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CHARACTERISATION OF WATERLOGGED WOODEN ARTEFACTS IMPREGNATED WITH STARCH. COMPARISON WITH PEGS METHODS

SANYA Emile Adjibadé[a], REZZOUG Sid-Ahmed[b*] and ALLAF Karim[b]

[a]Laboratoire d'Etudes et de Recherches en Techniques Industrielles-Ecole Polytechnique
Université d'Abomey - Calavi. 01 BP: 2009 Cotonou - Rép.du Bénin

[b]Laboratoire "Maîtrise des Technologies Agro-Industrielles" sarezzou@univ-lr.fr
Université de La Rochelle – Avenue Marillac 17042 - La Rochelle, France

Abstract

Experiments were performed using starch solutions and two PEGs (400 and 4000) as the impregnating materials for waterlogged woods treatment for conservation. This paper aimed to compare the devised starch impregnating method with the PEG treatments for waterlogged wood conservation. The proposed process consisted in using for wood impregnation coupled with a thermal treatment and a drying. The thermal treatment had two consequences: a total elimination of bacteria and a consolidation of waterlogged wood samples which was confirmed by a good dimensional stabilization of the treated samples.

This comparative study showed the proposed method give the same results as impregnation with the two resins in terms of dimensional stabilisation but better results in terms of colour preservation

Key-words: Starch Impregnation; Polyethylene Glycol; Dimensional stabilisation; Thermal Treatment; Anti-Shrink Efficiency.

1. Introduction

Numerous methods for waterlogged woods treatment for conservation have been experimented without any entire satisfaction (Ambrose, 1984; Drocourt and Deladalle, 1984; Cook and Grattan, 1984). Many investigations still ran for ideal and durable technique because conservation remained a real challenge (Foley, 1990; Watson, 1984; McCawley, 1977, Giachi et al., 2004). Archaeological waterlogged wooden artefacts were also numerous and still waited for the best treatment method. All the devised methods for conservation treatment accounted for the same goal that might be expressed in terms of the quality parameters .First was the dimensional stabilisation measured by Anti-Shrink Efficiency (ASE). The second important parameter comprised the surface checking aspects for the treated wooden artefacts that included no split at all or very slight and the colour preservation.

The colour measurement was essentially done for waterlogged woods by sensorial method which was often limited to the comparative observation between colour of a reference wood sample and that of treated samples (Macleod, 1987). The chosen reference was usually an untreated freely air-dried sample. Colour measurement method for the waterlogged woods could therefore be qualified as subjective.

Aesthetically pleasant treated woods with good dimensional stabilisation were obtained using a new treatment method, the starch impregnation coupled with a thermal treatment for waterlogged wood conservation (figure 1). It consisted of an impregnation phase in which starch was used as consolidating

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[*] Auteur à qui la correspondance devrait être adressée : sarezzou@univ-lr.fr

material. In a second phase, the starch-impregnated wood was submitted to a radiant heating thermal treatment in a high relative humidity conditions. A final phase consisted on treated wood drying using a recent drying process: successive pressure drops dehydration method developed in our laboratory ("Déshydratation par Détentes Successives": DDS) by Sanya et al., (2000). This paper aims to present a comparative study performed using the starch and Polyethylene Glycol (PEG) as consolidating treatment materials for waterlogged woods conservation. Two varieties of PEGs were used: low molecular weight PEG 400 that represented liquid rosins' class and PEG 4000 for solid rosins one. A mixture of starch and PEG 400 was also investigated. A comparison of measured Anti-Shrink Efficiency values and of colour analysis for the two conservation methods was performed. Although the PEGs 400 and 4000 were better absorbed by waterlogged wood samples than starch, the results of this study showed satisfactorily higher quality for the starch impregnated woods coupled with thermal treatment than that for PEG methods. The different sequences of the proposed process summarized in figure 1.

