

Original article

PRELIMINARY STUDY ON THE DIFFERENT EFFECTS OF CONSOLIDATION
TREATMENTS IN HEARTWOOD AND SAPWOOD OF A DECAYED
GYMNOSPERM WOOD

El Hadidi, N.¹ & Darwish, S.²

¹Assist. Prof. Conservation dept., Faculty of Archaeology, Cairo Univ., Giza, Egypt

²Assist. Prof. Conservation dept., Faculty of Archaeology, Cairo Univ., Giza, Egypt

E-mail: nelhadidi@gmail.com

Received 2/11/2013

Accepted 27/2/2014

Abstract

The aim of this research is to study and compare the different effects of some natural and synthetic polymers dissolved in different solvents on sapwood and heartwood samples taken from an archaeological decayed Cupressus sempervirens, a gymnosperm wood that had been often imported into Egypt throughout history. Five commonly used adhesives were chosen for this purpose: Paraloid B 72 dissolved in acetone (3% w/v), Methyl cellulose dissolved in water (1.5% w/v), Funori dissolved in ethyl alcohol 70% (3% w/v), Gum Arabic dissolved in water (3% w/v) and Poly vinyl acetate (PVAc) diluted in water (50% v/v). Untreated sapwood and heartwood samples and treated sapwood samples were examined using scanning electron microscope (SEM-EDS). For monitoring the chemical changes and modifications, which occurred in the wood due to the chemical effects of the consolidants, untreated and treated sapwood and heartwood samples were analyzed with an FTIR spectrometer.

Keywords: *Cupressus sempervirens, common adhesives, sapwood, heartwood, SEM-EDS, FTIR*

1. Introduction

Often old wooden objects present evidence of biological or chemical degradation which seriously reduces their mechanical properties. A consolidation treatment of wooden objects tends to render their mechanical strength and cohesion back; therefore it is an essential process for the conservation of old historical wooden artifacts. A high retention and a deep penetration and uniform distribution of the consolidant into the wooden object are actual goals of any consolidation treatment. Wood is an anisotropic and inhomogeneous material;

and it is relatively difficult to presume that all parts of wood will absorb polymer and solvent in the same efficiency. One of the factors that can be expected to significantly influence the performance of consolidants used for treating deteriorated wood is their distribution within the wood structure following treatment with either natural or synthetic resins dissolved in solutions/ solvents. Temporary expansion or swelling during treatment occurs, until the solution/ solvent evaporates. The 'initial' chemical effect of materials used in the

consolidation of wood needs thorough studies; because chemical reactions (between wood components and polymer or wood components and solvent) during and after treatment cannot be avoided. The aim of this research is to monitor and compare reactions and the different effects of some natural and synthetic polymers, which had been dissolved in different solvents, on sapwood and heartwood samples taken from the same tree trunk. There is a difference in the chemical composition of softwoods and hardwoods, and it was therefore necessary to decide to work on one type of wood for this preliminary study. The opportunity to find part of a tree trunk exposed to the same natural ageing conditions, containing both sapwood and heartwood, is rare, but not impossible. Fortunately a decayed wooden block cut from a cypress tree in the past was found in an old storage; therefore samples were taken from the decayed *Cupressus sempervirens*, for this study. Cypress is a softwood (gymnosperm) that had been often imported into Egypt, since as far back as Dynasty IV (ca. 2613 – 2498 BC) [1]. For wood treatment five commonly used adhesives were chosen for this study: **a)** Paraloid B72 is a well-known and studied consolidation material and has been extensively used in the consolidation of degraded wooden artifacts [2][3][4][5]. This synthetic polymer is composed of two monomers, methyl acrylate and ethyl methacrylate. **b)** Poly vinyl acetate (PVAc) emulsion is used most commonly in furniture and other wood product manufacture. It is a linear amorphous polymer with a weak polar interaction among the molecular chains, which results in a relatively low glass transition temperature (Tg) (about

28°C, from differential scanning calorimetry) [6]. The uses, properties and performance of PVAc on wood have been previously reviewed and discussed [7][8][9][10]. **c)** Funori (known also as JunFunori) is a polysaccharide extracted from the red algae *Gloiopeltis furcata*, which typically grows in the intertidal zones of the Pacific coast of Japan, Korea, South China and North America [11][12]. Investigations of the structure of the polysaccharide from the *Gloiopeltis* family showed that the monomer units of the polymer are comparable to those of agar and carrageen [11][12][13][14] [15][16]. One of the isolated regular repeating units was $[-\rightarrow 3) \beta\text{-D-galactose 6-sulphate-}(1\rightarrow 4) 3, 6\text{-anhydro-L-galactoseose } (1\rightarrow) \text{galactose}$, which is an ideal 6-sulphonated agarose. **d)** Gum Arabic, also called acacia gum, is a complex arabinogalactan-type polysaccharide exuded by *Acacia* trees. The main structural feature is a backbone of β -galactopyranose units with 1, 3 bonds and side chains of 1, 6-linked galactopyranose units terminating in β -D-glucuronopyranose and 4-O-methyl- β -D-glucuronopyranose [17]. **e)** Methyl cellulose is a non-ionic ether produced by many manufacturers in various grades, viscosity and degrees of polymerization (DP). The best methyl celluloses for use as consolidants are the highly purified varieties produced for adhesive applications (adhesive grades). Methyl cellulose is a more flexible adhesive than starch or gelatin. Low DP methyl celluloses can be made into solutions of 1-2% with water and used for consolidating large areas of weak paint layers. Methyl cellulose is not soluble in water at temperatures above 38° C [18].

