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EVALUATION OF POLYVINYL BUTYRAL AND ZINC OXIDE NANO-COMPOSITE FOR CONSOLIDATION OF HISTORICAL WOODS

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Abstract

Consolidation of degraded wooden artifacts by natural and synthetic polymers in a solution is an important step in the treatment process of wooden heritage. This treatment is basically depended on the penetration, distribution and retention of the consolidate in the wood structure. One of the most frequently used consolidate for wooden material is polyvinyl butyral (PVB). Present research aims to evaluate polyvinyl butyral and zinc oxide as consolidate of old dried wooden material and investigate the efficiency of zinc oxide as a supplement on the distribution, penetration and retention of the consolidate in the "patanus orientalts-L" wood samples. Samples used for this research all belong to Qajar period. They were obtained from the same artifact and had the same, relatively sound condition. Cross sections were cut and obtained in a chamber with controlled temperature and relative humidity and weighted afterwards. Zinc oxide was used in 0.5, 1.0 and 1.5 concentrations in the polyvinyl butyral matrix of 10% concentration. Efficiency of consolidate was evaluated by weighting, distribution and penetration in the wood and were examined by Fe-SEM and EDX. Concentrations 0.5 and 1% of Nano- zinc oxide increased the penetration of consolidate and all three concentrations of zinc oxide increased the retention. Penetration of Nano- zinc oxide in the lumen as well as uniform distribution of it in the wood structure was also observed by microscopic observation.

Keywords: *Wood; Consolidate; Nano-composite; Polyvinyl butyral; Zinc oxide*

Introduction

Consolidation treatment is of a particular importance in the conservation process, especially because most wooden objects are inevitably subjected to chemical and biological degradation which seriously affect their integrity and mechanical strength [1]. Before any consolidation treatment the goal should be identified, in other word it should be clarified why and for what purpose the wooden object needs to be consolidated. Generally, the purpose of consolidation is to restore the cohesion, physical properties and mechanical strength of the wooden material in a way that consolidation won't threaten the authenticity of the object [2, 3]. Finding the suitable consolidate, the type of solvent, concentration of the solution and appropriate treatment method are among the most important factors in the consolidation treatment. In choosing the consolidate, the nature of the object, the type of the tree, and its condition should be considered [1]. Different methods and materials have been used for consolidation of wooden object but polymeric solutions are most popular ones [3-5]. Several

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thermoplastic resins have been used for consolidation of degraded wood, but Paraloid B72 and polyvinyl butyral (PVB) have proven to be the most effective materials [4, 6-8] Of them, PVB is more in use and seems to be the more suitable option [6]. On one hand, the application of PVB solutions alone presents disadvantages such as insufficient penetration [3], short time retention of the consolidate in wood [9] and undesirable mechanical strength [10]. On the other hand, these are the most important factors of a good consolidate [1, 11, 12]. Retention of a resin is particularly important because the effectiveness of the consolidate is highly depended on the amount of the resin injected into to the wood [8, 13]. Therefore higher and deeper penetration are desirable qualities one can see in a consolidate [1]. In addition, the function of consolidation is a result of the consolidate properties and its distribution in the wood structure [14]. Therefore it is necessary to take measures in order to improve the consolidation properties of this polymer. Much effort has been taken to upgrade the quality of different polymers using nano-particles [15-19].

Same investigations have been accomplished in the field of wood consolidation [1, 11, 20-22] Some studies have been devoted to improve the biological properties of PVB in wood treatment [23]. Thus, a material should be sought which can improve the penetration and retention qualities of consolidate. To achieve this, nano-materials could be used because of their tiny particles and high distribution quality. Among these, nano-zinc oxide can be an appropriate choice due to its resistance to moisture, UV, fungi and microbial deterioration and leaching [11, 24-27] as well as being cost effective, bio-friendly and high hydrophobic quality [27].

With the mentioned qualities in mind, this research aims to evaluate the penetration, uptake, distribution and retention properties of PVB Nano-composite and zinc oxide, as a consolidate for dried old wood, in *patanus orientalts-L* wood samples.

Materials and Methods

Wooden Samples

In this research samples were obtained from the wooden stakes of a door of a building in Birjand in the east of Iran belonged to Qajar period. Samples were found in a same, relatively sound condition. Radial, tangential, and transversal sections were cut respectively in 10, 20 and 30mm [24]. After sanding with sandpaper H 240, samples were placed in a chamber in the laboratory (200±2ºC, 50±5RH) for 30 days to achieve weight stability and being prepared for treatment [5]. *Patanus orientalts-L* type was chosen because it is local to Iran [28, 29]. It has been employed in many wooden artifacts, particularly in historical buildings [30-33] and plays an important role in Iranian wood art.