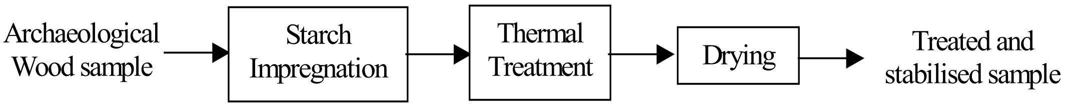

Figure 1.Sequences of the process developed by Sanya et al., (2000) for the conservation of waterlogged woods

2. Experimental

2.1 Wood samples and impregnation methods.

The waterlogged wood samples used in these investigations were provided by three museums and archaeological centres: the Centro Restauri Gallo (Italy), the Centre Camille Julian of Marseille (France) and the Centra Arqueologia Subaquatica Catalunya, (Girones, Spain). The wood samples belonged to shipwrecks such as Grado Julia Felix Grande (GJF 13), Dramont (Dram 9), Cavalière (15 E), Giens (ECBL) and different waterlogged wooden artefacts such as those called Culip, La Draga Neolithica, etc. Parallelepiped cut samples of 52×48×64 (r×t×a mm) were used. The maximum water content (MWC) which is a relevant physical characteristic for archaeological waterlogged woods (Macchioni, 2003) was determined from different cut parts of each wood type. Considered values of MWC were the average of six to eight trials, depending on wood availability. Impregnation of wood samples was carried out by immersing samples in the suspensions of consolidating materials (starch or/and PEGs) which were maintained in permanent stirring using Rotolab-France ROTO-020 model magnetic stirrer. For the PEG 400, the pure resin was used for impregnation while for the PEG 4000, the procedure was set up by using 50% (w/v) solution of PEG in desalting water because this polymer was provided in solid form. The starch impregnating solution was composed of a mix containing two types: a white dextrin (2/3) and a granular cationic maize starch (1/3), both of them were available as a free-flowing white powder. The Brookfield viscosity of the starch impregnating solution was about 225mPa.s at 100 rpm.

2.2 Impregnation rate control

Two methods were used for to determine the quantity of absorbed starch: dried material content and starch content determination based on Karkalas method [14]. Only the first procedures were applied for absorbed PEG quantification.

Initial sample weight and its gained mass were measured by the following procedure: the cut samples, were first rinsed with ordinary water, superficially dried using absorbent paper, measured and conserved in desalting water for two days before impregnation. When wood sample was taken out of the desalting water for the initial mass measurement, the absorbent paper was used again. The same operation was repeated after a fixed impregnation periods. For the dried material determination (d.b), cut wood samples of identical dimensions were taken off one after another at fixed period intervals during the impregnation experiments. The major inconvenient of this method was the wood sample loss. Procedure for the starch content determination in the treated wood samples was more fastidious. All these quantitative parameters allowed establishing the different impregnation rates presented in table 2.

2.3 Starch determination in treated wood samples.

Absorbed starch in the treated waterlogged wood samples was quantified using Karkalas' method for starch determination in food materials (Karkalas, 1985).The results of starch content of woods, expressed in percentage of initial treated wood samples basis, were gathered in the table 2.

2.4 Thermal treatment of wood samples.

In figure 1 is presented the thermal treatment devised for the developed starch impregnation process. On the photo was shown the horizontal opened reactor in which impregnated woods were treated. On the table appeared a digital mettler-indicator and the control Computer. Procedure in the thermal treatment consisted in placing the impregnated samples on a grid support inside autoclave and submits them to radiant heating at 140°C for a duration that depended on the wood thickness. The wood samples were only subjected to the radiant heating in the high relative humidity conditions. In this plant, the heaters consisted of external electric jacket made of resistance that supplied up to 180 - 190°C inside the autoclave.

Figure 1 – experimental apparatus for thermal treatment and D.D.S drying devised plant for the waterlogged woods treatment for conservation.

