Using SEM in monitoring changes in archaeological wood: A review

Safa A. M. Hamed*, Mona F. Ali, Nesrin M. N. El Hadidi

Conservation Department, Faculty of Archaeology, Cairo University.

* Corresponding author, E-mail: safu_an78@yahoo.com, safyhamed15@yahoo.com.

This paper focuses on the role of scanning electron microscope in understanding and assessing the changes in the anatomical structure of archaeological wood caused by deterioration agents and treatment procedures. Scanning electron microscopy is considered an important tool for observing the structural changes in degraded wood tissues at the level of cell wall, evaluating their damage, and identifying the causal agent of decay patterns. Additionally, it is very helpful in the assessment of materials and methods used in treatment of archaeological wood, especially during cleaning and consolidation processes which have different effects on the wood structure. Such valuable information helps in developing appropriate procedures for conserving wooden artifacts. Although the data obtained from SEM examination illustrates the morphological and structural changes of the wood, it sometimes provides an indication to the changes in its chemical composition. Therefore, investigations based on SEM examination seek to determine the condition of archaeological wood.

Key words: SEM, Archaeological wood, Deterioration, and Treatment.

1. Introduction:

Methods for characterizing surface properties of wood may be divided into three broad categories: microscopic, spectroscopic, and thermodynamic. Microscopic methods provide information about surface morphology; spectroscopic methods provide information about its chemistry; and thermodynamic methods provide information about the surface energy. Many types of microscopic methods are available for characterizing the physical properties of various material surfaces, but only a few have been particularly useful for characterizing the physical properties of wood surfaces such as scanning electron microscopy (SEM) (1). The SEM technique proved to be highly considered in its application to Cultural Heritage in general and in archaeological wood in particular since information on the unique features associated with different types of decayed wood are important to plan appropriate conservation procedures, and to select or develop special consolidation procedures or other treatments for each decay case (2).

One of the latest developments in electron microscopy is the environmental scanning electron microscope (ESEM), which enables soft, moist or electrically insulating materials to be viewed without pre-treatment, unlike conventional scanning electron microscopy, in which specimens must be solid, dry and usually electrically conductive (3). In conservation science, it is often necessary to preserve the specimens intact or in their natural state (4). Therefore, a study using the ESEM technique was performed on wood objects in order to assess the particular advantages, possibilities, and limitations of this microscopic tool. In contrast to conventional high vacuum SEM, in ESEM specimens can be investigated in a gaseous atmosphere, usually of water vapour. This enables the observation of wood in its natural state, without drying, evacuating, or sputtering them with a layer of carbon or metal (5). The comparison of ESEM micrographs with conventional SEM images revealed specific advantages and shortcomings of the ESEM technique in studies on different types of wood objects, such as finished or unfinished wood surfaces and polychrome wood. Merits of the application of ESEM technique for wood are related to the absence of preparation of the sample, such as sputtering irregularities or defects due to shrinkage in vacuum drying. The wood imaging using ESEM proved inferior to that of conventional SEM in terms of lower magnification, sharpness, and contrast (6).

Since no preparative technique is used which would interfere with the surface of the weathered wood and due to the deep three-dimensional change in the structure, the scanning electron microscope was found to be the ideal instrument for the study of the structure of weathered wood at both high and low magnification with excellent resolution of detail (7). Electron microscopy techniques (high vacuum scanning electron microscopy and environmental scanning electron microscopy) have been successfully employed in analysis of weathered wood. Observation of the effects that the photo-induced degradation may have on ultra structural and structural integrity of wood surface help in understanding the degradation process (8). Furthermore, the use of the scanning electron microscope for the study of the structure of wood under stress and the mechanism of its cohesive failure can supply information which seems to be unobtainable by any other method (9). In addition to SEM and ESEM, scanning electron microscopy–energy dispersive spectroscopy (SEM-EDS) have proven to give a lot of information not only about the morphological changes of archaeological wood, but also about the elemental composition of the different layers that were used to cover and decorate wood in the past.
2. Changes in archaeological wood due to deterioration:

Archaeological and historic wood are subjected to different types of decay resulting in distinct changes within the anatomical structure of wood. The morphological degradation patterns can be used to determine the type of decay and the causing agent (11). Decay can be closely studied and documented prior to treatment procedures. Often SEM is used to monitor these changes, which reveal and explain important facts (12, 13, 14, 15, 16, 17). A recent study, for example, revealed that spring wood is more susceptible to damage than autumn wood in different wood species which can be explained by the fact that cells in spring wood have thinner and weaker walls than those in autumn wood (16).