2. Materials and Methods

Five commonly used adhesives were chosen to study their effect on a decayed *Cupressus sempervirens* wood block. Sapwood and heartwood samples (ca. 0.5x0.5x1cm) were each treated separately. In the case of PVAc which

was diluted in water (50% v/v) it was not possible to immerse the samples due to the viscosity of the polymer. Therefore the polymer was applied by brushing. In the other four cases the consolidants were dissolved as follow: - Paraloid B 72

dissolved in acetone (3% w/v) - Methyl cellulose dissolved in water (1.5% w/v) - Funori dissolved in ethyl alcohol 70% (3% w/v) - Gum Arabic dissolved in water (3% w/v). Finally, the samples were immersed in the solutions for 15 min. Samples were left to dry for one month, before analysis and investigation could be undergone. Additionally sapwood and heartwood samples were treated separately with the same solvents used in diluting the polymers, in order to eliminate the effects of the solvent while studying the effect of the polymer during FTIR interpretation. Untreated sapwood and heartwood samples were examined using scanning electron microscope (SEM-EDS). After treatment only sapwood samples were examined using SEM, due to the difficulty of assessing the effects of

polymer in heartwood that is rich with secondary accumulations. The samples were mounted on aluminum stubs with double-sided cellophane tape. After gold coating using a JEOL-JFC-1100E ion sputtering device, the samples were examined by SEM (JEOL scanning electron microscope JSM-5400 LV SEM-EDS). For monitoring the chemical changes and modifications, which occurred in the wood due to the chemical effect of consolidants, untreated and treated sapwood and heartwood samples were analyzed with an FTIR spectrometer (Model 6100 Jasco, Japan). Spectra were obtained in the transmission mode with TGS detector using KBr method and represent (2mm/Sec) co-added scans at the spectral region ranging from 4000 to 400 cm^{-1} with resolution of 4 cm^{-1} .

3. Results

To evaluate the effect of different consolidants on wood the work was built on three major stages, which began by assessing the difference between sapwood and heartwood of the decayed wood. This was followed by studying the effect of the three solvents commonly

used in diluting polymers or resins during wood treatment using FTIR spectroscopy, so as to exclude their effects on wood. This was then followed by monitoring the chemical changes in wood after treating the wood with five consolidants.

3.1. Differences between sapwood and heartwood in an archaeologically decayed gymnosperm

In wood treatments it is advisable to use at least two methods to evaluate any treatment. In this research it was necessary to start off with SEM, which was followed by the interpretation of the effect of treatment using FTIR analysis. SEM micrographs taken from the decayed wood block showed the vast differences in the cells of sap and heartwood. The sapwood sample clearly shows that the wood suffered from fungal decay, mechanical fissures around the pits and slightly scattered deposits, fig. (1- a, b). Accumulations of secondary compounds are clearly evident in the sample taken from the heartwood, fig. (1- d). The cell walls are totally covered with a layer of storage products, hiding the main features of the wood elements in some parts. The cell walls that remained uncovered showed a slight scattering of

secondary compounds, fig. (1-e). Further investigations showed that the percentage of mineral nutrients in sap and heartwood varied, tab. (1) & fig. (1-c & f). The percentage of Na, Mg, Al, Cu and Zn decreased in the heartwood samples, whereas Si, S, Cl, K and Ca decreased in the sapwood samples. P and Fe were only present in heartwood. The results of FTIR analysis of both heart and sapwood samples showed a strong contrast between the relative intensities, and slight variations especially in lignin signals. Lignin is present in wood to the extent of 17-40 percent and whose structure varies from species to species of timber. Aromatic skeletal vibrations at 1510 cm^{-1} and C-O stretching of guaiacyl ring of lignin at 1226 cm^{-1} in addition to C-O stretching in cellulose and hemicelluloses at 1114 cm^{-1} were absent in heartwood compared

to sapwood. Band assignments according to literature [19] and band shifts of the analyzed samples are listed in tabs. (2 & 3) and fig. (3). Methoxyl C–H stretching at 2835-2840 cm^{-1} , asymmetric C–H bending from methoxyl group of lignin and $-\text{CH}_3$ and $-\text{CH}_2-$ groups at 1460 cm^{-1}

1 , C=O valence vibration of acetyl- or COOH-groups of hemicelluloses at 1735 cm^{-1} disappeared in both heart and sapwood samples. Deficiency of these bands may be due to the degradation of the wood samples resulting from exposure to uncontrolled environments.

