

Wood Surface Protection against Artificial Weathering with Vegetable Seed Oils

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Effects of UV-light irradiation and water spray on the mechanical strength and surface characteristics of untreated and pretreated Scots pine sapwood samples were studied. The specimens were treated with parsley seed oil, pomegranate seed oil, linseed seed oil, nigella seed oil, canola oil, sesame seed oil, and soybean oil. The compositional changes and surface properties of the weathered samples were characterized by Fourier transform infrared (FTIR-ATR) spectroscopy and color and surface roughness measurements. The results showed that all vegetable oils provided lower color changes than the control group after 600 h of exposure in a weathering test cycle. The least color change was found on the Scots pine surface pretreated with pomegranate seed oil. The vegetable oil treatment retarded the surface lignin degradation during weathering, indicating that the surface roughness values of pine wood treated with vegetable oils decreased with irradiation over time compared with those of control samples. The effect of artificial weathering on mechanical strength was determined with a compression strength test. It was observed that the compression strength values of Scots pine samples treated with vegetable oils was higher than that of untreated samples after 600 h of weathering exposure.

Keywords: Artificial weathering; Color change; Compression strength; FTIR-ATR spectroscopy; Surface roughness; Vegetable oil

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INTRODUCTION

Weathering leads to surface degradation of wood that is initiated primarily by solar radiation, but other factors are also important. The wetting and drying of wood through precipitation, diurnal and seasonal changes in relative humidity (RH), abrasion by windblown particulates, temperature changes, atmospheric pollution, oxygen, and human activities such as walking on decks and cleaning surfaces with cleaners and brighteners, sanding, and power-washing all contribute to the degradation of wood surfaces (Williams 2005). Some changes to the wood surface include grain loosening, roughened surfaces changing color, and checks and splinters and fragments breaking off the surface. The photon energy in solar radiation is the most damaging, initiating a wide variety of chemical changes at the wood's surface (Feist 1988). Color change on the wood surface is also related to the rate of formation of carbonyl groups and the degradation of lignin (Pandey 2005).

In recent years, many different methods have been discovered in the development of protective systems for wood to prevent photodegradation during outdoor weathering. Several approaches have been developed to prevent the photodegradation of wooden surfaces during outdoor weathering. One of the approaches considered is the application of clear-coating, which is thought to be the easiest and most common method (Yang *et al.* 2001; Chang and Chou 2000; Decker *et al.* 2004; Chou *et al.* 2008; Dawson *et al.* 2008; Forsthuber and Gröll 2010; Saha *et al.* 2011; Ozgenc *et al.* 2012; Corcione and Frigione 2012; Forsthuber *et al.* 2013). The other main approach considered for enhancement of weathering resistance is wood treatment (Temiz *et al.* 2005; Zhang *et al.* 2009; Ozgenc *et al.* 2012). Another method is the chemical modification of the molecular structure of polymers as a fundamental approach to improving the resistance of materials to photodegradation (Evans *et al.* 2000; Pandey and Chandrashekar 2006; Evans 2009; Hill 2011). New trends in wood preservation focus on products and processes that utilize environmentally friendly technologies and sustainable resources using recycled materials or byproducts from other industries (Temiz *et al.* 2007). There is growing interest within Europe in the use of oils, which is usually known as the Royal process, and water repellents for wood preservation at both industrial and research levels. This interest focuses on the screening of different natural and synthetic oils and on the process development of wood preservation technology (Palanti and Susco 2004). Linseed oil, tall oil, orange oil, soybean oil, nut oil, and hemp oil have been used either commercially or on a laboratory scale for wood preservation (Van Acker *et al.* 1999; Treu *et al.* 2001; Nakayama and Osbrink 2010). Traditional wood protection methods are highly effective against weathering, but in recent years, their use has been restricted due to the toxicity of traditionally used agents, which results in environmental hazards. With regard to developing environmentally benign wood preservatives without any toxicity to humans, the activities of various essential oils and extracts from plants against wood decay and termites have been investigated in recent studies (Yamaguchi *et al.* 1999; Kartal *et al.* 2006; Chang *et al.* 2008; Sen and Yalçın 2010). Another study investigated the water repellent efficiency of crude tall oil and crude tall oil emulsions, and the possibilities of reducing the amount of oil needed with the emulsion technique. Natural oils (*e.g.* tall oil, linseed oil) appear to be capable of preventing water uptake by wood. Tall oil treatments reduce the water uptake into sapwood. With tall oil emulsion treatments almost equal water repellent efficiencies are reached as with pure tall oil, even when the oil retentions are considerably lower (Hyvönen *et al.* 2006).

