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EVALUATING THE EFFECTS OF COMMONLY USED CONSOLIDANTS ON ZIZIPHUS SPINA-CHRISTI WOOD

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Abstract:

Wooden artifacts, like all other objects made of organic materials are susceptible to deterioration, and have to be continuously monitored and treated during their exhibition. Prior to the recent opening of the Grand Egyptian Museum (GEM), all the artifacts that were chosen for display had to be retreated and prepared for mounting and exhibition. The most prominent attraction in the museum is the Tutankhamun collection, which has been subject to many years of treatment since the discovery of the tomb and during its exhibition at the Egyptian Museum in Tahrir (EMC). Over the years several polymers have been used to treat wood, such as Paraloid B72, Klucel G, Methyl Cellulose and Funori. Their application on decayed wood makes some of these polymers susceptible to microbiological decay, which means that there is a probability that the treated wood may degrade again after treatment, if not kept in a controlled museum environment. In this article the decay is evaluated on Ziziphus spina-christi wood treated with the four polymers over a period of 18 months. The results obtained from the light optical microscope, scanning electron microscope and Fourier Transform Infrared spectroscopy showed that the polymers were affected differently by fungi, and even the same polymer dissolved in different solvents did not give the same results.

1. Introduction

Wood is a natural material that can be attacked by biological growth such as fungi, bacteria and insects. The microbiological agents play a key role in wood degradation due to their enzymatic activity. Fungi and mold decompose and destroy wood, and although mold fungi may cause minor or no significant damage to the structural elements of wood, they have a detrimental effect on the appearance of wood [1]. Biological processes thus cause the degradation of wood components, and soft rot is one of the main causes of wood degradation, because these fungi withstand environmental conditions suitable for their growth and thus lead to large-scale wood degradation over long periods of time [2,3]. Old wooden pieces often bear evidence of biological or chemical degradation that seriously affects their structural construction reducing their mechanical resistance [4]. It has been stated in previous research that biological degradation caused by fungi depends on environmental conditions, especially high relative humidity, which is often a preferred condition for microbes [1,5-8]. Other inappropriate environmental conditions that affect wood include poor ventilation, coupled with poor maintenance, which leads to a severe change in wood properties, for example wood becomes soft, fragile and weak, and is therefore prone to fracturing or disintegration into powder or dust at minimum mechanical pressure. This is because biological attack in conjunction with frequent expansion and contraction as a result of relative humidity changes significantly and affects the structural integrity and cohesion of wood materials, reducing their mechanical strength. “Long-lasting” wood is usually protected by an environment that limits microbiological activity, and these special conditions may allow wood to survive without degradation for centuries or over long periods, but even in these environments some physical and chemical changes of wood occur because of biological degradation. Microbiological degradation is one of the most serious types of damage to wood, because fungi can degrade cellulose, hemicellulose and lignin. They also cause colored patches on the surface of the wooden artifacts which stain the surface. From previous studies it is possible to conclude how various degradation processes occur on wood and how they affect its chemical composition leading to changes in the physical and mechanical properties of degraded wood [3,7]. Old wood pieces often bear evidence of biological or chemical degradation that seriously affects their structural construction reducing mechanical resistance [4]. However, it has been stated, that fungi that grow on wood, paper, wallpaper, books and leather surfaces are unable to remove cellulose, lignin or hemicellulose in wood cell walls while these fungi consume simple sugars and starch found in ray and axial cells [9]. In addition, they produce large quantities of colored dyes and stains on wooden surfaces, that reduce wood quality and show the appearance of damage in it, yet do not affect the strength of wood [1,8]. *Trichoderma* sp. and *Alternaria* sp. are the most common fungi that grow on decomposed wood and produce many enzymes. A colony is considered ready for freshly cut timber; particularly pine wood has a sophisticated lignocellulytic enzymatic system [8]. *Aspergillus niger*, a common fungus that causes soft rot, is very often identified in archaeological wood samples made of native Egyptian hardwoods such as *Ficus sycomorus* [10,11] and *Ziziphus spina-christi* [12], and in imported coniferous types of wood such as *Cupressus sempervirens* [13]. In addition to this fungal species, *Fusarium oxysporum*, *Alternaria