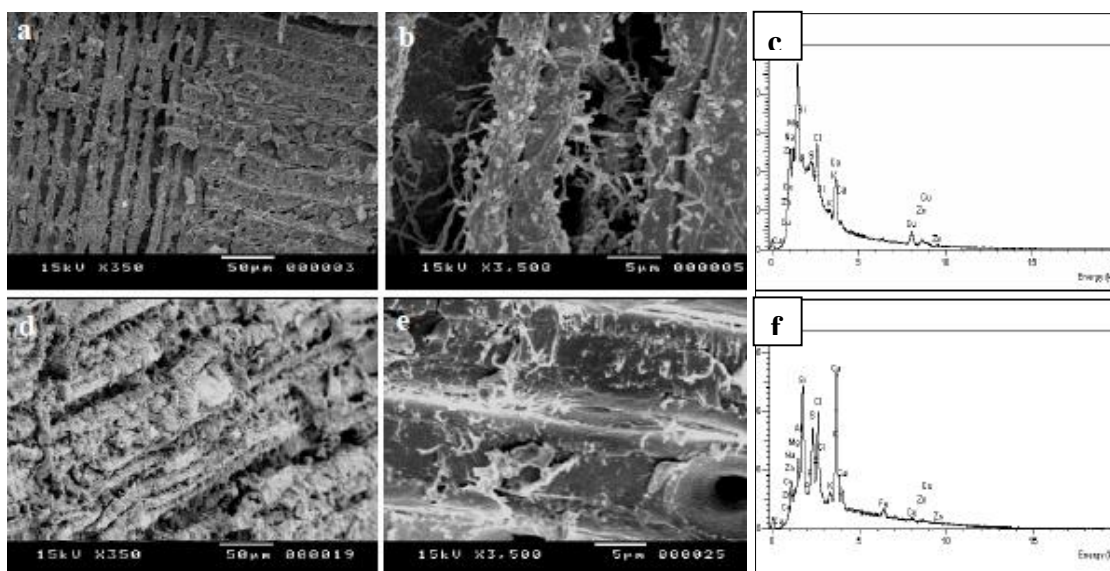


Figure (1) SEM micrographs of sapwood and heartwood **a** in longitudinal direction of the sapwood sample showing fissures in cell wall and scattered accumulations of foreign matter (bar = 50 μm), **b** in longitudinal direction of the sapwood sample showing fungal growth in cell walls (bar = 5 μm), **c** elemental analysis of sapwood using EDS, **d** in longitudinal direction of the heartwood sample showing dense accumulations of secondary compounds on the cell walls (bar = 50 μm), **e** in longitudinal direction of the heartwood sample showing fissures around bordered pits and in the cell wall, with the absence of fungal spores (bar = 5 μm), **f** elemental analysis of heartwood sample using EDS.

Table (1) elemental analysis of sapwood and heartwood samples using EDS

Elements	Sapwood		Heartwood	
Na	13.01	13.30	8.62	2.95
Mg	6.60	6.32	2.84	1.58
Al	30.22	27.23	5.43	4.96
Si	5.77	5.40	17.79	18.24
P	----	----	0.84	0.84
S	1.74	2.50	10.46	11.09
Cl	10.37	11.27	14.68	16.13
K	1.24	1.65	3.41	3.17
Ca	9.44	10.79	28.19	32.38
Fe	---	---	3.88	4.17
Cu	14.48	14.36	2.22	2.88
Zn	7.13	7.18	1.62	1.60

3.2. Effect of water, ethyl alcohol and acetone on sapwood and heartwood

Using FTIR, the molecular bonds in wood samples that were treated with different solvents and consolidants were closely studied and changes were noted as in tabs. (2 & 3). Wood absorbs organic solvents, which are retained in the wood cells for short periods of time, during

which the solvents may form complexes with wood components. After evaporation of the solvent, the chemical composition of wood components may undergo slight changes as follows: **a) Effect of water:** FTIR showed that no remarkable changes were noticed in all

bands of the sapwood except the O-H band which was shifted from 3411 cm^{-1} to lower wave number 3401 cm^{-1} . Heartwood absorbed water molecules. This is proven by the growth of a new band at 1616 cm^{-1} which is assigned to absorbed water. The band responsible for lignin component at 1599 cm^{-1} disappeared. The deficiency of this band may have resulted from solubility of lignin. This partially agreed with Horvath (2006) [20] who suggested that the swelling and solubility of lignin is greater with hydroxylated solvents (swelling solvents), e.g., methanol, ethanol, phenol, acetone and water than non polar solvents (non swelling solvents) like benzene and toluene. **b) Effect of ethyl alcohol:** Heartwood absorbed alcohol, displacing water molecules and leading to the formation of a complex with the two secondary hydroxyl groups in cellulose with breaking of hydrogen bonds. This is proven by shifting the O-H stretching band at 3421 cm^{-1} to a higher wave number at 3456 cm^{-1} with a growing new band at 1162 cm^{-1} . Effect of ethyl alcohol on sapwood was limited. Only the band at 1220 cm^{-1} assignable to C-C stretch

plus C-O stretch in xylan and hemicelluloses disappeared. **c) Effect of acetone:** Acetone, a less polar solvent, was chosen to test its influence upon the efficiency of Paraloid B 72 consolidation treatment. Slight changes were noticed due to the effect of acetone on sapwood. Both O-H and C-H stretching bands were shifted to lower wave number accompanied by the appearance of three new bands at 1454, 896.7 and 861 cm^{-1} assignable to CH_2 of pyran ring symmetric scissoring; $\text{C}_1\text{-H}$ deformation plus ring valence vibration and C-H out-of-plane, respectively. The effect of acetone on heartwood was relatively stronger. Many bands disappeared; asymmetric and symmetric C-H stretch in methyl and methylene groups in the region (3000–2842) cm^{-1} , aromatic skeletal vibrations of lignin at 1595 cm^{-1} , C-O valence vibration and/or calky-O ether vibrations at 1024.9 cm^{-1} . An adsorbed water band appeared at 1626.6 cm^{-1} . Some of these changes may result from the formation of wood - acetone complex due to the role of the polarity of acetone in the solubility of some wood components.

