

Preparation of some Water Soluble Polymers for Consolidation of Archaeological Wood

تحضير بعض البوليمرات الذائبة في الماء لتقوية الأخشاب الأثرية

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المخلص العربي :

في مجال الحفاظ على مكونات التراث الثقافي تم استخدام البوليمرات على نطاق واسع لتعزيز وحماية القطع الأثرية ذات القيمة التاريخية والفنية واشتملت دراسات واسعة على عناصر متنوعة مصنوعة من مواد مختلفة مثل الأخشاب والأحجار الخ. لذا كان الهدف من هذه المقالة هو تحضير لبعض البوليمرات الذائبة في الماء وتقييمها طبقاً لخصائصها واستخدامها مقوية للأخشاب الأثرية. إثبات الشكل الهيكلي لهذه البوليمرات المختلفة بواسطة تقنيات متنوعة منها الأشعة تحت الحمراء وتقييم أثار العلاج للعينات المعالجة باستخدام العديد من التقنيات مثل قياس صلابة السطح والمسح الإلكتروني.

ABSTRACT:

In the preservation of cultural heritage items, the use of polymeric materials for the consolidation and protection of artifacts with historical and artistic value is widely accepted. This area is vast and includes studies of various objects made of different materials such as wood, stone, textiles, and paper. The aim of this article is the preparation and evaluation of some Water Soluble polymers according to its properties for consolidation of archaeological wood. Elucidation the structure of the synthesized polymers by using different spectroscopic techniques such as Fourier transforms infrared spectroscopy (FTIR). Evaluation of the performance characteristics of the treated specimens by several techniques such as scanning electron microscopy (SEM) and Surface hardness.

INTRODUCTION

Wood is the main renewable material on Earth and is largely used as building material and in paper-pulp manufacturing (1). Historic and archaeological woods are important cultural objects that provide valuable information about the past (2).

One of the most important aspects of the preservation of wooden artefacts is consolidation of decayed wood which,

in the majority of cases, shows structural decohesion. One of the most common and most frequently criticized restoration operations is the application of synthetic products which can penetrate into the wood and restore sufficient mechanical resistance. The choice of consolidating agent is essential to recover or try to improve the physico-mechanical characteristics of a wooden artefact, especially if it falls into the category of

characteristics of a wooden artefact, especially if it falls into the category of historical and artistic cultural heritage(3). Notwithstanding that many classes of polymer materials are actually used in the conservation and restoration of Cultural Heritage items, with more or less satisfactory results, few scientific data are available on their chemical constitution and composition, structure and properties(4). The decision for the choice of the optimum consolidation treatment encompasses a wide range of issues such as, the vast variety of available commercial products, different application techniques, compatibility and performance characteristics of consolidants, re-treat ability, along with general conservation ethics. Therefore, it is generally suggested that the evaluation of different consolidation treatments is an essential step in every project and should be based on the systematic monitoring of quantitative and objective properties of treated specimens(5).

The present study deals with the evaluation of different consolidation treatments in order to reinstate the cohesion of the weathered material, enhance the durability of treated wood. The present study was focused on behavioral characterization of the two products, on a series of wood samples of two tree species belonging to the broadleaf and conifer classes, that have been both widely used in history of art and found as archaeological wood (3) and studying their chemical-physical characteristics. Evaluation of the performance characteristics of the treated specimens by several techniques such as scanning electron microscopy (SEM) and Surface hardness.

2. Materials and methods

2.1. Conservation materials

The conservation materials used in this work are selected polymers as (urea formaldehyde sulfonate, melamine formaldehyde sulfonate) and wood species such as sycamore (softwood) and pitch pine wood.

2.2. Synthetic polymers

2.2. A. Preparation of urea formaldehyde sulfonate:

Two hundred sixty-two grams of 24% formalin solution were heated to 80 °c and the pH was adjusted to 10. One hundred ninety-eight grams of water and 40 gm of urea were added. After 20 min, 313 gm of a 20% sodium bisulfite solution were added and the mixture was stirred for 60 min. The pH was lowered to 3.0 and the mixture was heated for 120 min, then it was cooled and its pH was raised to 9.0(6).