alternata*, and *Altenaria tenuis* were identified in both *Ziziphus spina-christi* and *Cupressus sempervierens* that had been treated with polymers such as Paraloid B72 in the 1950's of the last century [14]. Very often the wooden microbiologically infested artifacts are treated and retreated with polymers, as in the case of many artifacts from the collection of Tutankhamun since the discovery of the tomb over a hundred years ago [15,16]. *Ziziphus spina-christi* (L.) Desf./ sidder wood (Christ's Thorn Jujube, Rhamnaceae) was one of the original constituents of the wild flora of ancient Egypt with its various parts being used in medicine, diet, and rituals [17]. This type of wood like many other types with natural resistance to microbiological attack were often used in the past. It was extensively used throughout history in the joints of wooden artifacts, especially the wooden tongues and dowels, for its superior properties compared with other native wood types. It is characterized by its durability and resistance to warping, and it was used for making dowels and joints in various objects such as boats [12,18], large statues and coffins. In rare cases a complete coffin was made out of this type of wood [19]. In Tutankhamun's collection this type of wood was identified several times, especially in the shrines [20-22], and naos [23]. Recent pharmacological research undertaken suggests that sidder species possesses anti-inflammatory, hypoglycemic, hypotensive and anti-microbial effects. Gallocatechin and epigallocatechin are two of many other compounds that can be extracted from this tree. They have anti-inflammatory properties that were known to ancient Egyptians [24]. It has been demonstrated that the leaves and fruits' methanolic extracts have varying antifungal activity against *Aspergillus* sp [25], which was commonly identified in different types of wooden artifacts, as aforementioned. The extract-rich wood types resist biological attack [7], but even the most resistant timber is not totally immune from degradation. Therefore, due to the loss of wood integrity, archaeological wood consolidation has been one of the most important procedures particularly in the case of deteriorated artifacts. Consolidation or treatment with polymers is an essential step for preserving ancient historical wood and the process is intended to strengthen wood. Therefore, a polymer with sufficient physical, mechanical and durability properties must be introduced into the degraded wood structure to at least fill in the "excess porosity" resulting from degradation [4,5]. The idea of wood consolidation includes any procedures applied to stabilize parts damaged by either biological, mechanical or chemical degrading factors. The goal is usually to restore the original properties of wood [6] by introducing no more than exactly the necessary quantity needed of a polymer, in addition to strengthening the wood structure. However, some materials applied on wood may affect the dimensional stability of wood or encourage further microbial infestation. The problem of treating and strengthening weak and microbiologically damaged archaeological wood arises due to the difficulty of determining the optimal methodology for protecting these vulnerable objects. Many procedural treatments have been adapted and can be summarized in the following points: **1)** Strengthen wood and then inhibit microbiological damage. **2)** Resort to microbial treatment first and then strengthen weak wood after making sure that microbiological growth has been inhibited. **3)** Blend together consolidation and microbial treatments. Treatment materials and trends developed throughout the years, and properties of materials that were considered safe in the past have changed due to their degradation. Therefore, the aim of this experimental study is to examine wood samples that had been previously treated with some polymers that are commonly used in the treatment of archaeological wood in museums, namely Klucel G, Methyl Cellulose, Funori and Paraloid B72. It was decided to conduct this study on sidder wood samples that have been often identified in artifacts dating back to different eras in ancient Egypt, bearing in mind the fact that sidder wood extracts have antifungal properties.

2. Materials and Methods

2.1. *Wood samples (Experimental samples)*

Sidder wood/*Ziziphus spina-christi* was chosen for this experimental study for a couple of reasons. Firstly, because it is an extract rich wood that is not easily attacked by fungi, and secondly, because it was commonly used in joinery of wood panels. Samples were cut measuring 20×20×30 mm (radial, longitudinal, tangential, respectively).

2.2. *Consolidation materials*

Methylcellulose, Klucel G, Funori and Paraloid B72 are four commonly used polymers in the treatment of decayed wood [26-30]. These four polymers, which were selected for this study, were prepared by dissolving the first three polymers in either ethyl alcohol or distilled water, while the fourth polymer was dissolved in either toluene or acetone. Concentrations of the prepared polymers varied from one polymer to the other to obtain a low viscosity solution suitable for wood impregnation, tab. (1).