The goals of thermal treatment consisted of polymerizing absorbed starch in wood structure. It also brought an important reduction of shrinkage to thermally treated woods and favoured the micro-organisms and eventually any living organism destruction. As it was done for the starch-impregnated samples, some of the PEGs-impregnated wood samples were also thermally treated and dried.

2.5 Drying of treated wood samples.

The drying of wood samples by D.D.S ("Déshydratation par Détentes Successives") method was performed in the same pilot plant shown in the figure 1. The DDS drying method, employed in the devised process of conservation treatment for waterlogged woods, was retained according to its higher yielded quality over the studied three compared drying methods. This drying technique was largely described by Sanya et al. (2003) and by Maache-Rezzoug et al. (2002) in previous publications.

The well known freeze-drying method had been taken as reference for dimensional stabilization: freezing temperature about -40 °C followed by sublimation from -40 °C to 3 °C at 1.5-3 Pa.

2.6 Dimensional s characterisation

The sample weight was recorded until a constant mass was attained, then they were stored in polystyrene bags at room temperature (15 - 20°C) and a relative humidity of about 48 – 52 %, before the final measurements of dimensions. Dimensional stabilisation was measured with a 1/100-sliding calliper. The samples were measured on three positions of the parallel faces, before and after treatment. Axial (a), radial (r) and tangential (t) dimensions were measured and the percentage shrinkage in the i-direction (S_i) was calculated using Eq (1) :

$$S_i = \left[\frac{D_{0i} - D_i}{D_{0i}} * 100 \right] \tag{1}$$

where i = (a, r, t) and D_{0i}, D_i represented the initial and final dimensions in the i-direction. Volumetric Shrinkage (S_v) was then calculated. In the quality control of dried fresh wood, it is generally admitted that volumetric shrinkage can be calculated as the sum of radial and tangential shrinkage since axial shrinkage is generally negligible. Axial shrinkage when drying waterlogged wood is greater and so must be taken into account. Thus, volumetric shrinkage (S_v) for waterlogged wood was determined as the sum of the three components:

$$S_v = \sum S_i \qquad \text{where } i = (a, r, t) \tag{2}$$

2.7 Scanning electron microscopy

Scanning electron micrographs were taken with a Jeol 5410 LV SEM. The samples were first splutter-coated with a thin gold film using a Cressington metallizer. Very soft wood samples were difficult to cut in such small dimensions without deformation. We solved this problem by first hardening the wood samples in liquid nitrogen before cutting.

2.8 Colour measurement

Another important quality factor for museum acceptability in all the developed treatments for waterlogged wooden artefacts conservation was the colour preservation for dry objects (McLeod, 1987) In this study, a DIN 6174 CIELab-system apparatus devised for colour analysis was used. This colour device consisted of a camera plant that was connected with a Computer for data acquisition via an electronic Hund Wetzlar light deliver. The acquired data analysis was performed with the StatGraphics plus software. Reference colours for comparison were those of the control samples free air-dry at room temperature between 10 and 20°C, 48 to 52% relative humidity.

3. Results and discussion

3.1 Waterlogged wood characterization

The different species of waterlogged wood were divided into three groups (table 1) according to their maximum water content (MWC). Highly deteriorated wood had a MWC of more than 500 % (class 1), intermediately degraded wood in the range 200% - 500 % (class 2) and slightly degraded wood <200% (class 3).

Table 1: The maximum water content (MWC %) and the species of the different waterlogged woods used in this study

	MWC (%)	Class	Wood species
11 E	187	3	*quercus*
15 E	390	2	*Abies alba*
ECBL	759	1	*Olea europea*
GJF 13	955	1	*Picea abies*
Dram 9	776	1	*quercus*

Microscopic analysis for wood samples showed diversity of degradation. Some woods contained much deteriorated part generally made of the external part surrounded the inner core slightly degraded. Other woods were highly and uniformly deteriorated and looked very spongy at touching. These kinds of woods were of particular species because of the difference of structure that was not comparable to the habitual known structures. An example of these woods was that shown in the figure 5 (ECBL waterlogged wood)

