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Surface Characterization of Some Woods Exposed to Accelerated Weathering

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ABSTRACT

In this study, the photo degradation of beech (*Fagus orientalis*), oak (*Quercus robur*), ash (*Fraxinus* spp.), and poplar (*Populus euramericana*) wood samples were investigated by accelerated weathering test in order to determine the chemical change by Attenuated total reflectance-Fourier transform infrared (ATR-FTIR), surface degradation by Scanning Electron Microscopy (SEM) and colour measurements by portable spectrophotometer. For this purpose, weathering of wood samples was performed in an accelerated weathering tester using ultraviolet irradiation with 0.85 W/m² at 340 nm for 1000 h. According to results after 168 hours of weathering, the exposed samples showed considerable change in colour, which accompanied with the chemical change in wood components. After that time the total colour change showed a decrease. During the remaining time in weathering process total colour change lowered in comparison to 168 hours. Overall, the highest colour change was obtained with ash samples after weathering. SEM analyses showed cracks on the surface of the wood samples exposed to 1000 hours of weathering.

Key words: Wood, Accelerated weathering, SEM, FTIR

1. INTRODUCTION

Wood and wood-based materials have been commonly used in the interior spaces for centuries and also constitute preferred multi-purpose materials for exterior applications. However, wood is damaged by the exposure to various biotic (insect defoliation, and borer attack, infection by pathogenic fungi, microorganisms) and abiotic factors (air pollution, nitrogen eutrophication, soil chemical stress, solar radiation, moisture) in the external environment (Thomas *et al.*, 2002; Zhang *et al.*, 2009).

Among the factors affecting the environmental degradation of wood, accelerated weathering reproduces photodegradation the fastest and effective, but the other factors are also important (Can and Sivrikaya, 2016). Photodegradation leads to surface degradation of wood and is defined by colour changes, loss of gloss, roughening and cracking (Cogulet *et al.*, 2016). Degradation of wood by weathering primarily affects the wood components; in particular, results in the degradation of lignin and hemicellulose (Jin *et al.*, 1991). Lignin is able to absorb UV light at a short wavelength below 500 nm and is responsible for the colour change when wood exposed to weathering (Sivrikaya *et al.*, 2015; Cogulet *et al.*, 2016). Especially in the range from 295nm to 400 nm (UV-A and UV-B), the absorption of UV light in to the wood can be explained by the detection of discolouration and formation of chromophoric groups in wood (Feist and Hon, 1984; Hon and Chang, 1984; Zhang *et al.*, 2009).

The effect of photodegradation has been studied by authors who asserted two approaches to better understanding of wood weathering. One of these approaches is the colour measurement of wood according to CIELAB system using colour scale. Secondly, Fourier transform infrared (FT-IR) spectroscopy analysis of the surface allows the study of chemical changes in wood due to the photodegradation. It requires a simple sample preparation step and small amount of sample (Tolvaj and Oscar, 1995; Muller *et al.*, 2003; Cogulet *et al.*, 2016).

Vibrational spectroscopy methods such as infrared and Raman spectroscopy are used to detect mechanism and monitor the extent of wood degradation. Both techniques (FT-IR and Raman) are non-destructive, require few samples, have a simple preparation step and provide some information about the lignin or holocellulose (Long *et al.*, 1986; Rowell, 2012; Ozgenç *et al.*, 2017).

In this study, these techniques (FTIR-ATR) were used to investigate the effect of photo degradation in terms of colour change by spectrophotometer, chemical changes by FTIR and surface degradation by SEM in hardwoods such as beech, oak, ash and poplar, exposed to accelerated weathering for 1000 hours.

2. MATERIAL AND METHOD

Beech (*Fagus orientalis*), oak (*Quercus robur*), ash (*Fraxinus spp.*), and poplar (*Populus euramericana*) specimens, free of defect and fungal infestation, were prepared from sapwood blocks with dimensions of 15x75x150 mm (H x W x L) according to AWWPA Standard E4-03. Prior to weathering wood samples were put in the conditioning room at 12% RH and 22 °C until the constant weight.