Table (1) polymers used for wood treatment

Polymer	Conc. %	Solvent	Abbreviation
Methylcellulose	1	Alcohol	MC/Alc
		Distilled water	MC/W
Klucel G	1	Alcohol	Klu/Alc
		Distilled water	Klu/W
Funori*	2	Alcohol	Fu/Alc
	2	Distilled water	Fu/W
Paraloid B72	3	Acetone	B72/AC
		Toluene	B72/T

***:** *Funori does not dissolve in alcohol, therefore it was first dissolved in water and diluted in alcohol to reach* 2% conc

2.3. *Simulating ageing conditions*

A data logger inside the wooden cupboard at the Egyptian Museum in Cairo (EMC), in which miniature tools from the collection of Tutankhamun had been kept for decades recorded a fluctuation in environmental conditions, with the relative humidity (RH) ranging from 35% to 58% and the temperature from 15 °C to 34 °C [31]. To simulate similar conditions, the samples under study were placed in locked boxes with a source of moisture, to enhance natural chemical and microbial decay, without performing any inoculation. Thirty milliliters of each dissolved polymer were poured into polystyrene Petri dishes, and the mixture was left to dry for several days in a well-ventilated room in order to form a film layer. Simultaneously eight sidder samples were treated by immersing each wood block in one of the aforementioned solutions for 5 minutes. The wood samples were left to dry under normal environmental conditions in the laboratory. All samples were kept in the aforementioned boxes in a laboratory at Cairo University for 18 months with similar conditions as the EMC. A preliminary microbiological investigation was conducted to determine the most prominent type of fungi that had attacked the wood treated with polymers during a period of 18 months. The sample treated with methyl cellulose dissolved in distilled water was chosen for investigation for this purpose, because from visual investigation it was the most badly infested sample. The sample was cultivated in a Petri dish of potato dextrose agar (PDA medium composed of 200 grams of potato starch, 20 grams of dextrose, 20 grams of agar and 1000 ml distilled water) and then sterilized at 121° C for 15 minutes. For a period of three to seven days of incubation at room temperature, the dishes were mainly investigated on a daily basis. *Aspergillus* sp., fig. (1) which is one of the most commonly identified species in archaeological samples in Egypt, was identified.

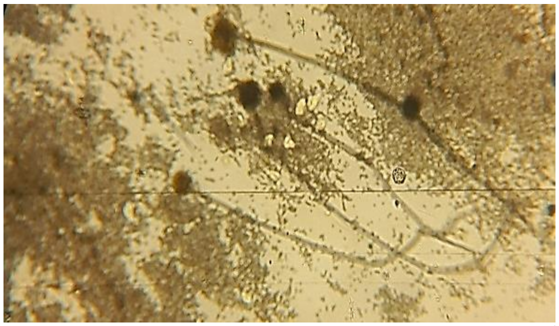


Figure (1) *Aspergillus niger* during preliminary investigation of samples

2.4. *Evaluation methods*

2.4.1. Digital and light microscopes

Noticeable color changes to the eye (visual characteristics), the growth of fungi on sidder wood samples and polymer films were examined using a digital microscope model: X4_500-1600X and light microscope model LABOMED: 400X.

2.4.2. Scanning electron microscope (SEM)

The surface of treated wood samples that had been infested with fungi were studied using a Quanta, FEG 250 SEM-EDX after gold sputtering using VAC coat DSR1

2.4.3. Measurement of color change

The changes in the color parameters L, a, and b were measured with a Mini Scan-EZ MSEZO693 Hunter lab colorimeter; **L** index of color represents black-to-white color, **a** index represents green-to-red color, and **b** index represents blue-to-yellow color. The overall change in color indices were calculated twice (ΔE after treatment with polymer and ΔE after fungal infestation of treated wood samples were compared to the measurements of the control sample), where **ΔL**, **Δa**, and **Δb** are the differences between the values of the color indices. The numerical values between 3 and 6 indicate a slight and noticeable color shift, values higher than 6 indicate a considerable and noticeable color change, whereas values less than 3 are not noticeable [10,32].

2.4.4. Fourier transform infrared spectroscopy analysis (FTIR)

FTIR was used for studying and comparing the effect of the chosen polymers on wood, in addition to observing changes and modifications that occurred in the wood after treatment [33]. The spectra of treated and untreated samples were recorded by means of FTIR spectroscopy which was carried out on a Nicolet 380 FT-IR Spectrometer, in the frequency range of 4000-400 cm^{-1} with resolution of 4 cm^{-1} in transmission mode using the KBr pellet technique at the National Institute for Standards (NIS) in Giza, Egypt. Peak heights and width of absorption bands were measured by essential FTIR software (version 310.041).