2.2. B. Preparation of melamine formaldehyde sulfonate:

The procedure is divided in four steps as follows:

Step 1. A formalin solution of 18% concentration is prepared by dissolving 50.34 g m of 94.6% Para formaldehyde in 230 ml of water. The reaction mixture is heated at 50°C for 30 min after its pH is raised to 11.0 by adding 0.5 ml of 10N NaOH solution. After the solution becomes clear, 88 ml of water is added and it is heated at 50°C for an additional 15 min. Then, the pH of the solution is raised to 11.35 and 50g of melamine are added to it. Upon addition of melamine, it was noted that the temperature of the reaction mixture increases 4-5°C and then falls back to 50°C within 15 min, during which time the melamine dissolves completely by reacting with the formaldehyde. Sodium

metabisulfite (37.7g) and water (20 ml) are then added to the solution, causing an increase in temperature of 4-5°C while the sulfite salt is dissolving.

Step 2. The solution is kept at around 50°C for 5 min and then the temperature is raised to 80°C in 15 min and kept at the new temperature for 45 min; the same pH is maintained.

Step 3. The solution is then cooled rapidly (approximately 5 min) to 50°C and 12 ml of 14.5 N H₂SO₄ is added, causing a drop in pH to 3.50 and an increase in temperature of 4-5°C. The temperature drops back to 50°C within 15 min, and the solution is kept under these conditions with continuous stirring for 95 min, during which time it becomes very viscous. The solution is then neutralized by careful addition of slurry of calcium oxide (CaO) in water. The amount of CaO needed is approximately 8.0g.

Step 4. After neutralization, the solution is heated to 80°C in about 20 min and kept at that temperature for 60 min with continuous stirring. The solution is finally filtered to remove calcium sulfate and other solid particulates, cooled to room temperature, and treated with sodium hydroxide to adjust its pH to 9.5.

The solution prepared according to this procedure has a solid content of approximately 23% (determined by total water evaporation at 60°C). The solid content is adjusted to 20 % by adding water, and the final viscosity of the solution at 20°C is 4.20 Cp (7).

2.3. Wood species

The woods used for experimentation were sycamore (softwood) and pitch pine. They were chosen both for their historical use in wood artefacts especially in Egypt. The two woods have different mechanical behavior of

each wood species at two different concentrations

2.4. Application of products and aging procedures

Eight samples, measuring 3 cm×3cm×3 cm, of the two wood species were prepared and each consolidant was applied to two samples of each wood species at two different concentrations. Before the treatment with the polymers, The treated and untreated (control) wood samples were artificially thermally aged at 140°C in precision forced convection oven for 72 h according to **Kerretal** is equivalent to about 100 years of ageing under normal conditions. Measurements were carried out on the wood samples after the thermal treatment, aimed at reproducing a naturally aged wood, and after the application of polymers at different weathering times.

After full characterization for polymers, polymeric solutions were applied by brush up to complete imbibition on aged wood samples set horizontal. Treated samples were maintained horizontal at room temperature for 3 weeks to allow solvent evaporation and then kept at T= 40°C and RH = 60% until constant weight. The amount of applied polymer was determined by weight difference. Preliminarily, the quantity of absorbed product was evaluated using the following equations:

$$\Delta\% = (M_f - M_0 / M_0) \times 100$$

Where M₀ is the weight of the untreated stone (in grams) M_f is the weight of the wood after treatment (in grams).

Measurements were made at least 30 days after application. For each experiment, the averages of data obtained from each single sample of each series were calculated. In the double treatment, a 3% concentration of (UFS, MFS) was applied and also a 10% concentration of (UFS, MFS).

2.5. Characterization and experimental testing

2.5.1. FTIR spectra analysis

FTIR spectra were obtained with a Perkin Elmer spectrometer (Model Paragon 500) using 15 scans summation and equipped with a universal ATR, with range 450–4000 cm^{-1} and resolution 4 cm^{-1} was used to identify the molecular structure of polymers. The analysis was carried out on thin films obtained by grinding the polymers with potassium bromide (KBr).

2.5.2. Microanalysis of carbon, hydrogen, nitrogen, oxygen and sulfur

The elemental analysis of carbon, hydrogen, nitrogen, oxygen and sulfur were carried out using Perkin-Elmer 2408CHN analyzer at the micro analytical center, Cairo University, Giza, Egypt.