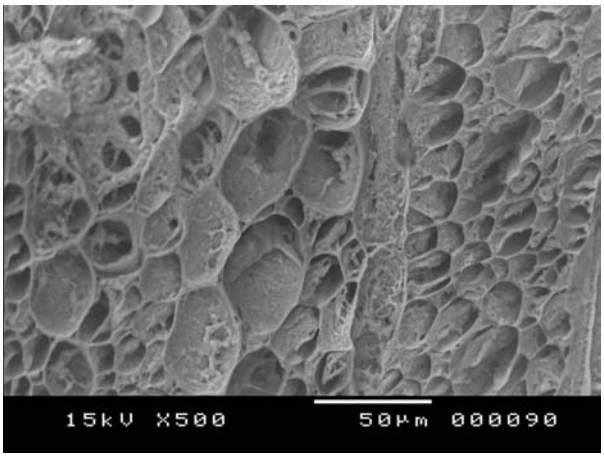

Figure 2: SEM photo of ECBL wood sample structure.

The heterogeneity of some of the waterlogged woods makes the classification very difficult. Although some wood species have exhibited high MWC, the SEM analysis seemed to show the relative well preservation of their internal structure. The maximum water content or the density of woods alone seemed not to be a reliable indicator of woods' degradation measurements. Some of the wood samples density were relatively higher enough and corresponded to our sensorial observations at the sampling moment but shown high MWC. The chemical analysis results for various wood samples were also of complex interpretation. However, the result for the chemically analysed samples showed that the lignin content of woods were almost higher than cellulose components contents (Sanya, 2003). These results confirmed that the treated samples belonged really to the waterlogged woods as MWC showed it.

3.2 Impregnation ratio results

The impregnation ratios were calculated as the difference in the dry basis between the initial and final states (after one month of impregnation) divided by the final dry basis. The results for starch content of the treated wood samples are shown in table 2. It can be seen that the starch content of wood samples determined by Karkalas method almost well corresponded to the impregnation ratio determined on the drying material basis (d.b).

The results also showed that high quantities of PEG 400 were absorbed for the highly degraded woods. The d.b material passed from 24.4 % to 44.9 % for woods from class 2 and 3 whereas that of highly deteriorated wood samples passed from 10 % to 91.5%.

Table 2: impregnation rate of the different consolidating materials including Karkalas starch determination method

Sample	PEG 4000	PEG 400	Starch	Starch (Karkalas method)
15 E	44.3	45.0	33.7	32.4
11 E	41.3	36.7	38.9	34.8
ECBL	72	81.5	70.2	77.7
GJF 13	48.1	88.9	54.0	69.3
Dram 9	66.3	65.2	42.6	37.2

According to these results, we could say that, the PEG 400 completely loaded the more degraded wood samples. The amount of PEG 400 absorbed by the relatively hard wood samples showed that this low molecular weight resin also encountered some difficulties for penetrating some wood structures. However, he amounts of PEG 400 that penetrated the different classes of woods were higher than those of PEG 4000 which was initially in solid form and then mixed with water solution 50 % (w /v). It might be thought that the solubilization of PEG 4000 in water probably lowered the molecular weight of solution but the obtained solution was visually more viscous than did the pure PEG 400. Moreover, the amounts of

PEG 4000 absorbed solutions did not significantly different for that of starch. It could be concluded that the PEG 4000 in 50 % (w/v) solution encountered practically the same difficulties for wood structure penetration than did the used starch.

