USING NANO-MATERIALS IN SUPPORTING THE SUBSTRATE OF AN EGYPTIAN COPTIC FRESCO PAINTING

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Abstract

There is no doubt that many mural paintings in museums suffer from the heavy loaded added gypsum layers to the background of them for supporting. Nano materials produce successful way for supporting. Currently a comparison between nano materials (Carbone nano tube, nano calcium hydroxide, nano calcium carbonate and nano silicon dioxide) and the nature calcium carbonate which added to the background of the mural painting, The mechanical characteristics of the treated models were improved in all cases but in different values scanning electron microscope to determine the change in properties of the interior structure of the treated models.

Keywords: Nano-materials; CNTS; Nano CaCO3; Nano Ca(OH)2; SiO2; Fresco painting

Introduction

Deteriorated murals have been treated by conservators in a variety of ways but little scientific testing on the techniques, their reversibility, and ageing characteristics exists in searching but the nano-materials proved its success in essentially the nano calcium hydroxide dispersions (usually 2-propanol) has been developed by the Florence unit of the CSGI (center for colloid and surface science) [1]. This new method has been mainly used to support the mechanical properties. It is exhibit a good mechanical properties due to the nano-lime companied with the carbon dioxide in the surrounded air to produce new calcium carbonate (new born) which filled the gaps and connected the compounds each other inside the interior structure [2], as the following reaction:

$$\text{Ca (OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} \quad (1)$$

And the nano-materials such as nano calcium carbonate, nano silicon dioxide and used as filler to fill the gaps inside the object structures, it's success with many objects (lime stone and sand stone objects) were proved, According to the carbon nano tube which probably used with cement mortar which improved 10 times after treatment [3], one other hand all the treatments caused a visual discoloration even in the most successful nano-material (nano Ca(OH)2) a wide variation in color currently in this paper that disadvantage can be fixed by turning the mural paintings upside down to consolidate and support the substrate as the Canadian institute cares about removing the gypsum layer which was added to the backside of the mural paintings as a support in the last century now it becomes a too high load on the mural paintings with all problems of gypsum like salts, humidity etc. (the current fresco painting suffers from the added gypsum layer) [4]. So using nano-materials in consolidate the substrate (backside) of mural painting can solve all problems related to the color change as the treatment
applied from the back side and The mechanical characteristics of the treated models were measured using hardness and bursting strength detectors to reveal any improvement happened.

**Material and Methods**

**Materials**
All the chemicals were of analytical grade and were used without further purification. Purified MWCNTs (diameter 40–70nm, length 2–5μm, purity >95%) were procured from Nano tech company Ltd., Water was purified by a Millipore Elix 3 apparatus: the resistance of the ultra-pure water was 18MΩ·cm.

**Synthesis of nano-materials**
The nano lime was synthesized according to [5] Silica nanoparticles were prepared according to [6] CaCO₃ nano-particles were prepared according to [7].

**Preparation of the mixed nano-materials system**
The four nano-materials were sonicated in ultrasonic power 100 for 1 hour to make a homogenous suspension. Preparation of the nano-materials/ethanol system was carried out as follows: 2g nano-materials is dispersed in 98mL of ethanol (initial concentration 20 g/L), at room temperature [8]. The composition and the appearance of the obtained mixed system are listed in Table 1.

<table>
<thead>
<tr>
<th>Nano-materials</th>
<th>SiO₂</th>
<th>CaCO₃</th>
<th>Ca(OH)₂</th>
<th>CNTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>98</td>
<td>98</td>
<td>98</td>
<td>98</td>
</tr>
<tr>
<td>Nanomaterial</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
</tbody>
</table>

**The fresco painting condition**
The pictorial layer suffered from severe loss and color change around the lost areas [9] and the whole fresco painting suffered from weakness as there were a vital cracks (Fig. 1A). The four models of Egyptian Coptic fresco were exposed to artificial aging to create a similar circumstances for the original fresco painting then they were treated with three different system described in Table 1.