2.1. Accelerated weathering tests (QUV)

Accelerated weathering tests was performed using UV-light irradiation for 24 hours (ASTM G154 1998). The average irradiance level was 0.85 W/m² at 340 nm and the temperature in the chamber was set to 50 °C. Four replicate samples of each treatment were exposed to accelerated weathering for 4, 24, 48, 96, 168, 500, 1000 hours respectively.

2.2. Surface characterization

2.2.1. Colour measurements

Colour measurement was performed according to ISO 7724. The CIELab system is described by three parameters: L* represents the lightness, a* and b* are the chromaticity coordinates; a*>0 describes red, a*<0 green, b*>0 yellow and b*<0 blue. L* varies from 100 (white) to zero (black).

The colour coordinates L*, a* and b* were determined for each sample before and after exposure to accelerated weathering. The colour was measured by a colour measurement device using a D65 light source. These values were used to calculate the colour change ΔE^* as a function of the UV irradiation period according to Equation 1

$$\Delta E^* = [\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}]^{1/2} \quad (1)$$

Where ΔL^* , Δa^* , and Δb^* are the changes between the initial values and the value after certain time periods of exposure. A low ΔE^* corresponds to a low colour change or a means stable colour (ISO 7724-2 1984).

2.2.2. ATR-FTIR spectroscopy analysis

Fourier Transform Infrared Spectroscopy (FT-IR) analysis has been used as a technique to obtain information about the structure of the wood constituents and chemical changes taking place in the wood weathering process. FTIR spectra were obtained by a Shimadzu IRAffinity-1 equipped with a Single Reflection ATR pike MIRacle sampling accessory. Wood surface contacted the ATR crystal, and the evanescent wave could be absorbed by the powder. The resultant attenuated radiation produced an ATR spectrum, similar to a conventional absorption spectrum (Khoshhesab, 2012). Four accumulated spectra with a resolution of 4 cm⁻¹ were obtained for wavenumbers from 700 cm⁻¹- 4000 cm⁻¹ with 32 scans for each sample.

2.2.3. Scanning electron microscopy

The morphology of the surfaces under nitrogen were observed with an environmental scanning electron microscope (ESEM) (Phillips Electroscan 2020) with an accelerating voltage of 5 kV. The radial surface of all samples was sputter-coated with gold using a Denton sputter coater for enhanced conductivity. Wood structure and the degradation caused by weathering were investigated.

3. RESULTS AND DISCUSSION

It is known that UV radiation plays the most important role in the degradation of organic materials when exposed to exterior conditions, with the breaking of the chemical bonds by means of the energy present in the UV rays that results in the reducing of the service life of wood material. At the end of the present study, some changes in colour towards greyish were observed when examined the wood surface with the increasing of the weathering time. For instance, the brightness of the surface decreased, and the colour turned to greyish as a result of accelerated weathering after 1000 h.

Tables 1-4 present the colour changes of the Beech, Oak, Poplar and Ash samples in the form of CIELAB parameters, namely L*, a*, b*, and ΔE^* after were exposed to weathering.

Table 1. Average values of the chromatic coordinates as function of irradiation duration of Beech

Irradiation durations (hours)	L	a	b	ΔE
0	67,28	10,30	19,68	-
4	62,72	10,01	21,78	5,12
24	62,19	10,43	24,31	6,96
48	62,37	10,36	24,52	6,97
96	62,47	10,32	24,38	6,82
168	62,56	10,14	23,71	6,37
500	64,49	9,43	21,97	3,93
1000	66,06	8,99	20,38	2,49

Table 2. Average values of the chromatic coordinates as function of irradiation duration of Oak

Irradiation durations (hours)	L	a	b	ΔE
0	65,51	6,86	21,03	-
4	61,24	7,29	23,57	5,02
24	58,91	8,51	27,03	9,11
48	58,3	8,96	27,4	9,90
96	57,72	9,35	27,02	10,18
168	57,22	9,61	26,12	10,15
500	57,06	9,24	22,71	8,97
1000	58,37	8,83	20,33	7,5

As shown in Table 1, the light stability (L*) value of beech (*Fagus orientalis*) and oak (*Quercus robur*) sapwood samples decreased with increasing irradiation durations (h), whereas tended to increase after 500 h. In case of the poplar and ash woods, L* value stabilized after 500 hours of aging. After accelerated weathering, the lowest value regarding light stability was found 62,56 in beech, followed by 57,06 in oak, 74,13 in poplar and 69,08 in ash samples. In the early stages of the accelerated weathering, dark-coloured woods are turned to greyish, whereas light-coloured woods darkened (Feist and Hon, 1984). Temiz *et al.* (2007) obtained

negative ΔL^* values due to the darkening of the wood surfaces after the weathering. In another research performed by Salla *et al.* (2012), L^* values decreased when the samples subjected to 200 hours of weathering.