3. Results

3.1. *Digital, light and SEM*

Digital and light microscope of polymer films showed that *Cladosporium* sp. and *Aspergillus* sp. were identified in both films of methyl cellulose dissolved in water and alcohol, while *Aspergillus sp*. was identified in polymer films of Klucel G and Funori dissolved in water. In the case of Klucel G dissolved in alcohol, Paraloid B72 dissolved in toluene and acetone the mycelium is not visible in the film samples, figs. (2 & 3). Images taken by the digital microscope are in agreeance with the SEM micrographs of the polymer films and sidder wood samples treated with methyl cellulose, Klucel G, Funori, which were all dissolved in either water or alcohol. In both samples treated with methyl cellulose, and the samples treated with Klucel G and Funori dissolved in water, the presence of mycelium due to a fungal infestation and germinated spores is noticeable, yet in the cases of Klucel G and Funori dissolved in alcohol there were no traces of fungi, figs. (2-7). In the samples treated with Paraloid B72 coverage of the wood surface occurred displaying the smoothness of the polymer film containing shiny remnants and an irregular distribution of the polymer which was dissolved in toluene when compared with the polymer dissolved in acetone. It was difficult to compare the microscopic images of this polymer with the SEM micrographs, because of the film layer that covered the wood surface. In the microscopic images it was possible to notice that the films formed by the polymer dissolved in toluene and acetone, and the wood treated with polymer dissolved in acetone were not attacked by fungi, yet the wood treated the polymer dissolved in toluene was infested with fungi, figs. (3 & 7).

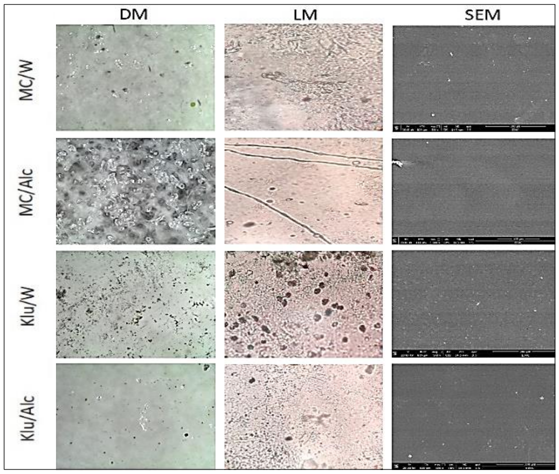


Figure (2) digital and light microscope images and SEM micrographs of polymer films. *Cladosporium* sp. and *Aspergillus sp*. were identified in both films of methyl cellulose dissolved in water and alcohol, and *Aspergillus sp*. was identified in polymer films of Klucel G dissolved in water. In the case of Klucel G dissolved in alcohol, the mycelium is not visible in the film samples.

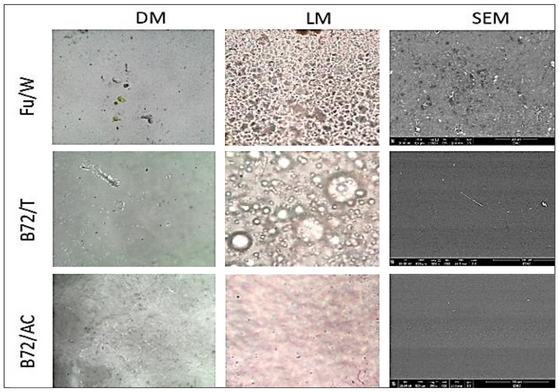


Figure (3) digital and light microscope images and SEM micrographs of polymer films. *Aspergillus sp*. was identified in polymer film of Funori dissolved in water. In the case of Paraloid B72 dissolved in toluene and acetone, the mycelium is not visible in the film samples.