In a last experiments series, the adopted 66-g of dry starch per litre of water were mixed with pure PEG 400 for comparative impregnation study using the same wood samples (GJF 13). The results were those presented in the figure 3. As previously described, the gain of dried material by impregnated wood samples with starch solution alone was lower than that obtained for PEG 4000 alone. The uptake was about 33 % that meant 322 % of dry matter increase against about 38 % i. e 370 % for PEG 4000. The uptake of starch by wood samples were also lower than the gain of the starch – PEG 400 mixture that reached 42,3 % i. e. about 413 % dry matter increase. The observed difference between the two uptakes amounts might be attributed to each of the consolidating materials. This was justified by the fact that the PEG 400 in the mixture could not preferentially load the wood. Water in starch solution modified PEG 400 conditions compared to the pure state. Moreover, we have observed a less change of colour for the impregnated wood samples by this mixture

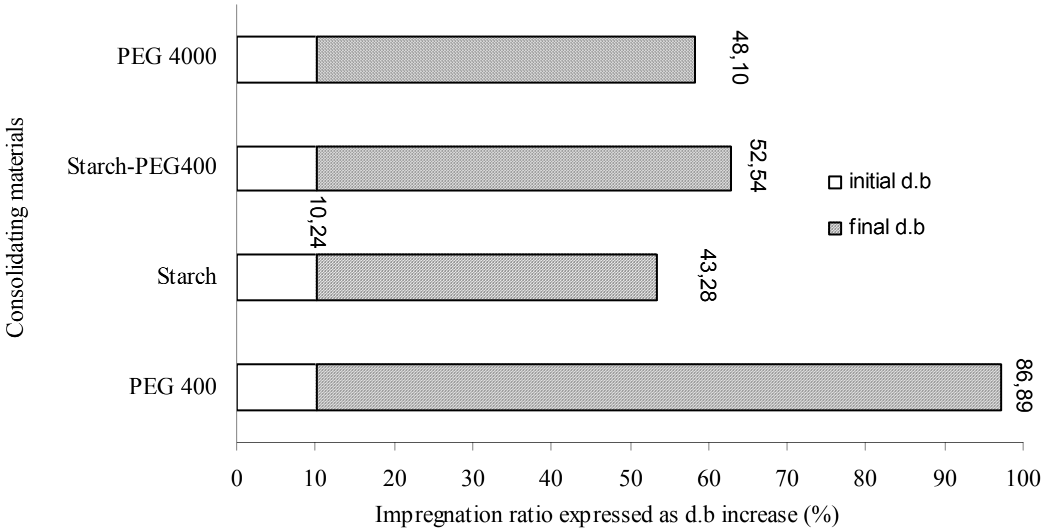

Figure3. Compared dried material gains by impregnated wood samples using respectively the PEG400, the PEG 4000, the PEG400 / Starch mixture and the Starch alone during the same period of one month impregnation (waterlogged wood: GJF-13).

In these comparative experiments also, all the three previous consolidating materials uptakes were far lower than that of the PEG 400 impregnation alone. For the latter, the wood samples absorption reached 76.4 % that meant 746 % dry matter increased based on the initial matter content.

3.3 Dimensional stabilisation of the waterlogged wood samples

After the thermal treatment and the drying of samples according to the conditions described in experimental section, the waterlogged wood samples were measured for the evaluation of shrinkage values. It was not possible to perform the measurement for the shrinkage values for the samples impregnated with PEG 400. This is probably due to the scrubbing phenomenon of the whole of wood structure induced by the thermal treatment. The samples recovered after the thermal treatment, was very soft and the absorbed resin seemed to reach the surface. These samples generally present important cracks after drying.

The shrink values in the three wood directions as well as the volumetric shrinkage are presented in table 3 for the samples impregnated with starch and with PEG 4000. For the latter samples, none resin was observed on the surface.