2.5.3 Performance test and structure characterization

2.5.3. a Surface Hardness test

The hardness of treated and untreated (control) wood samples were measured using a Wilbert Hardness tester HT2004 according to the DIN 53 456 standard.

2.5.3. b Scanning electron microscopy (SEM)

Scanning electron microscopy (gold coating, Edwards Sputter Coater, UK) was performed using a Jeol 6310 (Jeol Instruments, Tokyo, Japan) system running at 5-10keV.

3. Results and discussion

3.1. Molecular structure identification

3.1.1. Infrared spectroscopy

FTIR spectroscopy is a powerful tool for studying the physicochemical and conformational properties of polymers. In Fig.1 The spectra of the conventional and the innovative resins are almost identical and the peaks revealed could be

attributed to the characteristic functional groups of the resin such as C=O at 1639 cm^{-1} , C-N stretching band at 1181 cm^{-1} , the stretching band at 1408 cm^{-1} is related to stretching vibration of S=O, the band at 1036 cm^{-1} is due to ether linkage group (C—O—C) and the band at 1570 cm^{-1} is related to bending absorptions of >N-H. The most characteristic difference is at the spectral area 3700–3000 cm^{-1} . The sharpening and the shifting at 3361 cm^{-1} of this band indicate the formation of bonded NH group.

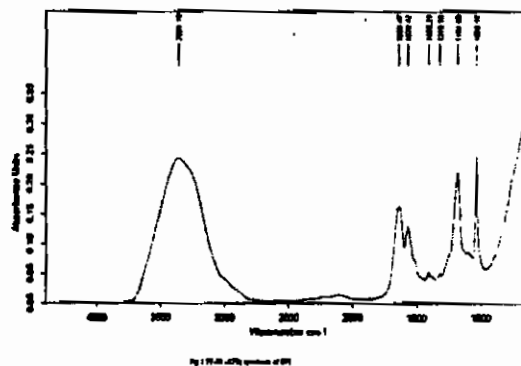


Fig.1 FT-IR (ATR) spectrum of UFS

In Fig. 2 The characteristic IR absorption bands of MFS are as follows : a broad band at 3334 cm^{-1} is attributed to N-H and O-H groups ; at 2987 cm^{-1} for stretching vibration of C-H groups . Three absorption bands at 880, 809 and 1549 cm^{-1} are related to melamine ring. The broad band at 1175 cm^{-1} is related to stretching vibration of S=O and the band at 1039 cm^{-1} is due to ether linkage group (C—O—C).

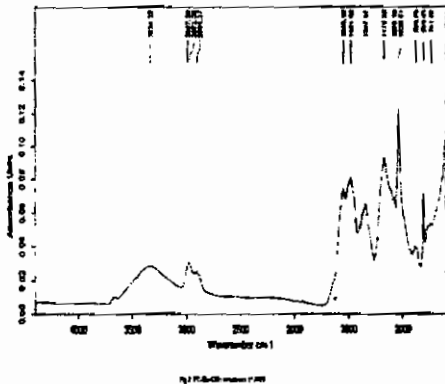


Fig.2 FT-IR (ATR) spectrum of MFS

3. 1.2. Elemental analysis

The results of elemental analysis of (UFS, MFS) are given in table 2. The data of elemental analysis of polymers are in agreement with molecular structure of polymers

Polymers	C%		H%		N%		O%		S%	
	Calc	Found	Calc	Found	Calc	Found	Calc	Found	Calc	Found
UFS	17.04	17.06	1.40	1.41	13.11	13.1	39.3	39.2	17.8	17.8
MFS	25.8	25.5	1.8	1.8	9.5	9.5	22.2	22.0	11.3	11.3

3. 2.Evaluation of consolidated wood samples

3.2.1. Scanning electron microscopy (SEM)

Fig. 3 shows the morphology of the untreated sycamore wood when zooming at 400 X , also describes the layers of wood fibers associated with the top of each other and describes the roots of the cells as illustrate some of the cells that contain the pits on their roots and there remains some parts of the cells.



Fig. 3 The morphology of the untreated sycamore wood

Fig.4 shows the morphology of the sycamore wood treated with UFS 3% when zooming at 400X and describes the spread of polymer within the wood fiber and polymer deposition on the roots of the cells as a thin layer of the association appear clearly on the wood fiber.