Consolidate solutions

In this research polyvinyl butyral (as the polymer matrix) and zinc oxide nano-particles (as the filler) have been combined and used for consolidation of the wooden artifacts. For making the Nano-composite, PVB (ACROS 33143) made in USA and zinc oxide Nano-particles with size of 29nm particles and 99.983% purity (“research” trademark made in Spain) were used.

PVB was diluted using ethanol and 10% PVB solution was prepared. Different concentrations of nano-zinc oxide (0.5, 1.0 and 1.5%) were added to PVB solutions separately and were dispersed using Ultrasonic Prob.

Numbers of consolidate solutions used in this research are shown in table 1.

Table 1. Samples code

Samples Code	Soluble compound
A1	A4+ 0.5 % nano ZnO
A2	A4+ 1.0 % nano ZnO
A3	A4+ 1.5 % nano ZnO
A4	PVB 10% in ethanol

Treatment process

Samples which achieved weight stability were weighted (m_i) and immersed in the consolidate solutions for 1, 2, 3, and 24 hours and weighted respectively ($1m_u$, $2m_u$, $3m_u$ and $24m_u$) [24]. According to the density difference between wood and the solution, to avoid the movement of samples and to make a uniform condition and constant contact of the solution on the wood surface, the samples were suspended in the solution using pin and stainless wire. Samples were held in a plumbed (plasticized) box during the treatment (Fig. 1).

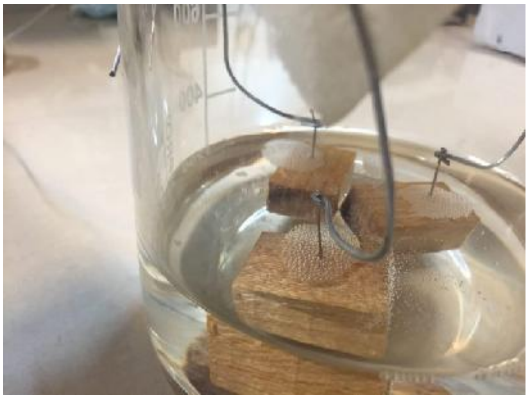

Fig. 1. Immersion of wood samples in the consolidate solution

Uptake and retention test

The application of consolidate was examined by weighting the samples. Taking into consideration the weight of the sample before and after treatment, the uptake of the resin in the saturated state and then after the evaporation, and the retention of the consolidate were examined [24].

Uptake of the consolidate was measured using the following equation:

$$CSP = 10^{-3}\,\frac{(Mu-Mi)}{Volume\ sample}\ kg/m^3 \qquad (1)$$

where: *Csp* - consolidate solution uptake, in [kg/$^{m3]}$; m_u - mass of the treated sample immediately after immersion, in [g]; m_i – initial mass of the sample, in [g];

Treated samples were held in the laboratory for 48 hours until the solvent evaporated and consolidate deposited. Samples were held in the same condition (20±2ºC and 50±5RH) until the weight was fixed and they were weighted (m_f).

Consolidate retention was measured using the following equation:

$$(WPG) = \frac{(m_f)-(m_i)}{(m_i)} \times 100 \qquad (2)$$

where: *WPG* - weight percent gain, in [%]; m_f - final mass of the treated and conditioned sample, in [g]; m_i - initial mass of the sample, in [g].

Microscopic observation

Microscope was used to prove the presence of zinc oxide in the samples. For this purpose some samples were cut from the treated wood with the solution and were compared with the none-treated one.

Small samples were prepared according to the following instructions: treatment samples in the size of 20 × 20 × 30 mm were immersed in the distilled water for 72 hours in the room temperature. Cross section was obtained using a microtome. These small samples were washed in two ethanol bathes (50% and 70%) for 5 minutes to evaporate their moist and then dried out by air-flow oven (20-60°C).

In this research, a Tescan equipped with the elemental analysis instrument Rontec SEM-EDX was used. Samples were covered with gold and examined. Presence of zinc oxide in the wood samples was examined using elemental analysis technique.

The SEM analysis didn't provide the desired images, detailed enough to see the Nano-particles. This could be related to the small size of the particles. Therefore FESEM HITACHI S-4160 with 5nm resolution was used.

Results and discussion

The weight of the samples before the immersion and after the treatment stages has been presented in the table 2.