Table (2) FTIR bands in untreated and treated sapwood samples

Wave number (cm^{-1}) range of maxima	Band origin (assignment) with comments	Wave number (cm^{-1}) of treated sapwood								
		Standard	H ₂ O	Ethyl alcohol	Acetone	PVAc	Methyl cellulose	Gum Arabic	Paraloid B-72	Paraloid B-72
3460-3200	Broad band due to Bonded O-H stretch	3411.4	3401.8	3415.3	3417.2	3431.7	3411.4	3415.3	3406.6	3419.1
3000-2800	Asymmetric and symmetric C-H stretch in methyl and methylene groups	2930.3	2943.8	2927.4	2925.4	2928.3	2941.8	2905.2	2939.9	2935.1
1740-1730	C=O stretch in ester groups of B-72	---	---	---	---	---	---	---	---	1730.8
1625-1640	Adsorbed water	---	---	---	---	1628.5	---	1627.5	---	1628.6
1605-1593	Aromatic skeletal vibrations of lignin plus C=O stretch	1601.6	1599.6	1602.5	1601.6	---	1599	---	1599.6	1599
1515-1505		1510.9	1510.9	1510.9	1510.9	---	1510.9	1510.9	1511.9	1510.9
1470-1455	CH_2 of pyran ring symmetric scissoring, OH plane deformation vibration	---	---	---	1454.0	---	---	---	---	---
1430-1416	CH_2 scissoring	---	---	---	---	1419.3	---	---	---	---
1375-1385	CH deformation vibration	1384.6	1384.6	1384.6	1383.6	---	1384.6	1384.6	1384.6	1384.6
1270-1266	Guaiaacyl ring structure in lignin and C-O stretching in xylan and hemicelluloses.	1268.9	1268.9	1268.9	1269.9	1267	1267.9	1267.9	1267.9	1267.9
1230-1221	C-C plus C-O plus C=O stretch	1220.7	1222.6	---	1225.5	---	1220.7	1220.7	1220.7	---
1162-1125	C-O-C asymmetric valence vibration	1144	1143.6	1143.6	1147.4	1127.2	1141.6	1141.6	1141.6	1144.5
1086	Aromatic C-H in plane deformation	---	---	---	1091	---	---	---	---	---
1060-1004	C-O deformation in secondary alcohols and aliphatic ethers	---	---	---	---	---	---	---	---	---
1060-1004	C-O valence vibration mainly from $\text{C}_3\text{-O}_3\text{H}$, plus Calky-O ether vibrations	1036.5	1036.5	1033.6	1034.6	1041.3	1033.6	1033.6	1032.6	1028.8
1035-1030	Aromatic C-H in plane deformation, plus C-O deformation in primary alcohols, plus C=O stretch (unconj.)	---	---	1033.6	1034.6	---	1033.6	1033.6	1032.6	---
895-892	$\text{C}_1\text{-H}$ deformation, ring valence vibration	---	---	---	896.7	---	---	---	---	---
860-853	C-H out-of-plane	---	---	---	861.0	---	---	---	---	860
800	Pyran vibration	784.8	781.0	773.0	---	793.5	---	---	772.3	---
715	Rocking vibration CH_2 in cellulose	---	---	---	---	716.4	---	691.3	---	---
670	C-OH out-of-plane bending mode	682.6	---	---	663.4	---	---	691.3	---	---

Table (3) FTIR bands in untreated and treated heartwood samples

Wave number (cm ⁻¹) range of maxima	Band origin (assignment) with comments	Wave number (cm ⁻¹) of treated Heartwood									
		Standard	H ₂ O	Ethyl alc.	Acetone	PVAc	Methyl cellulose	Gum Arabic	Funori	Paraloid B 72	
3460–3200	Broad band due to Bonded O-H stretch	3421.6	3420.1	3456.7	3425.9	3439.4	3431.7	3422.1	3423.9	3422.0	
3000–2842	Asymmetric and symmetric C–H stretch in methyl and methylene groups	2921.6	2918.7	2918.9	---	2924.5	2919.7	2920.1	2934.1	2980.4 2942.8	
1740–1730	C=O stretch in ester groups of B-72	---	---	---	---	---	---	---	---	1726.9	
1635	Adsorbed water	---	1616.1	---	1626.6	1628.6	1627.6	1646.9	1628.6	---	
1605–1593	Aromatic skeletal vibrations plus C=O stretch	1599.6	---	1592.9	---	---	---	---	---	1599.6	
1515–1505		---	---	---	---	---	1509.9	1509.0	1509.9	1509.9	
1470–1455	CH ₂ of pyran ring symmetric scissoring, OH plane deformation vibration	---	---	---	---	---	1457.9	---	---	---	
1430–1416	CH ₂ scissoring	---	---	---	---	---	---	1419.3	---	---	
1375–1365	CH deformation vibration, aliphatic C–H stretch in CH ₃	1383.6	1386.6	1383.6	1384.6	1382.7	1383.6	1383.6	1384.6	1384.6	
1270–1266	guaiacyl ring structure in lignin and C–O stretching in xylan and hemicelluloses.	1266.0	1271.8	1264.1	1270.8	1257.3	1267.9	1268.9	1268.9	1268.9	
1230–1221	C–C plus C–O plus C=O stretch	---	---	---	---	---	---	---	1222.0	1220.7	
1162–1125	C–O–C asymmetric valence vibration	---	---	1162	---	---	1160.9	1138.7	1151.3	1145.5	
1140	Aromatic C–H in plane deformation	---	---	---	---	---	---	1138.7	---	---	
1060–1004	C–O valence vibration mainly from C ₃ -O ₃ H ₅ plus Calky-O ether vibrations	1024.9	1014.4	1014.3	---	1019.2	1020.1	1026.9	1031.7	1029.6	
1035–1030	Aromatic C–H in plane deformation, plus C–O deformation in primary alcohols; plus C=O stretch (unconj.)	---	---	---	---	---	---	---	1031.7	1029.6	
996–985	C–O valence vibration	---	---	---	991.2	---	---	---	---	---	
860–853	C–H out-of-plane	---	---	---	---	---	---	868.7	866.8	861.0	
800	Pyran vibration	792.6	---	787.7	---	---	---	775.2	768.5	---	
715	Rocking vibration CH ₂ in cellulose	---	754.0	754.0	699.0	---	697.1	702.9	---	---	
670	C–OH out-of-plane bending	691.3	688.4	697.1	671.1	---	672.0	670.1	---	653.7	