2.1. Physicochemical deterioration:

There are limited numbers of studies that investigated the effect of aging on the structure of archaeological wood. Dry wood in historical buildings, in panel paintings, and in sculptures often shows fine cracks under the microscope (18), and in the case of decayed archaeological objects a weakened ultrastructure, especially in the area of the middle lamella has been observed. Also, in the secondary wall, a recognizable separation between lamellae can occur (19). In spite of the breakdown of certain elements in wood at ultra structural level due to aging, the samples sometimes retained almost their normal macroscopic appearance and properties. As long as the main reinforcing structural elements, the microfibrils, remain intact, the major properties of wood do not apparently undergo drastic changes (20). Foreign deposits due to either the deterioration of the old wood finishes and varnishes or the erosion of solid particles are commonly seen scattered around the wood elements of samples taken from wooden parts exposed to natural weathering (14).

Kollmann and Sachs (21) found comparable features in spruce after thermal treatment between 190°C and 240°C. The authors noted that lignin had been found to soften under elevated temperature in the presence of moisture and pressure. SEM studies of the anatomical microstructure, the pits and pit membranes, were performed on heat-treated as well as on untreated wood. The results revealed damage in heat-treated and dried pine sapwood mainly in pit membranes in the fenestroid crossfield pits connecting longitudinal tracheids with radial ray parenchyma cells. This damage is believed to play an important role in explaining the differences in water absorption between pine and spruce, since the piceoid crossfield pits in spruce seemed to be unaffected by heat treatment. In comparing the three different treatment temperatures in birch, no striking, visible differences were found that could shed light on the observed large differences in capillary water absorption (22). On the contrary, Boonstra et al. (23) investigated completely heat treated wood using SEM and mainly focused on the cross sectional and the radial sectional level of wood. They concluded that heat treatment did have an effect on the anatomical structure of wood, although this depends on the wood species and on the process method and conditions used.

Several publications describe microscopic changes caused by artificial and natural weathering (UV irradiation) of wood surfaces. Miniutti (24) reported changes in softwood surfaces after outdoor exposure. The first sign of deterioration was the enlargement of apertures of bordered pits in radial walls of earlywood tracheids. That was followed by the occurrence of microchecks, which enlarged principally as a result of contraction in cell walls. During weathering, the leaching and plasticizing effects of water apparently facilitated enlargement of the microchecks. Borgin (7) used the scanning electron microscope to study the changes in the structure and ultrastructure of wood exposed to natural weathering for several hundred years. The result revealed in detail the mechanism of the structural breakdown, and illustrated the gradual, very slow deterioration and ultimate destruction of the middle lamella, the various cell-wall layers, the separation of fibers and bundles of microfibrils from the surface and the enlargement of bordered pits and other pores. It also showed that these processes were confined to the surface layer (2-3 mm) and that most cell walls on exposed transverse surfaces are separated at the middle lamella region, apparently because of the degradation of lignin. However, tangential surfaces were quite resistant to UV light, compared to transverse and radial surfaces. Only microchecks were observed at the tangential cell walls (25).