The surface of current fresco painting has a gypsum spots and a black crust as shown in figure 1 [10] and the whole fresco painting suffered from weakness as there were a vital cracks. The models of Egyptian Coptic fresco were exposed to artificial aging to create similar circumstances for the original fresco painting which kept in the storage of national museum of
Egyptian civilization with registration number 7897 then the surfaces were treated with systems described in Table 1.

The preparation of the models

The models were prepared according to the original mural painting as follows a first layer of rough coating, this mortar is a mixture of hydrated lime - calcium hydroxide and coarse sand, the second layer consists of hydrated lime and well-filtered fine sand, the third layer is the pictorial layer made of pigments and pure water applied in several coatings with a brush [11] The calcified layer results from the carbonation of the lime mortar, while drying, produces a transparent protective crust (outer membrane that forms as a result of carbonation of lime). This pellicle includes the pigments and fixes them definitively [12].

The models of Coptic fresco paintings were treated with the previous components using brushes (Fig. 1D) [11] from the backside after turning them upside down as shown (Fig. 1C) and the model treated with nature calcium carbonate after mixture of calcium carbonate with water the mixture added with a spatula as a separate layer on the back side of the model (Fig. 1E). The models were subjected to different accelerated ageing test to simulate the most Common outdoor heritage deterioration processes due to weathering agents. so they were exposed to temperature 25°C for 12h then up gradually to 60°C for 8h then left them in room temperature for 24h this round repeated 10 times to define the state of models after exposing for changing in temperature [13].

Characterization

The morphology was examined by scanning electron microscope model Quanta 250 FEG Field Emission Gun) attached with EDX Unit (Energy Dispersive X-ray Analyses with accelerating voltage 30kV, magnification 14× up to 1000000 and resolution for Gun.1n. FEI Company, Netherlands). Sample preparation consisted of application of a superficial gold film by sputtering to prevent electro-static charge.

Hardness and Bursting

The Shore D scale is based on ASTM D2240. The test involves the use of a hardened steel rod 1.1 - 1.4mm diameter, with a 30° conical point, 0.1mm radius tip. This exerts 44.64N of force [14] The measured hardness is determined by the penetration depth of the indenter under the load maximum penetration for each scale is 2.5-2.54mm, the amount of penetration is converted to hardness reading on scale of 100 units maximum hardness value 100 shore corresponds to zero penetration which can be converted in to newton to be 44.45N [15].

Tinuis Olsen H5KT machine was designed for using in Research and Quality Control to measure material’s strength and performance. All tests are designed and implemented by Tinuis Olsen in accordance with key international testing standards including ISO, ASTM, EN and other industrial standards. The load measurement accuracy: +/- 0.5% of applied load from 2% to 100%, and position measurement accuracy: +/- 0.01% of reading or 0.001 mm [16].

Results and discussion

The four nano-materials improved the mechanical properties of the treated models, as the nano-materials increase the models strength to the exogenous factors as the mechanical properties were tested using the hardness tester and the bursting strength detector, on other hand the nature calcium carbonate which applied as a separate layer cracked after ageing (Fig. 2) and as shown in Table 2 the weight of model's treated with nature calcium carbonate is increased so the difference in weight is wide but the nano-materials penetrate the substrate and consolidate the treated models and the weight of them increased a little bit. There aren't any over load happened but the mechanical properties improved widely in compared with the untreated model and the traditional way in consolidation of substrate by adding a separate layer of calcium carbonate, the calcium hydroxide depend on the chemical bond as shown in the upper formula, the silicon dioxide and calcium carbonate act as filler depending on the physical bond. In the case of carbon nano tube is given the widespread specific surface area of the nano particles and due to van der Waals which tend to favor the formation of agglomerate the CNTs Bridge the cracks for connecting.
Fig. 2. The models substrate which treated with four nano materials: A. carbon nano tube; B. nano Ca(OH)$_2$; C. nano CaCO$_3$; D. nano SiO$_2$; E. the normal size calcium carbonate