Table 2. Weight of the samples before the immersion and after the certain times of treatment

Code Samples	Initial Weight	After 1 h	After 2 h	After 3 h	After24 h
A1	7.40	9.32	10.09	10.97	12.20
A2	6.97	8.63	9.12	9.52	11.09
A3	6.67	8.40	8.98	9.20	10.56
A4	7.18	9.31	9.71	10.3	11.30

According to the data presented in the table 2 and the mass of the samples, solution uptake was measured using equation 1.

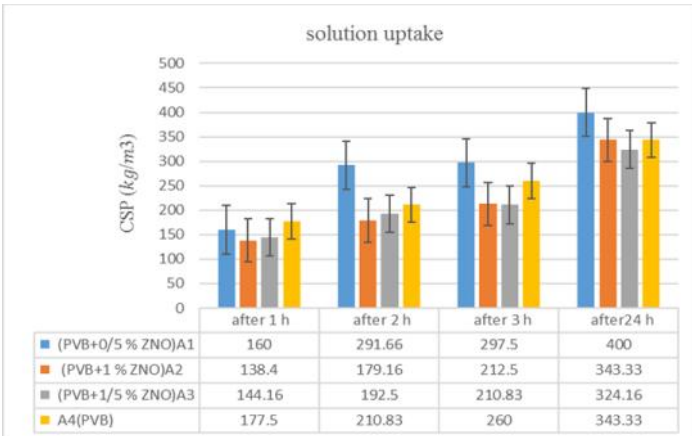

Fig. 2. Comparative solution uptake of *Patanus orientalts*-L samples treated by total immersion

As expected, the speed of solution uptake was fast at the beginning of the treatment (one-third of the whole solution in 24 hours), and then uptake speed reduced over time (Fig. 2.).

Adding nano-zinc oxide to PVB solution led to increasing uptake rate of the solution which is defined as kg/m^3. According to the data presented in the table 1, adding different values of nano-zinc oxide to the PVB solution showed different results. After the first hour of the immersion of the samples in the treatment solution, the maximum uptake was achieved in the zinc-oxide-free consolidate which was 177.5kg/m^3. Over time, different irregular uptakes were observed. After 24 hours immersion, PVB solution containing 0.5% nano-zinc oxide (A1) showed significant uptake (400kg/m^3), while zinc-oxide-free sample (A4) showed 343/33 kg/m^3 uptake. The interesting point was about the uptake reduction in A2 and A3, so that adding 1.0% and 1.5% values of nano-zinc oxide to PVB solution decreased solution uptake compared to the 0.5 value. This test showed that the 0.5% value of nano-zinc oxide in PVB solution had a better result on the consolidate uptake in the *patanus orientalts-L* wood samples 1.0% and 1.5% values reduced the solution uptake.

Consolidate retention

During the consolidation process, after the immersion step, the next step is ventilation, in which the solvent evaporates and the consolidate remains in the wood structure and increases the weight along with improving the cohesion and strength of the wood. Treated samples were held in the lab for 48 hours to let the solvent evaporates and allow the consolidate to reside in the wood. After this period of time, the weight of the samples was stabilized (m_f). After the evaporation of the samples, consolidate increased the weight of the treated samples. This weight is measured by equation 2:

Fig. 3. Comparative data of the weight percent gain of *Patanus orientalts*-L samples treated by total immersion in the four consolidate s A1, A2, A3 and A4 of PVB

As shown in the figure 3, the more nano-zinc oxide is added to the PVB solution the more consolidate retention is achieved. In the sample with no nano-zinc oxide, retention is 7.1%, while in the sample A3 which contains 1.5% nano-zinc oxide, retention gained its maximum 9.89%. Retention depends not only on the solution uptake, but also on the concentration of the solution. Considering the fact that concentration functions in two ways, lesser concentration helps the solution to be absorbed better, but sometimes high concentration ensures the higher amount of the solid consolidate.

Result of microscopic observation

SEM was used to study the presence and distribution of the consolidate in the wood structure, the penetration slits and the presence of nano-zinc oxide (Fig. 4).

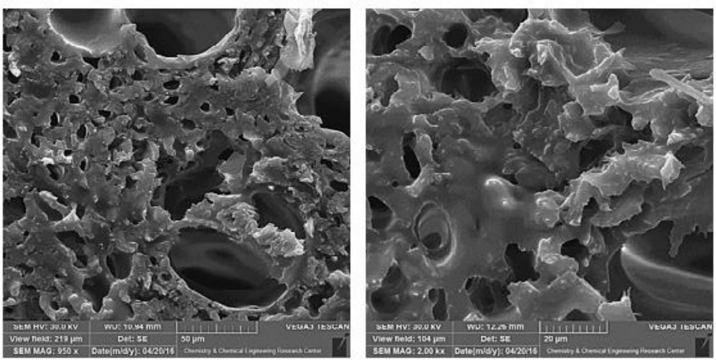

Fig. 4. SEM micrographs of treated (a) Patanus orientalts-L samples in PVB solution (A4) and (b) treated in PVB solutions with nano-ZnO additives in 1.0% ZnO, magnification 500X: a and b: cross section: consolidate is visible through vessels and fibers as white bubbles.