3.3. Effects of treatments after consolidation of samples

3.3.1. SEM investigations

SEM investigations were used to verify that the five chosen polymers actually penetrated the cell lumen and adhered to the cell walls. For comparison the SEM micrographs of sapwood sample before treatment, fig. (2-a) and after all five treatments, figs. (2-b, c, d, e, f) were grouped according to the direction of the

3.3.1.1. Longitudinal Direction:

PVAc and Paraloid B72 gave the most evident coverage of the wood cells in the longitudinal direction. An uneven ‘plastic’ layer of the polymer covered in both cases the wood cells. The tracheids and parenchyma which are totally covered with the polymer had been lined with a film hiding some of the anatomical features, such as the pits. This was most evident in the case of Paraloid B72, fig. (2-c). Methyl cellulose formed a very thin film in some parts of the cell wall, fig. (2-d), but like Paraloid B72 it hid some of the anatomical features of the cell wall. A ‘wavy surface’ is seen in all three cases; in the case of PVAc the distance between the ‘wavy lines’ is far smaller,

sections. The longitudinal direction showed clearly how the tracheid walls were covered with the polymer. The transverse direction gave an indication of how the polymer entered the wood via the cell lumen and helped in binding the cell walls together.

fig. (2-b) than in the case of Paraloid B72 and methyl cellulose. A possible explanation is that when water molecules diffuse into the adhesive layer of PVAc, they can act as a plasticiser and make the chains more flexible [6]. In the case of Paraloid B72, solvent type plays a major role in solution uptake and consolidant retention. Polar solvent mixtures tend to result in higher solution uptake and consolidant retention [21]. Methyl cellulose tends to remain on the surface for a few seconds before sinking in [18]. Funori and gum Arabic gave a totally different type of film, fig. (2-e, f). They both penetrated the wood and covered the cell walls, forming a

uniform, but blistered layer due to the absence of plasticizers. Both films cracked and blistered in the same

3.3.1.2. Transverse Direction:

In the transverse directions the cell walls are covered with a film of polymer, which has clearly thickened the cell walls and maintained their original shape in two of the five polymers. Cell walls seem to be intact after treatment with PVAc and Paraloid B72, fig. (2-b, c), but the thick PVAc film inside the cell wall is not uniform and the “wavy and uneven surfaces” are evident as in the longitudinal section. In

direction of the openings of the cupressoid type cross-field pits in the radial surface of the ray cells.

the case of methyl cellulose the secondary wall layers remain detached after treatment and the presence of the polymer cannot be easily monitored due to the minute thickness of the film, fig. (2-d). In the case of funori and gum Arabic, in addition to the cracked and blistered film, the cells are slightly deformed due to the contraction of the adhered film, fig. (2-e, f).

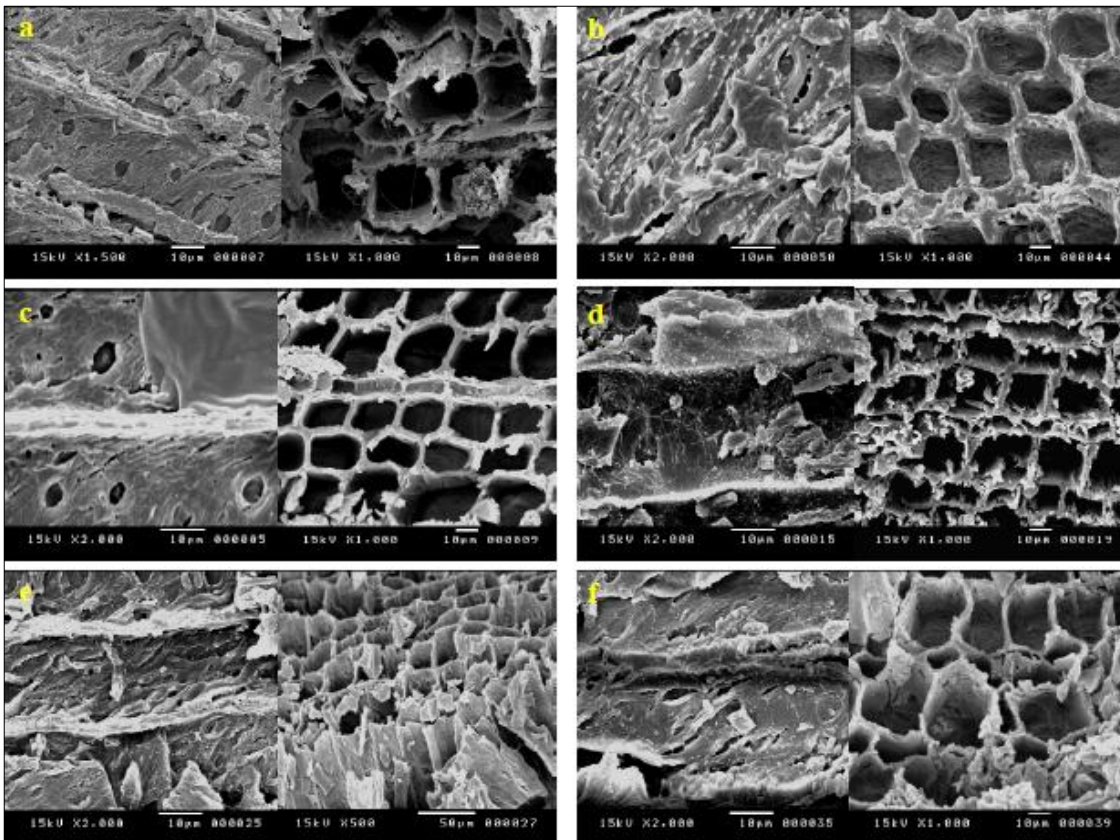


Figure (2) SEM micrographs of sapwood in longitudinal and transverse sections **a** before treatment showing fissures in cell walls, **b** after treatment with PVAc showing a wavy plastic layer on the cell walls, **c** after treatment with Paraloid B 72 showing uneven distribution of the polymer in the longitudinal direction, **d** after treatment with methyl cellulose showing uneven distribution of the film, **e** after treatment with funori showing a blistered film, **f** after treatment with gum Arabic showing cracks and blisters in the cell wall.