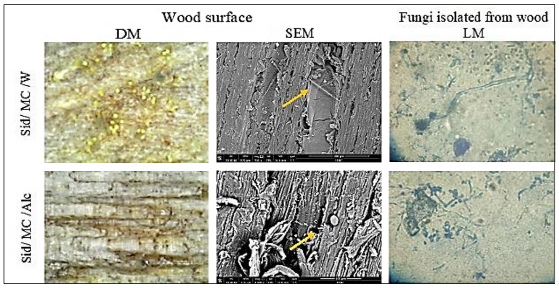


Figure (4) digital microscope images and SEM micrographs of samples treated with methyl cellulose, and light microscope images of fungi isolated from treated wood. *Cladosporium sp*. and *Aspergillus sp*. were identified in both wood samples treated with methyl cellulose dissolved in water and alcohol.

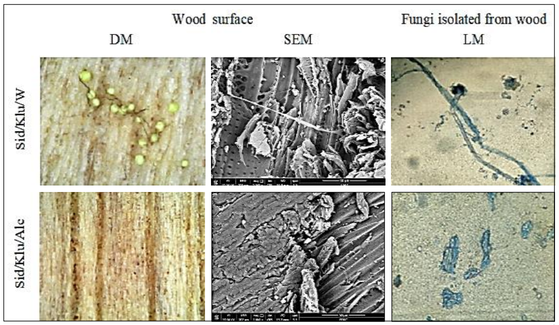


Figure (5) digital microscope images and SEM micrographs of samples treated with Klucel G, and light microscope images of fungi isolated from treated wood. *Aspergillus sp*. was identified in the wood sample treated with it, but in the case of the polymer dissolved in alcohol there was no infestation.

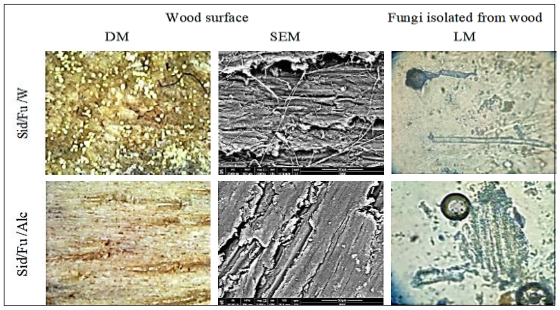


Figure (6) digital microscope images and SEM micrographs of samples treated with Funori, and light microscope images of fungi isolated from treated wood. In the case of Funori dissolved in water the treated wood was attacked by *Aspergillus sp*., whereas in the case of using alcohol for dissolving the polymer the treated wood was not attacked by fungi.

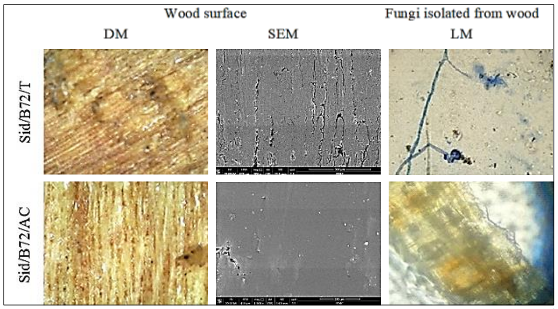


Figure (7) digital microscope images and SEM micrographs of samples treated with Paraloid B 72, and light microscope images of fungi isolated from treated wood. In the case of Paraloid B72 dissolved in toluene, the mycelium appears in a small proportion and is distorted in the wood sample, whereas in the case of the polymer dissolved in acetone the wood is free of fungi.

3.2. *Colorimetric measurements*

The color change results of the sidder samples, tab. (2) revealed that the majority of the samples showed a slight change in ΔE. This change was below 3 in the samples treated with Funori (dissolved in water and alcohol) and Klucel dissolved in water, while a value between 3 and 5 was measured in the rest of the samples. After 18 months of exposure to humidity and the slight infestation with fungi as previously mentioned in the microscopic investigation a decrease in the ΔE values was recorded, except for two samples, namely the one treated with Funori dissolved in alcohol, which became lighter in color, and the one treated with Paraloid dissolved in acetone, which darkened. These two samples showed no indication of a fungal infection during investigations; therefore, the changes could be either due to the effects of the polymer or the solvent.