In other studies, Hon and Feist (26) investigated the erosion of four hardwood surfaces that were exposed to outdoor weathering and to artificial ultraviolet (UV) light. SEM micrographs showed that all wood species exhibited surface deterioration after 30 days exposure to sunlight or 500 hrs to UV light. Loss of middle lamella, separation of procumbent cells, and damage of pit structures were observed on transverse sections for all species. On the other hand, Kučera and Sell (27) studied the erosion of the large rays in European beech in tangential surfaces exposed to natural weathering. The authors observed a differential shrinkage of the ray compared to normal wood tissue, partially combined with the photochemical degradation of the wood substance. Kuo and Hu (28) tracked UV radiation-peak at 254 nm which induced degradation of red pine (Pinus resinosa Ait.) for 3 to 40 days and showed the progressive degradation from the corners of the middle lamella to the cell wall. According to Turkulin (8), the most evident early structural sign of photodegradation on softwood surfaces is the damage of bordered pits. Only 4 days of natural exposure or 10 hours of exposure to fluorescent UV lamps cause the distinctive cracks of the torus, especially on aspirated pits. Longer exposures cause the pit domes to crack in diagonal progression, following the microfibril orientation in the domes. Eventually the widening of the aperture, thinning of the pit dome and complete destruction of the pit membrane mark advanced stages of weathering degradation. Simple pits do not disintegrate as fast as bordered...
pits. The evidence of fungal infection can be found after only 4 days of natural exposure, indicating that the growth of microorganisms begins by deposit of their spores into the microcracks. The general structural damage that could be seen on characteristic anatomical features is cracks on bordered pits, cross-field pits, surfaces of the lumina. William (29) emphasized that weathering causes two types of microscopic effects: destruction of middle lamella in both softwoods and hardwoods which support the premise that the lignin is the photosensitive component in wood; and the destruction of bordered pits and checking of cell wall in wood structure.

Owen et al. (30) revealed that degradation caused by the full weathering process, comprising both water and UV light, is considerably more rapid and more extensive than exposure to any parameter individually. SEM data, however, show that water has a deleterious effect on the physical characteristics of the surface. The swelling effect of water on wood, however, was detected clearly by SEM but not by infrared spectroscopy. Moreover, Park et al. (31) did a study using pH 2 sulfuric acid on hinoki wood (Chamaecyparis obtusa Endl) to investigate the acid effects on the weathering and evaluated the degradation using SEM. Acid-treated specimens had 1.5 times more degradation of the middle lamella and cell walls than specimens treated with water.

Iron or other metal corrosion products can weaken wood and cause significant cell wall alterations. Metal ions are active catalysts promoting chemical reactions that initiate a non-biological type of cell wall degradation. Moisture and soluble chlorides accelerate the corrosion process and the deterioration of wood. In certain circumstances, metal corrosion not only causes extensive cell wall degradation but produces iron or other metal pseudomorphs that display a replica of the woody cell wall (11). Remains similar to wood in superficial appearance are sometimes observed on the surfaces of corroded iron objects from archaeological deposits. Examination of this material with a scanning electron microscope suggests that deposition of iron corrosion products has occurred within the cell spaces. Subsequently the wood may have decomposed, leaving behind internal cell casts which mirror the original structure (32). According to Kepax (33), three types of wood replacement with iron corrosion products can be seen under SEM: negative impressions (casting), replaced wood, and double deposition.

Unfortunately, little is known about the non-biological degradative processes that take place when wood surfaces are in contact with alkaline substances for thousands of years. Surface deterioration has been found in wood that was in contact with potash for 40 years. The degradation caused a delamination of wood cells and a general dissolution of lignin. The cells appeared partially swollen and sustained cracks and fissures within the secondary wall. Potassium chloride crystals were deposited on surfaces between cells and within cell walls. In areas where potassium chloride crystals accumulated, a total hydrolysis of wall material was evident. A similar type of deterioration has been reported previously where alkali substances were in contact with wood for several years within a historic building (11).

2-2. Mechanical Deterioration:
Using SEM, Borgin (9) studied the mechanism of fracture and cohesive failure of the structure of wood and gave the following results: cohesive failure when the wood was exposed to shear along the grain and tension across the grain, showed clearly that the weakest part of the ultrastructure of wood under such conditions was the bonds between parallel strands of microfibrils which were pulled out with little resistance from the matrix. However, the adhesion between the middle lamella and the cell wall or the middle lamella itself failed when the wood was exposed to cleavage parallel to the grain. Loads and stresses caused mechanical damage to the wood cell walls where separations within the secondary walls and fractures in middle lamellae can be observed especially in the large wooden objects and structural wooden elements (11). In cases where weak wood is exposed to heavy loads the cell walls collapse (34).

Internal stresses caused by expansion or contraction of wood due to gain or loss of moisture can be obvious while studying samples using SEM. The cells take the same curvature as that of the warped wood (14).