Fig. 4 The morphology of the sycamore wood treated with UFS 3%

Fig.5 shows the morphology of the sycamore wood treated with USF 5% when zooming at 400X and describes the spread and penetration of polymer within the wood fibers and deposition of well-illustrated article about the roots of polymer fibers and cells of wood, but irregularly and heavily.

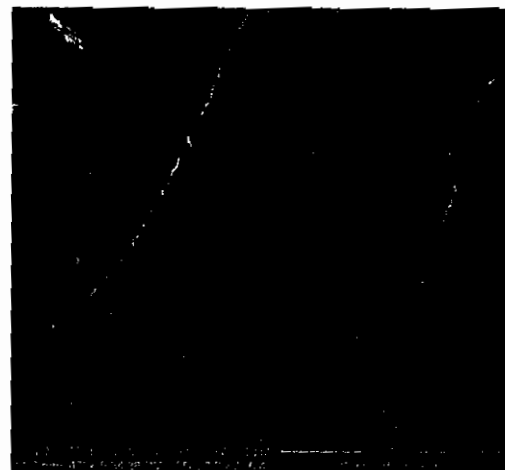


Fig.5 The morphology of the sycamore wood treated with USF 5%

Fig.6 shows the morphology of the horizontal section in sycamore wood treated with MFS 5% when zooming

at 400X and describes a wood fiber longitudinal and lateral deposition also shows a thin polymer layers on the fiber longitudinal and spin-off of wood as a polymer as a thick layer around the roots of the cells.



Fig.6 The morphology of the horizontal section in sycamore wood treated with MFS 5%

Fig. 7 shows the morphology of the cross- section in sycamore wood treated with MFS 3% when zooming at 400X and describes a wood fiber longitudinal and lateral deposition also shows a thin polymer layers on the fiber longitudinal and spin-off of wood a thin layer polymer around the roots of the cells.



Fig.7 The morphology of the cross- section in sycamore wood treated with mfs3%

Fig. 8 shows the morphology of the sample of untreated pitch pine wood with zooming at 300X which describes

the cells of wood, longitudinal and horizontal fibers and pits in the cells which are clearly appeared in the figure.

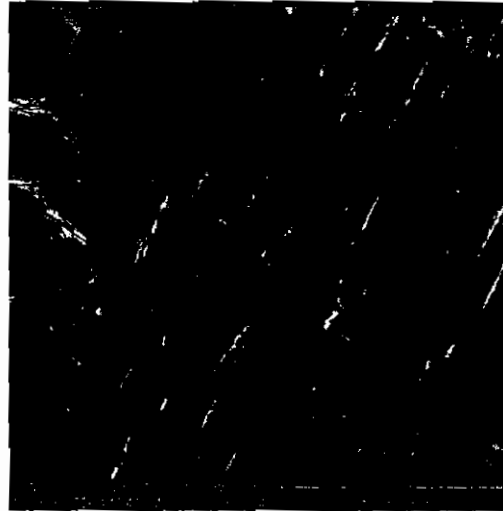


Fig. 8 The morphology of the sample of untreated pitch pine wood

Fig. 9 shows the morphology of the longitudinal sector in pitch pine wood sample treated with UFS 3% when zooming at 400 X describe high penetration and deposition of polymer and formation of a thin polymer layer on the root of the longitudinal fibers of the wood.



Fig. 9 The morphology of the longitudinal sector in pitch pine wood sample treated with UFS3%

Fig. 10 shows the morphology of the longitudinal sector in pitch pine wood sample treated with UFS 5% when zooming at 400X which describes the spread and deposition of high-polymer

as a thick layer of polymer on the root of the longitudinal fibers.

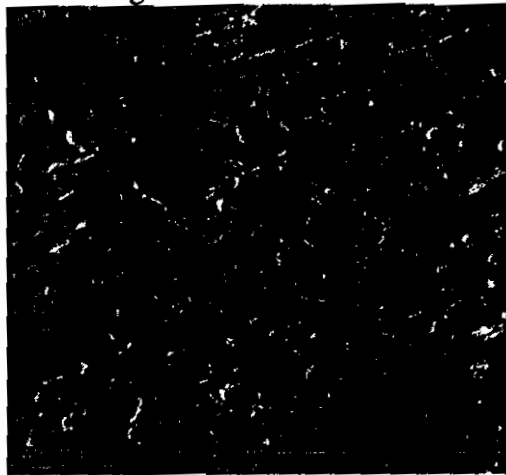


Fig.10 The morphology of the longitudinal sector in pitch pine wood sample treated with UFS 5%

Fig. 11 shows the morphology of the Cross-section in pitch pine wood sample treated with MFS 3 % when zooming at 400X and describes the spread of polymer within the wood fiber and polymer deposition as a thin layer appear clearly on the wood fiber without blocking the cells.