Table 2. The mechanical characteristics results of the models

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight of models</th>
<th>Average hardness shore D</th>
<th>Shore D (Newton’s)</th>
<th>Bursting strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated model</td>
<td>1051.67</td>
<td>19 ± 0.5</td>
<td>13 N</td>
<td>244N/mm$^2$</td>
</tr>
<tr>
<td>Nano-calcium carbonate</td>
<td>1060</td>
<td>40 ± 0.5</td>
<td>18 N</td>
<td>340N/mm$^2$</td>
</tr>
<tr>
<td>Carbon nano tube</td>
<td>1052</td>
<td>69 ± 0.5</td>
<td>31 N</td>
<td>500N/mm$^2$</td>
</tr>
<tr>
<td>Nano-calcium hydroxide</td>
<td>1056</td>
<td>47 ± 0.5</td>
<td>22 N</td>
<td>380N/mm$^2$</td>
</tr>
<tr>
<td>Nano-silicon dioxide</td>
<td>1070</td>
<td>35 ± 0.5</td>
<td>18 N</td>
<td>450N/mm$^2$</td>
</tr>
<tr>
<td>Natural calcium carbonate</td>
<td>1301.67</td>
<td>40 ± 0.5</td>
<td>18 N</td>
<td>300N/mm$^2$</td>
</tr>
</tbody>
</table>

The difference in weight after treatment

Table 2 show the weight of model's treated with nature calcium carbonate is 1301.67g the increased amount 250.76g so the difference in weight is wide but the nano-materials penetrate the substrate and consolidate the treated models and the weight of them increased 4.33-5g so there aren't any over load happened

The visual properties and the changes of colors after treatment

The purpose of comparison the changes of visual colors of substrate which always white after treatment (Fig. 2A) the carbon nano tube caused darkening. The models after treatment figure 2B, C and D, with nano-materials in sequence nano Ca(OH)$_2$, nano CaCO$_3$, nano SiO$_2$ shown as white and figure 2E the new added layer of nature calcium carbonate cracked.

Scanning Electron Microscope

Scanning Electron Microscope showing the results of consolidation as the nano-materials appeared inside the structure of the treated models as shown in figure 3.

Hardness and bursting

The Hardness Tests using Shore D

The Shore D scale is based on ASTM D2240. The test involves the use of a hardened steel rod 1.1 - 1.4mm diameter, with a 30° conical point, 0.1mm radius tip. This exerts 44.64N of force (Fig. 4) [17]. The measured hardness is determined by the penetration depth of the indenter under the load maximum penetration for each scale is 2.5-2.54mm, the amount of penetration is converted to hardness reading on scale of 100 units maximum hardness value 100 shore corresponds to zero penetration which can be converted in to Newton to be 44.45N [18]. Hardness tests for untreated model and treated models with the four nano-materials are presented in figure 4 and the treated model with nature calcium carbonate acts as a two layer connected together.
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Fig. 3. SEM images of pure nano-materials:
A. Ca(OH)$_2$ during the carbonation process; B. carbon nano tube inside the substrate structure;
C. nano-silica; D nano-calcium carbonate

Fig. 4. Testing samples for Hardness using Shore D and bursting strength test using Tinuis Olsen

The bursting strength Tests or compressive strength using Tinuis Olsen
Bursting strength or compressive strength express the ability of samples to bear compressive strength to be broken (Fig. 4) [18, 19]. Bursting strength for untreated model and treated models with the four nano-materials are presented in Table 2. The results proved that there is an improvement happened in the five models in different values the traditional way in adding a layer of calcium carbonate separated as a single layer under pressure.

Conclusions

This study focused on the difference of adding a layer of calcium carbonate like all the traditional ways in adding a new layer to be as support can be cracked and separated after ageing and in addition to cause over load to the mural paintings, but the nano- materials produce a simple way in consolidation the substrate of the mural painting from the back side to overcome the changes of the color painting which happened even in using the nano Ca(OH)$_2$. The bursting strength and hardness for the treated models were improved in different values the highest value in case of using the nano Ca(OH)$_2$ which act as it's natural to combine with carbon dioxide to produce calcium carbonate connecting the structure of mural painting and carbon nano tube which bridges the cracks without filling gaps inside the structure of the model depending on van der Waals bonds, on other hand the lowest value in case of using the added new layer of nature calcium carbonate which separated out of the backside under pressure in case of the nano silicon dioxide, nano calcium carbonate were acted as filler.

http://www.ijcs.uaic.ro
References