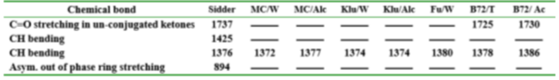
Table (2) colorimetric measurements and changes

Sample		L	A	B	EΔ
Sidder	Control	65.48	9.17	25.26	---
Sid/MC/W	After application	61.62	7.48	23.06	3.57
	After 18 months	63.40	7.48	22.53	2.38
Sid/MC/Alc	After application	60.58	7.47	21.50	4.59
	After 18 months	64.03	6.97	22.32	2.33
Sid/Klu/W	After application	67.42	8.31	26.54	1.94
	After 18 months	65.92	8.65	23.80	0.80
Sid/Klu/Alc	After application	69.69	7.21	26.00	3.83
	After 18 months	68.35	8.53	27.10	2.61
Sid/Fu/W	After application	67.78	7.64	28.05	2.87
	After 18 months	68.29	7.44	23.85	2.66
Sid/Fu/Alc	After application	67.95	7.02	24.33	2.65
	After 18 months	71.83	7.39	23.34	5.21
Sid/B72/T	After application	69.27	7.21	26.45	3.61
	After 18 months	68.07	9.08	26.38	2.17
Sid/B72/AC	After application	67.06	8.56	26.25	1.53
	After 18 months	55.48	13.73	30.34	9.36

3.3. *FTIR Analysis*

After 18 months of treatment the main wood components remained almost unchanged. This could be attributed to a number of factors, including the sidder wood's natural resistance to damage, the different types of solvent that may have helped reduce the fungal infestation, and the polymer coating and bulking of the wood cells. Only the two samples treated with Klucel G showed a noticeable change and increase in the OH stretching of cellulose. However, to understand the slight chemical changes that occurred in the wood treated with different polymers, it was necessary first to define the wavenumbers that the sidder wood samples and the polymers have in common. Table (3) shows that the CH bending band at around 1376 cm^{-1} was recorded in all polymer samples, while other weak bands were recorded in only some of the polymers. Consequently, these differences are clearly reflected in the lignin – carbohydrate ratio of the treated wood samples, especially the polymers that were dissolved in alcohol and acetone. For example, in the CH bending band at 1378 cm^{-1} of the treated samples there is a noticeable relative increase of carbohydrates when compared to lignin within the same sample.

Table (3) common wavenumbers in sidder wood and polymers



Chemical bond	Sidder	MC/W	MC/Alc	Klu/W	Klu/Alc	Fu/W	B72/T	B72/ Ac
C=O stretching in un-conjugated ketones	1737	——	——	——	——	——	1725	1730
CH bending	1425	——	——	——	——	——	——	——
CH bending	1376	1372	1377	1374	1374	1380	1378	1386
Asym. out of phase ring stretching	894	——	——	——	——	——	——	——

3.3.1. The effects of consolidants dissolved in different solvents

The chemical composition did not change significantly in the FTIR spectra of most of the treated samples, except for the intensities of some bands, fig. (8). The slight differences between the samples could be because of the different types of solvent used as well as the sidder extractives that may leach out due to the polymers' solvents during the impregnation process. The OH stretching broad band at around 3400 did not show significant change in most samples except for the sample treated with Klu/Alc, which became broader and the intensity decreased slightly, and the two samples treated with MC/Alc and Klu/W, which showed an increase in intensity, as in tab. (4) & fig. (9). Furthermore, the FTIR spectra of all the wood samples that had been affected by fungi (MC/W, MC/Alc, Klu/W, Fu/W and B72/T) showed a change in ratio between lignin and hemicellulose, except for the MC/W. Hemicellulose decreased in the case of MC/Alc, Klu/W and Fu/W, while a small increase was recorded in the case of the B72/T. In the sample treated with B72/Ac complete disappearance of the band at 1425 cm-1 was recorded, yet the FTIR spectra and the lignin/carbohydrate ratio indicate a clear increase of carbohydrate percentage at wavenumbers 1735 and 1375 cm^{-1}, tab. (5).

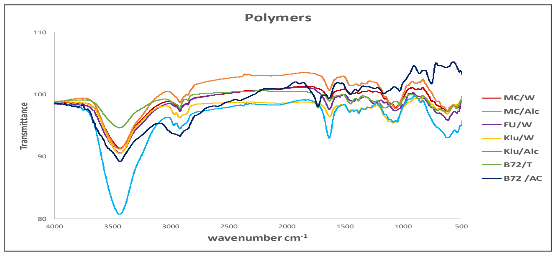


Figure (8) FTIR spectra in transmittance of methyl cellulose, Klucel G, Funori and Paraloid B72 in different solvents

