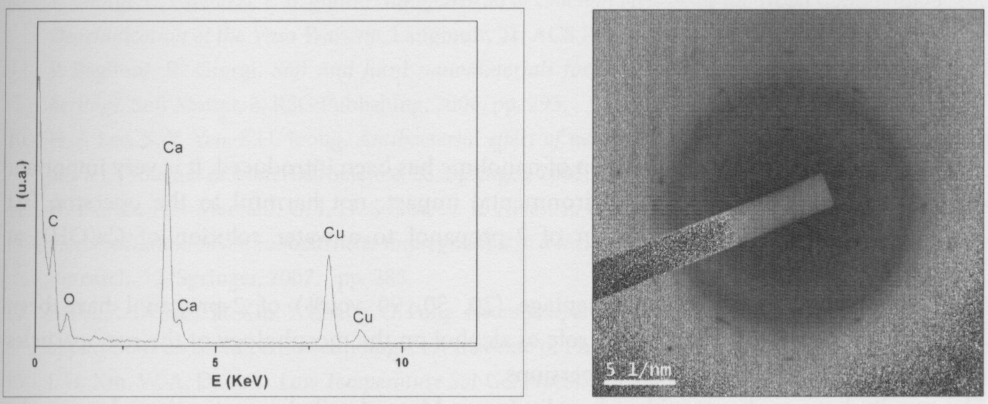

Fig. 4: EDS spectrum (at left) and SAED pattern (at right) of sample C.

The size distribution of nanoparticles was calculated and is shown in Fig. 5. Distribution of Sample C was not computed since particles are pretty monodisperse as shown in the inset of Fig. 3.

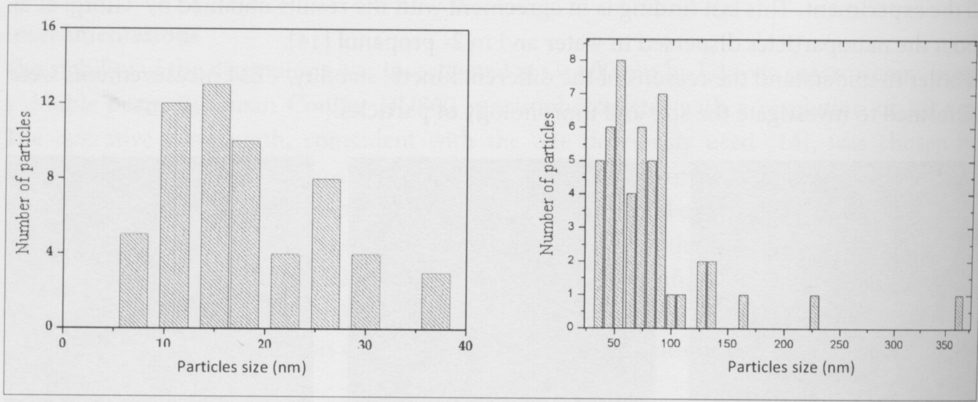

Fig. 5: Histogram of the size distribution for the sample A (at left) and B (at right).

The change in size can be rationalized considering that the dispersion particles are stabilized by a positive surface charge distribution as suggested by Giorgi et al. [8].
Based on the analysis conducted so far, this method looks promising: it is easy and allows to obtain the nanoparticles directly into the solvent to be used for applications. The limit, however, is the low amount of nanoparticles that can be achieved, because it is determined by the solubility limit of $Ca(OH)_2$ in water. Known that the solubility is greater at low temperatures, this study continues by examining the effect of temperature. This is particularly interesting because, in our view, temperature might play an important role on the morphology and particle size.

CONCLUSIONS

An innovative way for the preparation of nanolime has been introduced. It is very important and innovative because of low environmental impact, not harmful to the operator, fast and easy. It consist in the addition of 2-propanol to a water solution of $Ca(OH)_2$ at 90°C, under inert atmosphere.
Three dispersions at different percentage (20, 50, 90 vol.%) of 2-propanol have been prepared in order to understand the role of alcohol on the morphology of the nanoparticles and on the kinetic stability of the dispersions.
The results have to be considered preliminary. More detailed investigations have to be performed.

ACKNOWLEDGMENTS

TEM experimental data were provided by Centro Grandi Apparecchiature - UniNetLab - Università di Palermo funded by P.O.R. Sicilia 2000-2006, Misura 3.15 Azione C Quota Regionale.

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