Table 3. Average values of the chromatic coordinates as function of irradiation duration of Poplar

Irradiation durations (hours)	L	a	b	ΔE
0	88,59	1,67	15,42	-
4	85,06	2,22	22,41	7,86
24	81,01	4,78	28,99	15,86
48	79,39	5,99	30,35	18,06
96	77,89	7,13	31,04	19,70
168	76,47	8,08	31,09	20,83
500	74,88	8,78	29,35	20,80
1000	74,13	8,92	27,31	20,08

Table 4. Average values of the chromatic coordinates as function of irradiation duration of Ash

Irradiation durations (hours)	L	a	b	ΔE
0	84,60	3,75	18,38	-
4	80,37	4,12	25,04	7,91
24	76,36	6,65	31,17	15,50
48	74,69	7,89	32,54	17,78
96	73,11	9,06	33,16	19,46
168	71,56	10,08	33,13	20,68
500	69,95	10,93	30,69	20,45
1000	69,08	11,22	28,40	19,93

As can be seen from Tables 1-4, the changes in a^* and b^* values generally decreased in beech and oak wood samples, nevertheless increased in the cases of poplar and ash woods. a^* value showed a decrease in all periods in beech wood, while increased in oak wood through 500 h, following that decreased. For the b^* value, the first 48 hours of beech and the first 96 hours of oak, and the first 168 hours of poplar and ash exhibited an increasing followed by decreasing in the remaining time. In the CIELAB system, a positive Δa^* correspond to reddish, and a positive Δb^* show an increase of yellow colour. It is thought that the degradation of lignin and other compounds are caused by UV radiation after weathering, subsequently the generation of o- and p-quinoid groups is due to the lignin degradation that leads to colour change (Salla *et al.*, 2012; Feist *et al.*, 1984; Hon and Shiraishi 2001). Since the natural colour of beech wood is reddish white, therefore it was shown that the beech samples give the highest colour value of the red. It was reported by Keskin and Atar (2007), the red colour tone in the beech wood was found to be 26% greater than oak.

The increasing in the total colour change (ΔE^*) regarding the exposure time was different depending on the wood species; for beech in 48 h, oak in 96 h, poplar and ash in 168 h. The reason why the colour changes were relatively may be the absence of the water in the accelerated weathering process. Earlier workers (George *et al.* 2005; Williams 2005) reported that water contributes the removing of the fragments on the wood surface during the weathering process. When compared to colour change among wood species the highest change was obtained in oak wood (96 hours), in addition total colour change was high in beech and oak, whereas low in poplar and ash woods. This is because the tree species having dark surface exhibit less colour change than those having light surface. Some workers studied on weathering during 12 months with Scots pine and beech indicating that the reason of less colour change in beech was explained by its having dark surface, furthermore the differences in the ratio of main

and side compounds of wood that effect the photodegradation as well (Temiz *et al.*, 2004; Budakcı and Karamanoglu 2014).

The colour changes of wood surfaces is not only visible but also chemical changes. UV light is largely responsible for wood degradation. FTIR spectroscopy has done much to help us understand the chemical mechanisms of wood degradation. *Figures 1-4* show the changes in the wood surface as analysed by the FTIR method.