2-3. Biological Deterioration:
Several types of biodegradation have been recognized in wood, e.g. fungal decay, bacterial degradation and insect attack, but the greatest damage results from the fungal action.

2-3-1. Fungal Decay:
The ability of rot fungi to degrade wood varies among fungal species and depends on the chemical properties of wood and on its structural features. Wood decay is initiated by fungal enzymes, acting on the cell wall components of the wood. Although most of the wood-rotting fungi are able to degrade both cellulose and lignin, they exhibit different degradation rates for these substances. The growth characteristics of the microorganisms in wood and the type of degrading system produce different decay patterns. Depending on the type of decay, different physical, chemical and morphological changes occur in wood. According to the macroscopic differences of their substrate utilization, wood rotters are classified into three specific decay groups: white rot, brown rot, and soft rot fungi. (2, 35).

Certain ascomycetes fungi can cause soft attack on wood. These fungi are widespread in nature causing deterioration of wood in aquatic and a range of terrestrial environments. Soft-rot fungi show preference for cellulose and hemicellulose, and they do not appear to degrade lignin within the middle lamella. These fungi can be distinguished...
from other decaying fungi by the decay patterns they produce. Some soft-rot fungi produce cavities within the secondary walls of wood cells following the microfibrillar orientation of cellulose that changes in different layers of cell walls (Type I attack), while others may erode the secondary wall completely (Type II attack) leaving a relatively intact middle lamella. (2, 36, 37, 38, 39, 40, 41, 42). Soft-rot is more common in hardwood than in softwood. It has been suggested that the reason for this is the quality differences in the lignin of hard- and softwood. The methoxyl content of lignin in hardwood is usually higher than in softwood. However, few researches were conducted to study and evaluate the changes in the structure of wood degraded by soft-rot fungi (35, 43, 44, 45).

Brown-rot fungi are basidiomycetes that degrade polysaccharides by extensive depolymerization. In brown rot, the fungi cause the characteristic wavy appearance due to the lack of strength, particularly visible in the transverse section but also seen in longitudinal ones. The same group is distinguished by forming cubical cracks in the wood. In some advanced stages of decay, the cell walls begin to have a porous aspect as polysaccharides are extensively removed. Some of the brown-rot fungi also decompose lignin that may result in the destruction or an extremely fragile middle lamella that appears degraded. (2, 12, 14, 38, 39, 42, 46, 47).

White-rot in wood results from degradation by basidiomycetes and by certain ascomycetes that have the capacity to remove all cell wall components. The common feature of all these fungi is that they can degrade lignin as well as cellulose and hemicelluloses. However, the relative rates of decomposition of lignin and cellulose vary greatly according to the species of fungi and the conditions within the wood. White rot is subdivided into simultaneous rot and selective delignification. In selective delignification, lignin is degraded earlier in the decay process than cellulose or hemicellulose. The hyphae grow on the cell wall. The enzymes that they secrete are able to decompose all substances of the lignified cell wall. The decomposition takes place close to the hyphae involved, and results in the formation of erosion troughs where they grow on the cell wall. The enzymes that they secrete are able to decompose all substances of the lignified cell wall. The coalescence of the erosion troughs induced by numerous hyphae results in a general cell wall thinning from the lumen onwards. (38, 46, 47, 48, 49).

2-3-2. Bacterial Degradation:

Compared with insects and fungi, bacteria are much less important as agents of wood deterioration. Bacteria will attack the various structural elements of wood differently; therefore they are divided according to the structural damage pattern into: bacteria destroying pit membranes and bacteria destroying wood cell walls.

**Bacteria destroying pit membranes:** Some primary bacterial colonists of wood have been found to preferentially attack only pit membranes. Soft-woods are affected more than hardwoods; and sapwood more than heartwood. Destruction of pit membranes increases porosity and improves the permeability to fluids.