Elemental analysis was used to trace the presence of zinc oxide in the wood samples. The result of SEM revealed the evidence of penetration of nano-zinc oxide into the lumen. It also showed that distribution of the polymer into the wood structure in the sample treated with PVB nano-composite and zinc oxide is more uniform. Elemental analysis shows a small amount of zinc oxide (Fig. 5).

In the SEM images nano-particles are not very clear, therefore FESEM was used. Pictures of this analysis showed a uniform distribution of particles inside the wood structure. It also showed the approximate size of nanoparticles, between 25 to 38nm (Fig. 6).

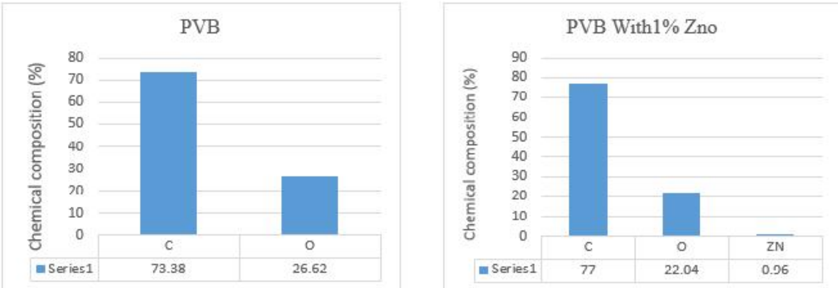

Fig. 5. Chemical composition (%) of samples treated with PVB (a); samples treated with PVB with nano-ZnO (b).

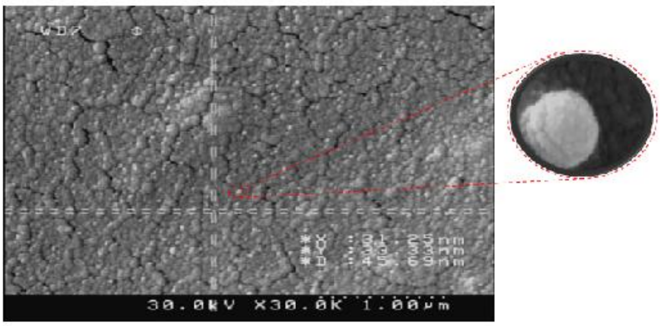

Fig. 6. FESEM micrographs of cross section, consolidated pieces by total immersion in PVB solutions with nano-ZnO additives in 1.0% ZnO

By comparing the SEM images taken from treated samples with PVB solution with those taken from samples treated with Nano-composite of PVB and zinc oxide it can be understood that zinc oxide Nano-particles has penetrated the deep structure of the wood. The advantage of treatment with Nano-composite compared with PVB solution is that one can see the zinc oxide Nano-particles even in the deep texture of the wood and it is not only a superficial treatment. Therefore it can be concluded that, after treatment with PVB nano-composite and zinc oxide, wood has a better functioning against environmental degrading agent and has a slower degradation process compared with nano-zinc-oxide-free PVB solution.

Conclusion

Synthetic resins are employed as consolidate for conservation of historical heritage. These resins may have some problems which can be improved by trying new methods and materials particularly mineral nano-particles. In this research nano-particle zinc oxide was added to the polyvinyl butyral (PVB) solution and the amount of uptake, penetration, retention and distribution of PVB and zinc oxide nano-composite in "*palatanus orientalts-L*" wood samples were measured and then compared with those of PVB solution. Concentrations of 0.5 and 1% of nano-zinc oxide increased the solution uptake. Concentrations higher than 1% of zinc oxide nano-particle reduced the consolidate uptake. All the concentrations of zinc oxide increased the solution retention. Retention is depended not only on the solution uptake but also on the concentration of the treatment solution. Therefore, concentration functions in two ways; the lesser concentration increases the uptake, but sometimes higher concentrations ensure higher amounts of the solid consolidate. The result of microscopic observation shows the deep penetration of zinc oxide nano-particles into the lumen as well as the uniform distribution in the wood structure.

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