It is clearly seen that the peak at $3400-3200\text{ cm}^{-1}$ refers to hydrogen bonded OH group stretch, CH bonds at $2800-3000\text{ cm}^{-1}$, and the peaks at 1743 cm^{-1} and 1605 cm^{-1} respectively, indicating the absorption peaks of C=O and C-O bonds present in the hemicellulose. Furthermore, the peak at 1653 cm^{-1} represents the absorbed OH groups. The peak at 1510 cm^{-1} originates from the lignin aromatic groups whereas the peak at 1251 cm^{-1} derives from the guaiacyl group present in wood. The peak at 1467 is due to C-H deformation in lignin and at 1427 cm^{-1} indicates the C-H group in carbohydrates. Previous authors reported the representation of the following peaks as follow: 1375 cm^{-1} indicates the C-H deformation in cellulose and hemicellulose, 1320 cm^{-1} shows the -CH vibration in cellulose and 1160 cm^{-1} comes up from the vibration of C-O-C group in cellulose and hemicellulose and 1058 cm^{-1} originates from the CO stretching in cellulose and hemicellulose, in addition 898 cm^{-1} reveals the C-H deformation in cellulose (Pandey, 1999; Baeza *et al.*, 2000; Tshabalala, 2005).

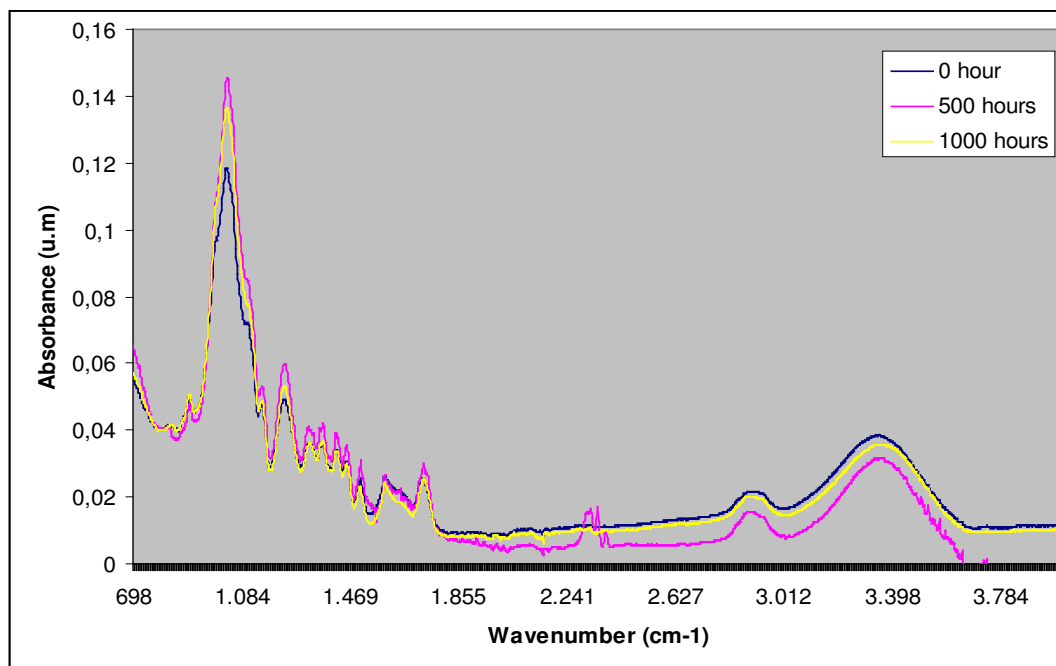


Figure 1. FTIR-ATR spectra corresponding to different exposure period of test and control beech sapwood sample

When the peak values described above are examined, we see no significant change in the case of beech wood. *Figure 1* shows the lignin bands and an increase in the cellulose at the wood surface. The lack of a significant change in peak values is thought to be due to the fact that only UV light was present during the weathering process. According to Andrew (2001) DRIFT spectra showed that the wood exposed to both water and light showed a much higher degree of weathering than did the wood exposed to either water or light by itself.