Table (4) The main bands in sidder wood samples treated with polymers

Chemical bond	Sidder	MC /W	MC/Alc	Klu/W	Klu/Alc	Fu /W	Fu /Alc	B72/T	B72/Ac
Bands assigned to Hemicellulose and Cellulose in Wood									
C=O stretching in unconjugated ketones	1737	1731	1735	——	——	1733	1737	1735	1731
		Sharp & strong		——	——		Sharp & strong		
CH bending cell.	1425	1423	1423	1425	1423	1423	1425	1423	——
				Sharp & weak					——
CH bending cell.	1376	1375	1376	1375	1376	1375	1375	1373	1375
	Weak	Weaka sharp	Strong & sharp	Strong & wide			Strong & sharp		
Asym. out of phase ring stretching cell.	894	892	894	896	892	894	892	896	894
	Sharp & weak	Weak	Sharp & weak		Wide & weak		Sharp & weak		
Bands assigned to Lignin in Wood									
C=C stretching vibration in lignin aromatic skeletal	1510	1510	1508	1510	1510	1510	1508	1508	1510
				Strong & sharp					

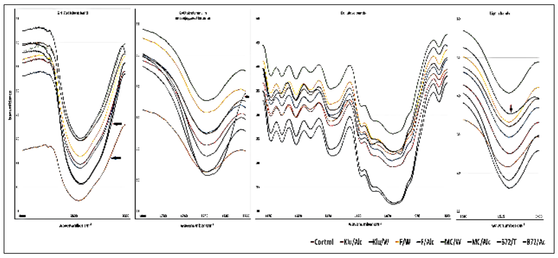


Figure (9) FTIR spectra in transmittance of sidder wood samples (control) and wood samples treated with methyl cellulose, Klucel G, Funori and Paraloid B72 after 18 months of treatment and exposure to humidity.

Table (5) showing how the ratio of lignin and carbohydrates in the treated sidder samples under study was affected by polymer treatment and fungal infection.

L/Carbohydrate	Sidder	MC /W	MC/Alc	Klu /W	Klu/Alc	Fu /W	Fu/ Alc	B72 /T	B72/AC
L/1735	1/1.2	1 / 1.13	1/ 0.47	1/ 0.42	1 /0.96	1 /0.85	1 /1.22	1 /1.39	1/8.9
L/1425	1/0.35	1 /0.40	1/ 0.53	1/ 0.44	1 /0.41	1 /0.40	1 /0.35	1 /0.38	1/ n.a.
L/1375	1/0.49	1 / 0.43	1 /0.61	1 /0.49	1 / 1.75	1 /0.57	1 /0.64	1 / 0.53	1/3.89
L/897	1/0.41	1 /0.32	1/0.36	1 0.47	1 /0.40	1 /0.40	1 /0.40	1/ 0.35	1 /0.31

3.3.1.1. *Polymers dissolved in water*

In all three cases a decrease occurred in the hemicellulose band at 1735, yet the highest decrease was in the Klu/W. In the MC/W and Fu/W, there was a clear decrease of C-O stretching intensity at (1000-1210) especially in the MC/W sample and a decrease was noticed in the C-O-C stretching and asymmetric out of phase ring stretching cellulose deformation at around 897. However, in the Klu/W sample, the C-O stretching band at (1000-1210), C-O-C stretching band at around 1163 and asymmetric out of phase ring stretching cellulose deformation at around 897 showed a slight increase in intensity.

3.3.1.2. *Polymers dissolved in ethyl alcohol*

The asymmetric out of phase ring stretching cellulose deformation at around 897 did not show any changes in all the samples treated with the polymers dissolved in alcohol, except for a slight decrease in the MC/Alc sample. In the MC/Alc sample the increase of intensities in the C-O stretching at (1000-1210) and C-O-C stretching at 1163 was also noticeable. In the case of the Fu/Alc samples the changes were similar to the Fu/W sample except for the slight increase in O-H stretching intensity at (3300-3450) due to the mixing of alcohol with water. In the Klu/Alc sample an increase occurred in the C=O stretching in unconjugated ketones at 1730 cm^{-1} and adsorbed water at 1643 cm^{-1} and a clear decrease in all the other bands. Which indicates the oxidation of cellulose and the formation of carboxylic acid.