Table 3: Shrink values in the 3 directions of wood impregnated by starch and by PEG 4000

Wood	Starch				PEG 4000			
	a	r	t	Sv	a	r	t	Sv
11E	2.11	2.47	0.12	4.70	2.46	3.57	0.79	6.82
15E	0.12	4.32	0.53	4.97	1.33	3.59	0.47	5.39
ECBL	5.80	17.73	3.60	27.13	7.51	13.22	2.48	23.21
GJF13	3.39	8.35	5.24	16.98	3.03	6.10	5.56	14.69
Dram-9	7.33	6.97	0.11	14.4	6.33	6.93	0.20	13.82

From table 3, it can be seen that the percentage reduction of shrinkage depended on the wood species. The samples from class 1 (the most degraded woods) exhibited a high volumic shrinkage compared to the waterlogged woods from class 2 and 3 and this although that for these samples a higher impregnation was observed.

The values of shrinkage obtained for samples impregnated with starch and those impregnated with PEG 4000 were similar. Although, we must precise that all samples impregnated with PEG 4000 were qualified as unpleasant. In fact, their final aspect was very dark, almost black while the one of samples impregnated with starch solution was qualified of "naturalness"

3.4 Colour measurements

The acquired data from colour analysis of the starch, PEG 400 and PEG 4000 treated wood samples were statistical compared with the free air-dry samples. Analysis of variance (ANOVA) and Kruskall-Wallis test were displayed for the wood samples colour. The obtained results were those depicted in the figure 4 which showed that there was no significant colour difference at the 95 % confidence level when starch treated wood samples were compared to the control samples. Contrary, higher colour change occurred when the wood samples were impregnated using PEG 400 or PEG 4000.

Although the PEG 400 and 4000 better penetrated the wood structure than starch, qualitatively, the PEG absorption did not conferred any aesthetic value to the treated waterlogged woods

The conservation treatment, using the starch impregnation coupled with thermal treatment, was satisfactorily successful because it allowed maintaining the initial colour for the treated wood samples and yield acceptable shrink values.

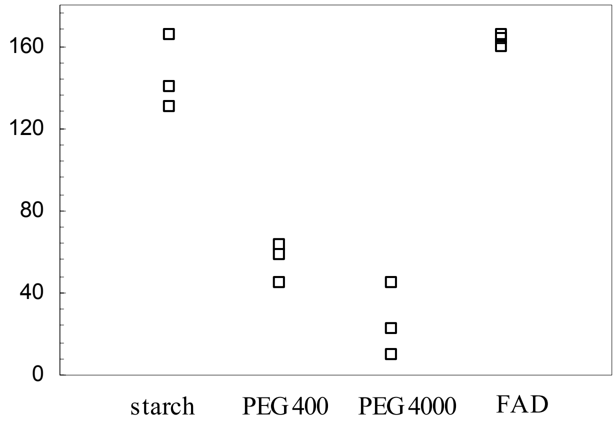

Figure 4. Colour analysis of the three impregnated wood (GJF-13 waterlogged wood) samples after D.D.S drying. FAD: free air drying (control)

Conclusion

This comparative study proved that the proposed starch impregnation coupled with thermal treatment process permitted to yield better wood qualities than did the pure PEG 400 and 50% (w/v) PEG 4000.

Although the impregnation ratio for starch remained lower than that of the two PEGs used in these investigations, good quality was for starch treated woods. The obtained results could also allow confirming that lower molecular weight favoured quasi complete loading of some woods' structure namely the highly degraded and spongy woods. The PEG 400 uptake by relatively mid-degraded woods was not as higher as that of the spongy woods. It was the proof that low molecular weight consolidating material did not automatically ensure the dimensional stabilisation and other required qualities for impregnated waterlogged woods . Contrary, the amount of PEG 4000 uptake was low but induced positive consolidation for the wood structure in the same manner as that of starch. Hardening property of PEG 4000 material favoured the resulting consolidation. The impregnation ratio for PEG 4000 was not so greatly different from that obtained with starch. Unfortunately, the colour change induced by usage of PEG 4000 and the humidity absorption by this solid resin in high relative humidity conditions constituted the major inconvenient of its use for wood conservation. The starch treatment yielded satisfactorily good quality for treated woods. Dimensional stabilisation was acceptable the colour preservation was largely better than PEGs impregnated samples.

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