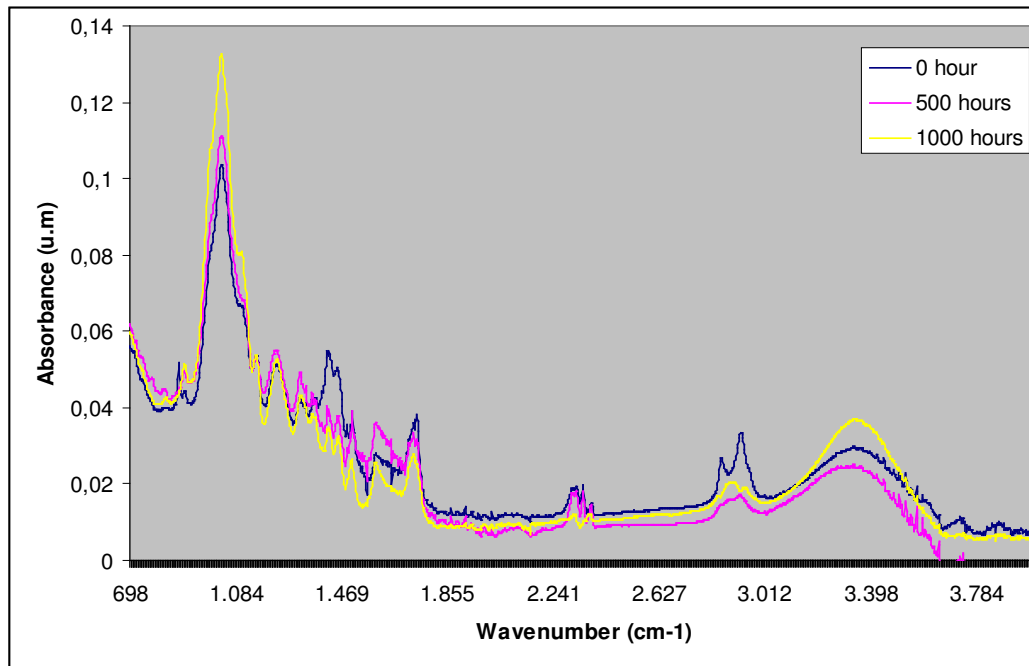


Figure 2. FTIR-ATR spectra corresponding to different exposure period of test and control oak sapwood sample

As can be shown from the *Figure 2*, while the C-H deformation peak in cellulose (898 cm^{-1}) increased, on the other hand significant decrease was found in C-H bonds in cellulose and hemicellulose. At the peak of 1743 cm^{-1} , it appears that there is a decrease with the increasing of exposure time. The peak of 2916 cm^{-1} shows the C-H bond in methyl and methylene groups. Consequently, these peak values mentioned above were significantly lowered in a short time (Socrates, 2004; Hesse, 2005).

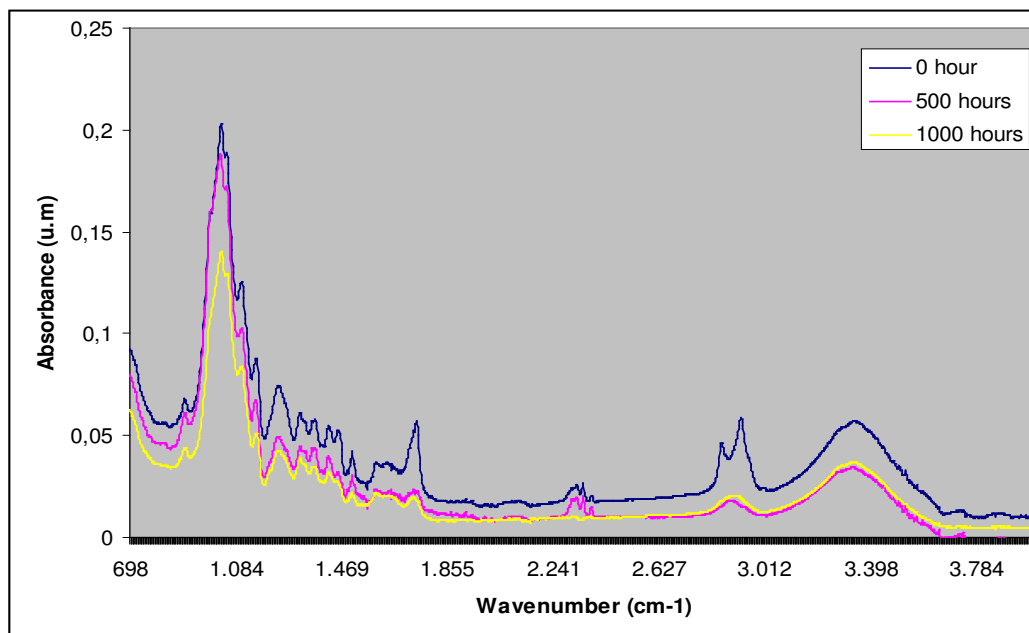


Figure 3. FTIR-ATR spectra corresponding to different exposure period of test and control poplar sapwood sample