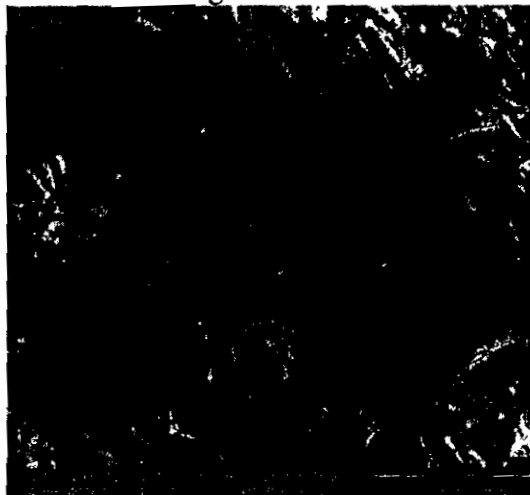


Fig. 11 The morphology of the Cross-section in pitch pine wood sample treated with MFS 3 %

Fig. 12 shows the morphology of the longitudinal sector in pitch pine wood sample treated with MFS 5% when zooming at 800X describes a wood fiber longitudinal and lateral deposition also shows a thin polymer layers on the fiber longitudinal and

spin-off of wood as a polymer as a thick layer around the roots of the cells.



Fig. 12 The morphology of the longitudinal sector in pitch pine wood sample treated with MFS 5%

3. 2. 2. Surface hardness

The results of the surface hardness measurements are summarized in table2 at the same weight 13.5kp. It is observed from the hardness given in table (2) that the hardness increases with increasing the concentration of consolidating polymers (UFS, MFS). Also in the case of pitch pine wood samples , It is observed that the hardness in case of 3% concentration of polymer increased in the following order MFS>UFS and in case of 5 % concentration of polymer increased in the following order MFS>UFS .On the other hand , also in the case of Sycamore wood samples , It is observed that the hardness in case of 3% concentration of polymer increased in the following order MFS>UFS and in case of 5 % concentration of polymer increased in the following order MFS>UFS. So a distinct increase of the surface hardness was observed due to the melamine treatment and the hardness of melamine. It is observed that the treated samples give the hardness above the untreated samples. The applied melamine treatment lead to

significant increases of surface hardness (table 2) as already reported.

table2. The measurements of Surface hardness for wood samples

Samples of wood	Control wood (untreated sample)	The concentrations of UFS		The concentrations of MFS	
		UFS 3%	UFS 5%	MFS 3%	MFS 5%
Sycamore wood	2.94 kg/mm ²	3.34 kg/mm ²	3.28 kg/mm ²	3.42 kg/mm ²	4.33 kg/mm ²
High Pine wood	3.79 kg/mm ²	4.56 kg/mm ²	5.28 kg/mm ²	4.97 kg/mm ²	5.91 kg/mm ²

4 Conclusion

In conclusion, the treatment of wood with urea formaldehyde sulfonat and melamine formaldehyde sulfonat is a possible mean to protect and consolidate wood against deterioration especially if it falls into the category of historical and artistic cultural heritage(4). A good penetration of the resin into the wood cell wall is the precondition for efficient treatment. The increase in hardness due to melamine treatment was well preserved after simulated long term weathering because of melamine formaldehyde sulfonate was given good penetration than urea formaldehyde sulfonate into the wood cell wall(8). In spite of Urea is rather inexpensive compared with melamine. Formaldehyde also is relatively inexpensive, and thus, together, they give a resin of low cost but nevertheless high performance (9). Since the sulphonated groups play a major role in solubilizing melamine-formaldehyde resins, both by ionic character and their ability to block bridging sites, namely, the N-methylol groups, they are expected to strongly influence the properties of the prepared resins (10).

The treated samples also showed advantages compared to untreated reference samples.

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