**Bacteria destroying wood cell walls:** Previous studies have shown that distinct patterns of attack occur, and several categories of bacterial decay have been described. These bacteria are further subdivided according to the microscopic structure of their attack, into erosion bacteria, tunneling bacteria, and cavity-forming bacteria; Erosion bacteria degrade secondary wall layers and deplete cellulose and hemicellulose from the wood. Both softwoods and hardwoods are attacked. Erosion bacteria attack the S3 layer of the wood cell wall from the lumen, and subsequently decompose the S2 layer. If the attack occurs in waterlogged wood under anaerobic conditions, the decomposition of the S2 layer is uneven. In most cases, even in advanced decomposition, non degraded wall materials, consisting of lignin from the secondary wall layers and compound middle lamellae remain resulting in a porous, high lignified residue. Tunneling bacteria characteristically produce minute tunnels that occur within the secondary cell wall. These bacteria penetrate the S2 layer of the wood cell wall, each tunnel being headed by a single bacterium. Division of the bacteria increases the number of tunnels rapidly, and a branched tunnel system is formed. Tunnels can also be found penetrating and degrading the middle lamellae, and even the highly lignin-rich primary structure of bordered pits in coniferous wood. Lignin may be degraded to a limited extent but large amounts of lignin present in wood with advanced bacterial degradation suggests that lignin loss is not extensive. Cavity-forming bacteria, like the tunneling bacteria, attack the S2 layer. They form angular cavities which extend at right angles to the long axis of the fibers. (18, 38, 39, 50, 51, 52, 53, 54, 55).

### 3. Changes in archaeological wood due to treatment procedures:

#### 3-1. Cleaning:

Hamed (16) studied and monitored microscopically the changes during cleaning of archaeological wood with commonly used solvents. The cells with a large diameter were easier to clean than those with small diameters and the SEM results showed that the deleterious effect of the selected solvents on wood structure varies depending on the type of the solvent.
A recent study investigated the effect of enzymes in cleaning archaeological wood and concluded that, enzymatic cleaning is an excellent method compared to traditional chemical cleaning (56); since chemical cleaning using organic and inorganic solvents adversely affect the anatomical structure of the wood and causes pressure and stresses on the cells as a result of expansion and contraction caused by penetration of the solvent during the cleaning process and its evaporation once the process is over (16).

3-2. Consolidation:

The aim of a consolidation treatment of wooden objects is to render their mechanical strength and cohesion back without depleting their authenticity. A consolidation treatment is therefore essential for the conservation of archaeological wooden artifacts. Changes in archeological wood by impregnation with consolidants can also be studied by SEM (57).

The distribution of synthetic resin consolidant after treatment of deteriorated wood by vacuum impregnation was studied principally by SEM. The samples had been completely saturated with consolidant solution during treatment, and accordingly, evidence of resin could be found throughout the cross section. However, the resin was not uniformly distributed. As revealed, some cells could be observed to have heavy deposits of resin, in some cases completely filling the cell lumen, while adjacent cells contained little or no resin. The percentage of earlywood cells with visible resin deposits in a given sample area was used as an indicator of resin content. It was found that there was greater concentration in the side grain surface layers than in the specimen core. There was also a tendency toward increasing concentration toward the end surfaces but this effect was not well defined (58).

Spirydowicz et al. (59) demonstrated that treatment of decayed archaeological wood with 10% Butvar B-98 solution can be carried out without significantly altering the micromorphological structure of the wood. At relatively high magnifications with microscopic observations, the consolidant can be seen to coat the cell walls and fill some of the lumina of small diameter cells. This type of treatment greatly aids the stability of the decayed wood without significant changes to the microstructure.

Moreover, Olsson et al. (60) studied transverse liquid flow paths in pine and spruce sapwood and heartwood vacuum impregnated with of a low-viscous epoxy. They proposed a damage hypothesis deriving from the impregnation procedure. For pine sapwood, the liquid flow was enabled through disrupted crossfield pit membranes. For spruce, the thicker ray cell walls in combination with smaller crossfield pits reduced permeability considerably. The reduced permeability in pine heartwood was believed to be the result of deposits of high-molecular-weight substances (extractives) on the cell walls and in the parenchyma ray cells. In a study of penetration of different wood coatings into predried pine sapwood and spruce, De Meijer et al. (61) found a substantially different behavior of liquid flow into ray parenchyma and ray tracheids between these two species. In pine, the major part of the coating flows through the ray parenchyma cells from cell to cell, while in spruce, the coating flows in ray tracheids solely. While some coatings only penetrated spruce in ray parenchyma into the first cell, the penetration depth in pine parenchyma was as deep as 1000 µm.