Among the wood species in the present study, poplar was the most influenced by the UV radiation. It is believed that UV has much higher impact on lignin than other wood components. This can be understood from the significant decrease in the peaks at 1510 cm^{-1} derived from

the aromatic groups, at 1461 cm^{-1} arising from the C-H deformation and at 1267 cm^{-1} due to guaiacyl groups in lignin. Likewise, CH stress peaks as well as decreasing in the C-O, C-O-C bonds in cellulose and hemicellulose were found. It was also indicated that the peaks at $1630\text{--}1660\text{ cm}^{-1}$ are associated with the aryl ketones bonded to the $\text{-C}=\text{O}$, unbound with $\text{C}=\text{C}$ in lignin and water band. The study showed that these peaks decreased in poplar samples after accelerated aging test (Temiz *et al.*, 2006).

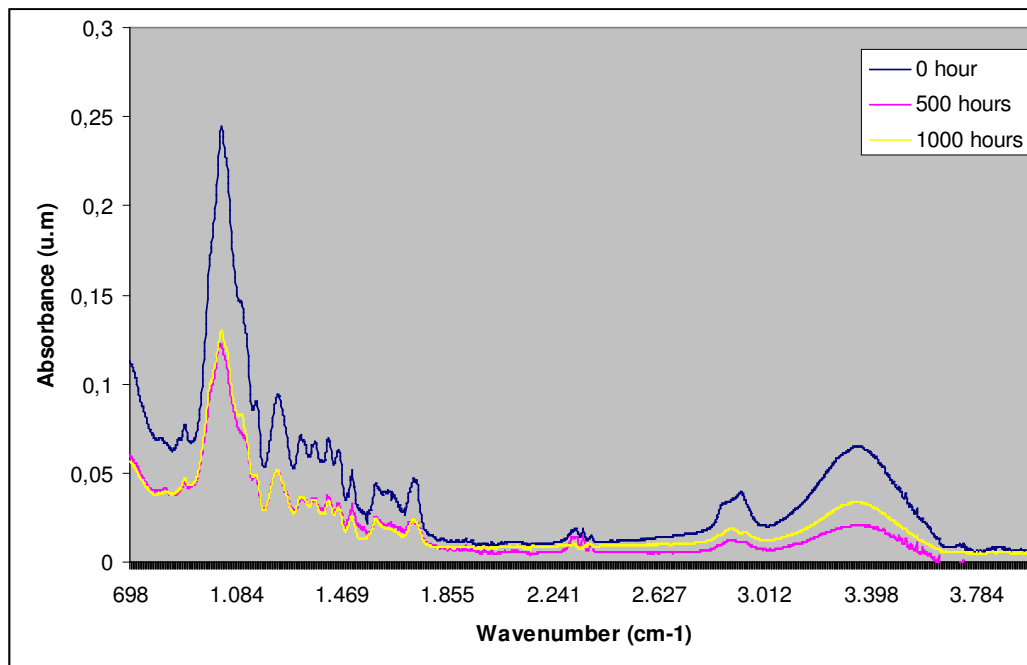


Figure. 4. FTIR-ATR spectra corresponding to different exposure period of test and control ash sapwood sample

After weathering, FTIR peaks at 1035 cm^{-1} and 1251 cm^{-1} were greatly diminished for ash wood. These bonds refer to C-O and C-O-C found in hemicellulose and cellulose. Similarly, there was a significant decrease at the peak of 1510 cm^{-1} representing the guaiacyl lignin, and at 1251 cm^{-1} which describes aromatic rings in the lignin.

SEM images of the Beech, Oak, Poplar and Ash sapwood samples were exhibited in Fig. 5-8, showing wood fibres, and decomposition of cell walls. Characterization of the weathered and control samples displayed in these images. In addition to colour and chemical changes, physical changes also occur on the wood surface that weakens the chemical bonds in the cell wall and leads to intercellular stretching and cracking. With the contribution of water, the cracks can cause erosion on the wood surface. However, as the water was not used in our experiment the crack formation was not observed. Still, very few micro cracks were observed on the wood surfaces with the 1000 hours of weathering. The changes in the anatomic structure resulting from the outdoor weathering were investigated by some authors (Hon and Shiraishi, 2001; Pandey and Pitman, 2002).