3.3.2. FTIR analysis

3.3.2.1. Applications of polymers diluted/dissolved in water

It is worthy to note that some of the changes recorded after treatment with the three polymers that were diluted or dissolved in water are due to the chemical effect of the polymer itself, and not the

water, although in some instances, especially the lignin band at 1595 and absorbed water at 1635 cm^{-1} , water may have strengthened the effect, tabs. (2 & 3), fig. (3). **a) Application of PVAc:**

Dilution of PVAc emulsion with water causes partial hydrolysis of acetyl groups to hydroxy groups. When applied to wood, the acetyl and hydroxy groups do not form covalent links to the components of wood. The interaction is through secondary forces [6]. Water molecules can easily penetrate into the wood/PVAc interface through the adhesive layer and through the wood. This is proven by the growth of a new band at 1628 cm^{-1} which is assigned to absorbed water in both sap and heartwood. The relatively weak links formed by the secondary forces between the chains of the polymer are easily broken by the intervention of water as well as the links between the polymer chains and wood. This appears clearly in shifting of the O-H stretching bands from 3411 cm^{-1} in the untreated sapwood, 3401 cm^{-1} in sapwood treated with water to 3431 cm^{-1} in the consolidated sapwood. While this shifting occurred in the case of heartwood from 3421 cm^{-1} to 3439 cm^{-1} . FTIR spectra show that PVAc has great influence on lignin degradation and carbohydrates. Bands corresponding to lignin at 1595 and 1510 cm^{-1} disappeared in both sap and heartwood after treatment. The band at 1385 cm^{-1} disappeared only in the case of sapwood

after treatment. **b) Application of Methyl Cellulose:** Application of methyl cellulose/water solution on sapwood gave good results. No remarkable changes occurred in the chemical bonds of all sapwood components. While in case of heartwood, many changes were observed: bonded O-H stretching band was shifted to a higher wave number, lignin band at 1595 cm^{-1} in heartwood disappeared, which could be due to the effect of water as previously noted, reappearance of lignin band at 1509 cm^{-1} was noted. **c) Application of Gum Arabic:** Due to the weak acidity of gum Arabic/water solution, C-H stretching bands of cellulose and hemicelluloses in sapwood at 2930 cm^{-1} were shifted to lower wave number at 2905 cm^{-1} proving the weakness of these bonds, whereas in heartwood the band was not shifted. Lignin band at 1595 cm^{-1} in sapwood also disappeared as a result of this acidity. In heartwood, immersion of wood samples in gum Arabic solution caused dissolution of some extractives surrounding lignin components. This may explain the absence of lignin band at 1509 cm^{-1} before treatment and its reappearance after treatment, on the contrary to sapwood.

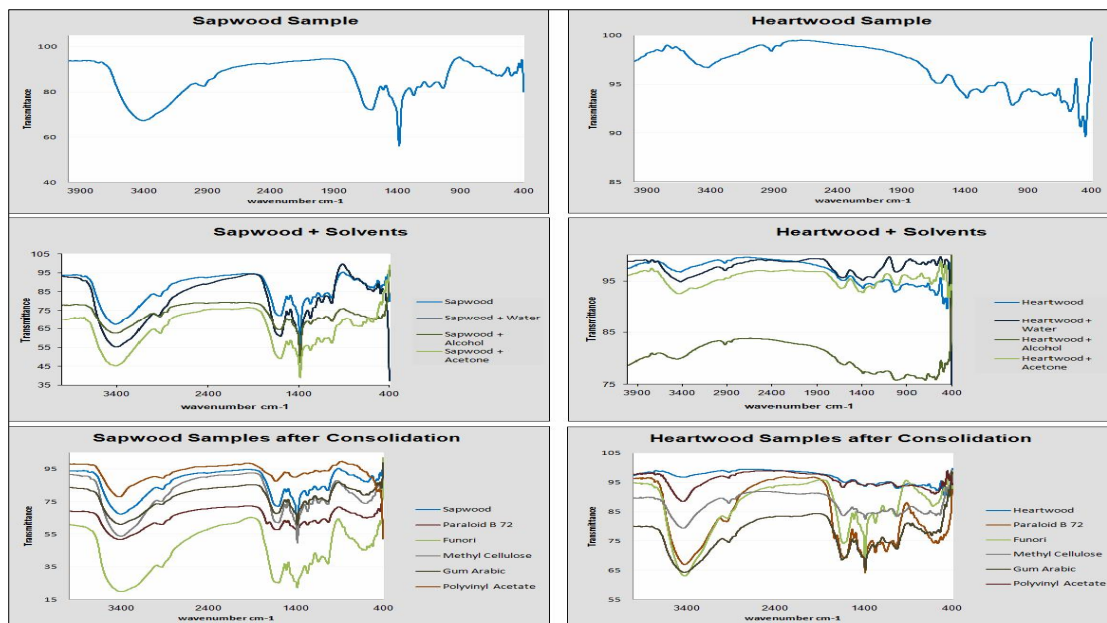


Figure (3) FTIR spectra of sapwood and heartwood samples before treatment, after treatment with different solvents separately; water, ethyl alcohol and acetone, after treatment with the five chosen polymers; Paraloid B72, Funori, Methyl Cellulose, Gum Arabic, Poly vinyl acetate.