3.3.1.3. *Paraloid dissolved in toluene and acetone*

In the B72/T sample, there was a broadening and slight decrease of intensity in (O-H) stretching in all the bands of cellulose, hemicellulose and lignin, while in the B72/AC sample, there was a decrease in all cellulose and hemicellulose bands and an extremely high increase in C=O stretching in unconjugated ketones at 1735 cm^{-1} which was the reflection of the oxidation of cellulose due to the high volatility of acetone and the increased band at 1735 cm^{-1} that might be due to the ability of acetone to degrade wood components specially lignin, which may have helped expose the carbohydrate bands.

4. Discussion

The microscopic investigation of the wood samples treated with methyl cellulose dissolved in either water or alcohol, Klucel and Funori dissolved in water and Paraloid B 72 dissolved in toluene had been affected by fungi. During investigation it was also noticed that the samples treated by polymers dissolved in ethanol were not affected in the same manner as the samples that were treated with the polymers dissolved in water. This results from the natural resistance of sidder extractives that were dissolved either by the alcohol or toluene in the polymer solution during the treatment process. These results are in agreeance with recent research, in which it was demonstrated that methanolic extracts from leaves and fruits have varying antifungal activity against *Aspergillus* sp. [25]. The results are also in agreeance with the findings of Nugari and Priori (1985) who noted that in the case of Paraloid B72 there was no significant weight loss in the polymer after inoculation. However, the fungal growth modified the polymers water affinity [34], and this was noticeable in the FTIR spectra of the OH stretching bands. However, these bands in the FTIR spectra of the sidder samples under study showed no changes, and the results here are not in agreeance with the aforementioned publication. In another experimental study by Li (2012) the results showed a high contamination in the 7% Paraloid B72 sample dissolved in acetone [35], on the contrary to the findings here, which showed no contamination in the acetone dissolved polymer and a contamination in the toluene dissolved polymer. An explanation for this could be that the acetone dissolved or released the wood extracts, which in turn work as antifungals, and thus prevent fungal infestation of the treated sample on the contrary to the sample treated with Paraloid dissolved in toluene. This was confirmed in a study on the effect of both acetone alone and Paraloid dissolved in acetone on *Cupressus sempervirens* samples, where it was noted that the acetone played a major role in causing changes to the main wood components, especially in the heartwood samples that contained a higher percentage of extractable materials [36]. None of the samples treated with MC/Alc, Klu/W, Fu/W and B72/T indicated a strong color change after 18 months of exposure to humidity, and the color change values further confirm the fact that slight whitening occurred in all of the wood samples, due to minute relative increase of carbohydrates, when compared to lignin. These results are a clear indication that the acetone dissolved the wood extracts and affected the crystalline cellulose, which in turn darkened the wood, but prevented the fungal infestation. However, as previously mentioned, the strong darkening of the sample treated with B72/Ac is not due to deterioration of all the wood carbohydrates.

5. Conclusion

Microorganisms quickly break down wood since it is an organic material, and fungi thrive in environments that are conducive to their growth, which causes extensive wood degradation over an extended period of time. The biodeterioration of wood treated with either natural or acrylic polymers is sometimes difficult to understand, because wood and polymers are susceptible to some form of biological attack when preventive measures in museums are not taken into consideration. In this experimental study a natural-resistant wood was chosen for evaluating the microbial susceptibility of wood treated with polymers dissolved in different solvents and exposed to humidity for 18 months. Results indicated that the fungal attack differed from one case to the other depending not only on the type of polymer, but also on the solvent. The FTIR results of the Klucel G treated samples showed a slight increase in OH stretching of cellulose which could be due to the hygroscopicity of Klucel which changed the water content. How-ever, there was no noticeable change in the chemical composition of the samples treated with either Klucel or Funori, even after the microbial attack. This may be due to the natural antifungals in sidder and their resistance to microbial attack. This preliminary study focused on the controlled natural aging in humid conditions of sidder wood, which contains natural extractives resistant to microbial decay. The results proved that the preservation of archaeological wood offers many challenges for researchers, because even if we are dealing with one type of wood, the microbial attack differed from one polymer to the other and from one solvent to the other, even when exposed to the same decay factors. Future examinations and analyses can be performed on samples of other wood types by using different aging methods including heat, moisture and light together to simulate open environments or museum environments in which many wooden artifacts can be found. Comparison between wood types that are less resistant to microbial decay would most probably give variable results not only due to the effect of the polymer and solvent, but also because of the higher possibility of fungal attack.

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