Figure 5 shows that no change in the pit structure was observed. This demonstrates that the accelerated weathering process without water does not bring any changes in the chemical structure of the beech wood (Fig. 1).

Structural changes in cell walls at the microscopic level were seen from SEM micrographs after the oak, poplar and ash wood specimens were exposed to 1000 hours accelerated weathering (Fig.6-8).

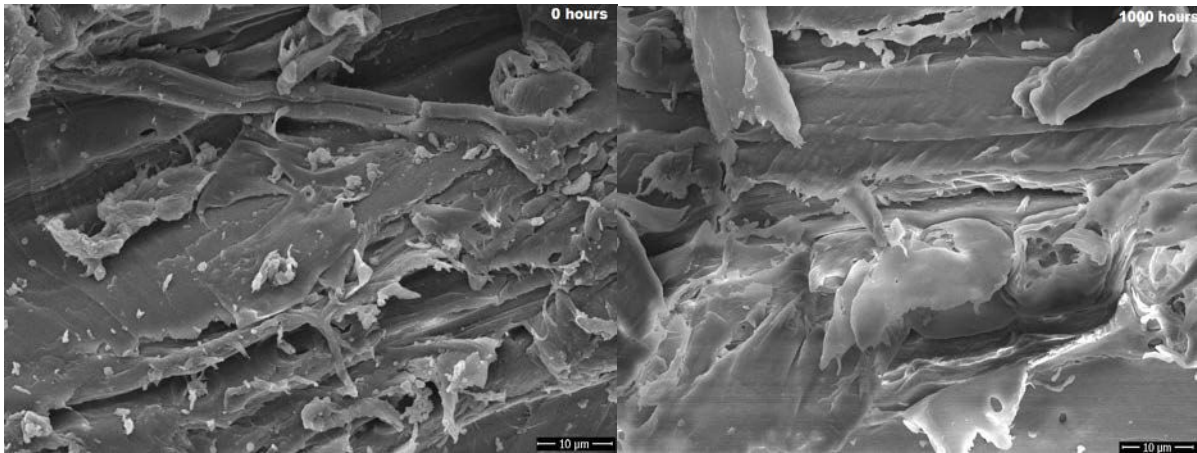


Figure 5. SEM analysis of the Beech wood, control (0 hours) and exposed to weathering (1000 hours) (10 μm , x5000).

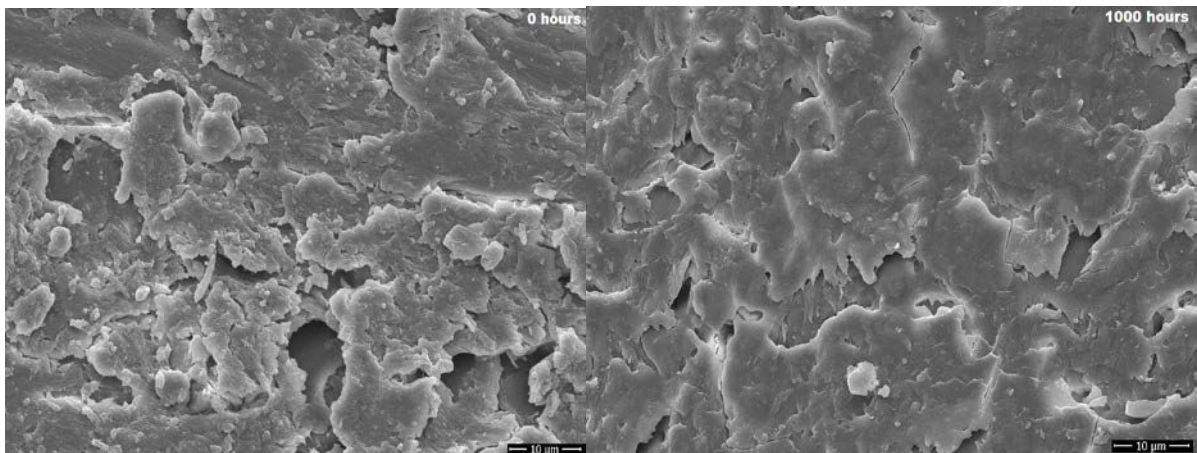


Figure 6. SEM analysis of the Oak wood, control (0 hours) and exposed to weathering (1000 hours) (10 μm , x5000)