3.3.2.2. Application of polymer dissolved in ethyl alcohol: 'Funori'

The efficiency of applying funori dissolved in ethanol to wood samples gave interesting results. The polarity of the solvent is compatible to wooden objects, which would mean higher solution uptake and consolidant retention. The FTIR spectra showed that the bonded O-H band at 3411 cm^{-1} in sapwood was broadened and shifted to a lower wave number, due to an increasing hydrogen bonding effect. While, no remarkable changes in this band were observed in heartwood. Water molecules were absorbed into the wood/funori interface giving a band of absorbed water at 1628

cm^{-1} . The band responsible for aromatic skeletal vibrations of lignin at 1595 cm^{-1} disappeared in heartwood indicating the degrading effect of funori/ethanol solution on lignin component. It is surprising to note that the C–O–C asymmetric valence vibration was present in sapwood prior treatment and after treatment with ethyl alcohol, but disappeared after treatment with funori. In heartwood this band was absent prior treatments only and reappeared after treatment with both ethyl alcohol and funori.

3.3.2.3. Application of polymers dissolved in acetone: 'Paraloid B 72'

The infrared spectra of both sap and heartwood samples treated with Paraloid B 72 resin remained almost unchanged except for C-H stretching at 2921 cm^{-1} in heartwood. This band was split and shifted to a higher wave number at 2980 and 2942 cm^{-1} . The interaction between polymer and wood is through secondary forces. Presence of a new band

at 1628 cm^{-1} in sapwood indicates absorption of water molecules, which also occurred after treating the heartwood with acetone. It is surprising to note though that effects of acetone on wood are not clearly evident after treating the wood with Paraloid B 72 that had been diluted in acetone.

4. Discussion

In trees the outermost wood layers that contain living cells are referred to as sapwood. Gradually the inner sapwood rings are eventually converted into heartwood, which does not contain living cells. It has been noted that during the conversion of sapwood into heartwood, extensive translocation of chemical compounds occurs. Secondary compounds tend to accumulate in heartwood, while storage products (starch), soluble sugars, amino-acids and mineral elements are removed from senescing sapwood rings [22]. Calcium is involved in lignin polymerization within the cell wall; low calcium content leads to lower lignin proportion [23]. A substantial proportion of Ca and Mg in wood is located in the cell wall either adsorbed on negatively charged exchange sites or incorporated in the form of pectates or in the lignin matrix. Ca and Mg are thus less mobile than N, P and K in the xylem [22]. The extremely high

increase in Ca in the heartwood sample may reflect accumulation of this element in the form of crystals or degradation of lignin leading to the exposure of calcium. SEM has been often used to monitor the changes that occur in wood prior or after conservation treatments, especially cleaning and consolidation. In a lot of research the even or uneven distribution of polymer or consolidant has been studied. In other cases the distribution of polymer inside the wood via longitudinal or cross section has been monitored [24]. SEM is a good tool that cannot be ignored in conservation, because it gives a relatively good idea of the treatments undergone, but it does not clearly indicate the chemical changes that may or may not occur during treatment process. FTIR is often used to characterize the analytical compositions of the compounds that occur at the different steps of wood decay of wooden beams, especially in the $1800\text{--}900\text{ cm}^{-1}$ region [25].

5. Conclusion

The fact that different polymers give different types of film and adhesive properties in wood is a well known fact. In general, the longer the molecule, the stronger the material [26]. There has been a lot of debate on the choice of polymers in conservation, but till this day most polymers are still in use. The main issue that has been overlooked in the past is that because wood is an inhomogeneous material polymers may react differently in the same block of wood that has aged naturally over the years and centuries. The effect of most materials used in treating wood starts right after its introduction into wood, before even being exposed to artificial ageing factors. As a preliminary study heartwood and sapwood samples were taken from the same wood block and treated with different materials. SEM, EDS and FTIR showed differences in cell composition between sapwood and heartwood, even before treating the wood. After consolidation SEM clearly showed how the polymer penetrated inside the cell and how the film that was formed appeared. In the interpretation of the FTIR spectra the effects of solvents were put into consideration, because solvents had different effects on both sapwood and heartwood. After treating both sapwood and heartwood with the same polymer differences were evident in several cases; PVAc affected both sapwood and heartwood, but in each case chemical reactions were different. Gum Arabic and funori affected mainly sapwood, but on the contrary methyl cellulose affected heartwood. Paraloid B 72 showed the least effects on either sapwood or heartwood. We can conclude from this preliminary study that it is necessary to specify the exact part and wood type from which the wood piece/pieces were taken in the past to form wooden artifacts, before actually attempting to consolidate the object.