A comparative study between two consolidant materials commonly used in the treatment of archaeological wood: Paraloid B72 and Tylose using SEM was conducted to demonstrate the efficiency of consolidation treatments and evaluation of their effect on the anatomical structure of wood, before and after conservation, as well as after artificial aging. Additionally, microscopic investigations were done after testing their reversibility from wood structure (16).

Tuduce Trăistaru et al. (62) investigated the presence and the distribution of the consolidant into the wooden support by SEM. The authors showed that the expected effect of the consolidation treatment was the filling of voids, so that this particular aspect would be relevant in the microscopic characterization of the efficiency of consolidation treatments. The main anatomical elements involved in the penetration of consolidants are the vessels and the rays, as well as the interconnecting pits, which observations confirmed in previous research regarding the distribution of consolidants. The SEM analysis of all the sections suggested an uneven distribution of consolidants into the wooden structure, and a better penetration occurred on the longitudinal direction via fibers and vessels.

4. Conclusion:

Scanning electron microscopy is considered an important tool for observing the morphological characteristics of degraded wood at the level of cell wall, evaluating their damage, and identifying the casual agent of decay patterns. Figures 1-5 are just an example of what we can obtain from the use of such a useful tool in the assessment of wood decay. Additionally it is very helpful in the evaluation of materials and methods used during the treatment of archaeological wood, especially cleaning and consolidation processes, because the effect of any process on the wood structure varies according to wood properties, decay and composition. SEM micrographs are valuable assets in developing specific consolidation and treatments procedures for every decay situation. SEM – EDS will be very useful in future research, because it has the additional privilege of identifying chemical elements of materials used in the decoration of polychrome wood, which would help understand ancient technologies and the deterioration of its different layers.
Fig. (1): SEM micrograph in longitudinal view showing deterioration of bordered pits of pine (*Pinus silvestris* L.) resulting from weathering, in addition to the foreign deposits on the wood surface (bar: 50µm).

Fig. (2): SEM micrograph of longitudinal view of pine (*Pinus silvestris* L.) showing deposition of corrosion products of iron gradually penetrating the wood elements and covering the wood structure (bar: 100µm).

Fig. (3): SEM micrograph of transverse view of sycamore wood (*Ficus sycomorus* L.), showing separations between cell walls, cracks and fractures in cell walls due to mechanical deterioration (bar: 10µm).

Fig. (4): SEM micrograph of *Ficus sycomorus* L., showing enlargement and deterioration of simple pits and detachment within cells due to fungal attack (bar: 50µm).

Fig. (5): SEM micrograph of longitudinal view of *Ficus sycomorus* L. showing foreign deposits presumably resinous material mixed with dust. Erosion and defibration of cell walls are evident. (bar: 10µm)
References:


[12] El Hadidi, N.M.N., Treatment and Conservation of Archaeological Wood with the application on Two Wooden Coffins at the Egyptian Museum–Faculty of Archaeology - Cairo University, M.A., Conservation Department, Faculty of Archaeology, Cairo University, 1998. (unpublished)

[13] Lokma, N.I., Studies of the treatment and conservation of dry wood applied on selected wooden statues from the Egyptian Museum, Ph.D., Conservation Department, Faculty of Archaeology, Cairo University, 2000. (unpublished)

[14] El Hadidi, N.M.N., A Study on some Physical, Mechanical and Chemical Changes of Deteriorated Archaeological Wood and it’s Consolidation, with the Application on some Selected Artifacts at the Islamic Museum of the Faculty of Archaeology, Ph.D., Conservation Department, Faculty of Archaeology, Cairo University, 2003. (unpublished)

[15] Hamed, S., Study of Technique, Treatment, and conservation of Archaeological Wooden Boats from Pharonic Age with The Application on Selected Model, M.A., Conservation Department, Faculty of Archaeology, Cairo University, 2005. (unpublished)


[17] Fawzy, M., A Study on Relation between Swelling and Shrinking in wood and its chemical compounds, with the application on Treatment, and conservation of Archaeological Painted Wood, M.A., Conservation Department, Faculty of Archaeology, Cairo University, 2010. (unpublished)