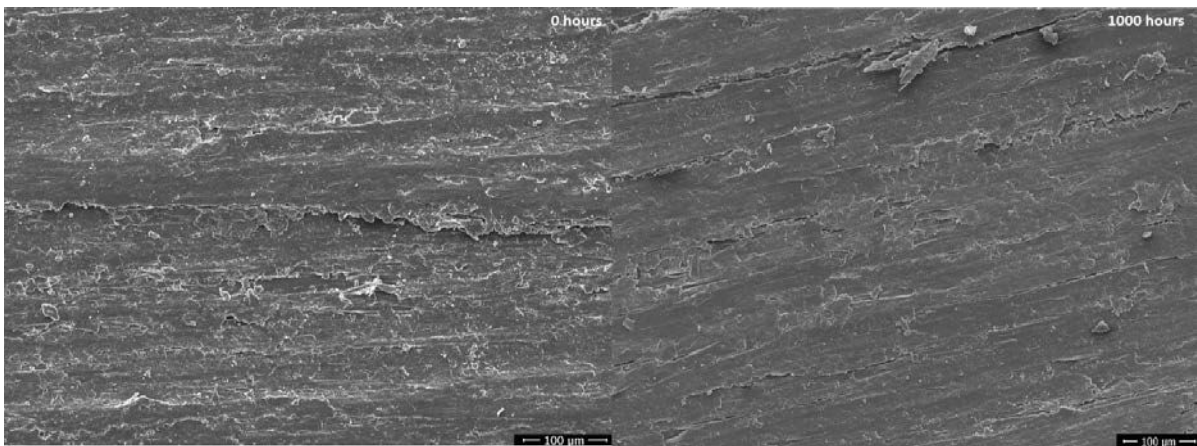


Figure 7. SEM analysis of the Poplar wood, control (0 hours) and exposed to weathering (1000 hours) (100 μm , x500).

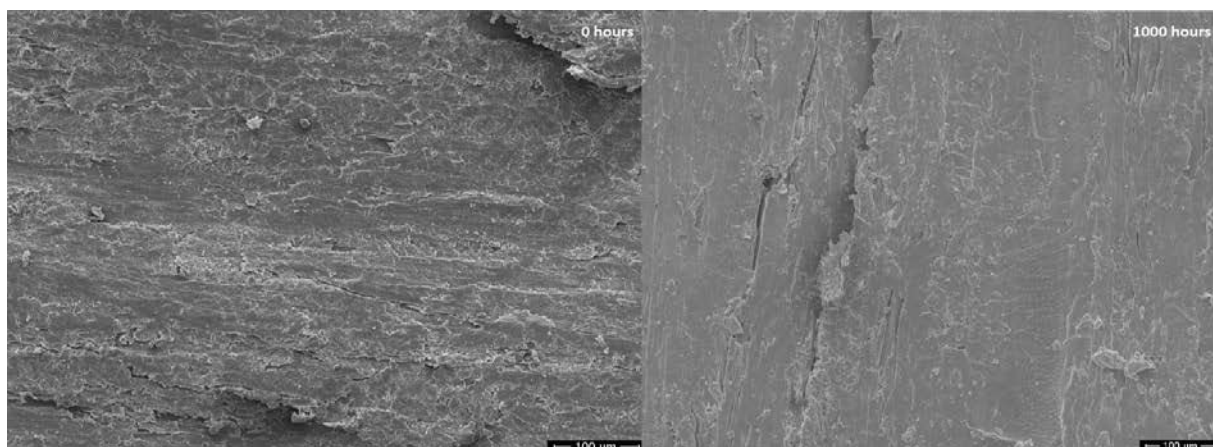


Figure 8. SEM analysis of the Ash wood, control (0 hours) and exposed to weathering (1000 hours) (100 μm , x500).

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