References

- [1] El Hadidi, N., (2005). The Cheops boat–50 Years Later, in: Tampone, G. (Ed.) *Proceedings of Int. Conf. conservation of historic wooden structures*. Florence: Vol. 1, pp. 452-457.
- [2] Chapman, S. & Mason, D., (2001). Literature review: The use of Paraloid B72 as a surface consolidant for stained glass, *JAIC*, Vol. 42, pp. 381-392.
- [3] Favaro, M., Mendichi, R., Ossola, F., Simon, S., Tomasin, P. & Vigato, P., (2007). Evaluation of polymers for conservation treatments of outdoor exposed stone monuments. Part II: Photo-oxidative and salt-induced weathering of acrylic-silicone mixtures, *Polymer Degradation and Stability*, Vol. 92, pp. 335-351.
- [4] Podany, J., Garland, K., Freeman, W., & Rogers, J., (2001). Paraloid B 72 as a structural adhesive and as a barrier within structural adhesive bonds: Evaluations of strength and reversibility, *JAIC*, Vol. 40, pp. 15-33.
- [5] Schniewind, A. & Eastman, P., (1994). Consolidant distribution in deteriorated wood treated with soluble resins, *JAIC*, Vol. 33, pp. 247-255.
- [6] Qiao, L. & Easteal, A., (2001). Aspects of the performance of PVAc adhesives in wood joints, *Pigment & Resin Technology*, Vol. 30 (2), pp. 79-87.
- [7] Warson, H., (1972). *The applications of synthetic resin emulsions*, Ernest Benn Limited, London.
- [8] Jaffe, H., Rosenblum, F. & Daniels, W., (1990). Polyvinyl acetate emulsions for adhesives, in: Skeist, I. (Ed.), *Handbook of Adhesives*, Van Nostrand Reinhold, NY, pp. 387-91.
- [9] Nakhla, S., (1986). A comparative study of resins for the consolidation of wooden objects. *Studies in Conservation*, Vol. 31(1), pp. 38-44.
- [10] Yang, B., (1996). Composition and properties of polyvinyl acetate emulsion, *China Adhesives*, Vol. 6 (1), pp. 46-50.
- [11] Takano, R., Hayashi, K., Hara, S. & Hirase, S., (1995). Funoran from the red seaweed, *Gloiopeltis complanata*: polysaccharides with sulphated agarose structure and their precursor structure, *Carbohydrate Polymers*, Vol. 27, pp. 305-311.
- [12] Takano, R., Iwane-Sakata, H., Hayashi, K., Hara, S. & Hirase, S.,

- (1998). Concurrence of agaroid and carrageenan chains in funoran from the red seaweed *Gloiopeltis furcata* Post, et Ruprecht (Crytonemales Rhodophyta), *Carbohydrate Polymers*, Vol. 35, pp. 81-87.
- [13] Izumi, K., (1971). Chemical heterogeneity of anhydrogalactose containing polysaccharides from *Gloiopeltis furcata*, *Agricultural and Biological Chemistry*, Vol. 35, pp. 633-657.
- [14] Takagi, T., Asahi, M. & Itabashi, Y., (1985). Fatty acid composition of twelve algae from Japanese waters, *Yukagaku*, Vol. 34, pp. 1008-1012.
- [15] Hirase, S. & Watanabe K., (1971). Fractionation and structural investigation of funoran, in: Science Council of Japan. (Ed.), Proceedings of the 7th Int. seaweed symposium, Section IV, Sapporo, Japan, John Wiley & Sons., pp. 451-454.
- [16] Hirase, S., Araki, S. & Ito, T., (1958). Isolation of agarobiose derivative from the mucilage of *Gloiopeltis furcata*, *Bulletin of the Chemical Society of Japan*, Vol. 31, pp. 428-431.
- [17] Sanchez, C., Renard, D., Robert, P., Schmitt, C. & Lefebvre, J., (2002). Structure and rheological properties of acacia gum dispersions, *Food Hydrocolloids*, Vol. 16, pp. 257-267.
- [18] Rodgers, S., (1988). Consolidation/fixing/facing, in: Ash, N., Hamburg, D., Page, S., Bertalan, S., Kruth, L., van der Reyden, D., Craddock, A., Maynor, K., Rodgers, S, Dwan, A, Mickelson, M. & Vitale, T, (Eds.), Paper Conservation Catalog, AIC Book and Paper Group, 5th ed., Ch. 23, pp. 1-18
- [19] Schwanninger, M., Rodrigues, J.C., Pereira, H. & Hinterstoisser, B., (2004). Effects of short-time vibratory ball milling on the shape of FT-IR spectra of wood and cellulose, *Vibrational Spectroscopy*, Vol. 36, pp. 23-40
- [20] Horvath, A., (2006). Solubility of structurally complicated materials, *J. Phys. Chem. Ref. Data*, Vol. 35 (1), pp. 77-92
- [21] Tuduca, A., Timar, M., Câmpean, M., (2011). Studies upon penetration of Paraloid B72 into poplar wood by cold immersion treatments, *Bulletin of the Transilvania University of Braşov, Series II: Forestry, Wood Industry, Agricultural Food Engineering*, Vol. 4 (53) No. 1, pp. 81-88
- [22] Meerts, P., (2002). Mineral nutrient concentrations in sapwood and heartwood: a literature review, *Ann. For. Sci.*, Vol. 59, pp. 713-722.
- [23] Fromm, J., (2010). Wood formation of trees in relation to potassium and calcium nutrition, *Tree Physiology*, Vol. 30, pp.1140–1147.
- [24] Hamed, S., Ali, M., & El Hadidi, N., (2012). Using SEM in monitoring changes in archaeological wood: A review, in: Méndez-Vilas, A. (ed.), Current microscopy contributions to advances in science and technology. Microscopy Book Series, Badajoz: Formatex Research Center, Spain, pp. 1077- 1084.
- [25] Genestar, C. & Palou, J. (2006). SEM-FTIR spectroscopic evaluation of deterioration in an historic coffered ceiling, *Anal Bioanal Chem.*, Vol. 384, pp. 987-993
- [26] Horie, V. (2010). Materials for conservation: Organic consolidants, adhesives and coatings, 2nd ed., Butterworth-Heinemann, Oxford, UK