The effects of novel organic product on compression properties of fir (*Abies alba*), beech (*Fagus sylvatica*), and deciduous oak (*Quercus* sp.) were investigated. The effectiveness of the chemical treatment changes from one botanical species to another morphological structure, which leads to different mechanical strength of each species to be impregnated and to retain the consolidation product (Lionetto and Frigione 2012). Effects of treatment of southern pine with some organic wood preservation system on mechanical properties are not deleterious when compared with untreated controls (Barnes and Lindsey 2009). The effects of vegetable oil treatments on mechanical properties have been found to be directly related to several key wood material factors and pretreatment, treatment, and post-treatment processing factors (Tomak 2011; Yıldız *et al.* 2011a).

The objective of this study was to investigate the influence of artificial weathering on color stability and chemical change occurring in the surface structure of vegetable oil-treated Scots pine wood (*Pinus sylvestris* L.). The effect on compression strength of artificial weathering in the case of Scots pine wood treated with vegetable oil also was investigated.

EXPERIMENTAL

Materials

Preparing wood samples

Scots pine sapwood (*Pinus sylvestris* L.) was prepared at 20 mm thick, 76 mm width, and 120 mm length (3 tests and 3 controls for each variation). The samples were planed and equilibrated at 65% relative humidity and 20 °C. Before applying the vegetable oil on the wood surface, the surfaces of the samples were sanded with 120-grit sandpaper. The vegetable oils were applied in three layers to only one surface of each sample by brush. Later, the specimens were kept at room temperature for a week. The retentions values of vegetable oils are shown in Table 1.

The seeds were washed several times with water, then cleaned for removal of sugars, adhering material, and foreign matter. Then seeds were dried under outdoor conditions. Their moisture content was 8 to 9 wt% (dry basis). Finally, the dried, clean seeds were extracted to obtain the oil, using the commercial cold press method.

The vegetable oil and control sample groups tested in the study included the following: A = Parsley seed oil; B = Pomegranate seed oil; C = *Nigella sativa* oil; D = Linseed oil; G = Canola oil; V = Sesame oil; M = Soybean oil; and K = Control.

The retention for each treatment solution was calculated following formula (1):

$$\text{Retention (kg/m}^3\text{)} = (M_{ys} - M_0) / V_0 \quad (1)$$

where M_{ys} is the mass of sample after application of vegetable oil, M_0 is the mass of sample containing 0% moisture, and V_0 is the volume of sample in cubic centimeters at 0% moisture content.

Table 1. Retention Values of Vegetable Oils for Scots Pine (*Pinus sylvestris* L.)

Group	A	B	C	D	G	V	M
Retention (kg/m ³)	4.3 (0.9)	5.5 (1.1)	5.1 (1.2)	5.0 (1.0)	4.2 (0.8)	3.8 (0.9)	4.7 (1.0)
*Values in parentheses are standard deviations. * A = parsley seed oil; B = pomegranate seed oil; C = <i>Nigella sativa</i> oil; D = linseed oil; G = canola oil; V = sesame oil; M = soybean oil; and K = control							

Methods

Accelerated weathering test (QUV/spray)

Artificial weathering was performed in a QUV/spray accelerated weathering tester (Q-Panel Lab Products, Cleveland, OH, USA) equipped with UVA 340 lamps; the temperature in the chamber was approximately 50 °C (ASTM G 53-96). The weathering experiment was carried out in cycles of UV-light irradiation for 2 h followed by a water spray for 18 min in an accelerated weathering test cycle chamber over 25 d (600 h). Four replicate samples for each oil-treated system were prepared for each artificial weathering test condition.

Color measurements

Color measurements were performed with a Konica Minolta CM-600d (Canada). The reflection spectrum was acquired from a measuring area of 8 mm in the 400- to 700-nm wavelength range, where four measurements at precisely defined points on the weathered surfaces of each sample were carried out periodically (ISO 7724-1). Thus, color changes during weathering were always monitored on the same spot of wood. The CIE (Commission Internationale de l'Eclairage) color parameters L^* (lightness), a^* (along the X axis red (+) to green (-)), and b^* (along the Y axis yellow (+) to blue (-)) were calculated using the Konica Minolta Color Data Software CM-S100w SpectraMagic NX Lite (ISO 7724-2), from which the color differences ΔE^* were calculated according to Eq. 2:

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

Measurements were always performed at the end of a UV irradiation step to provide consistent specimen conditions during color measurements. Five replicates were used for each sample to evaluate color change.

Surface roughness

A Mitutoyo SurfTest SJ-301 instrument was employed for surface roughness measurements. The R_a and R_z roughness parameters were measured to evaluate the surface roughness of the surfaces of unweathered and weathered treated and untreated samples according to DIN 4768. R_a is the arithmetic mean of the absolute values of the profile departures within the reference length, and R_z is the arithmetic mean of the 4-point height of irregularities (DIN 4768). The cut-off length was 2.5 mm, the sampling length was 12.5 mm, and the detector tip radius was 10 μm in the surface roughness measurements.

Fourier transform infrared spectroscopy

The FTIR spectra were obtained using a Perkin-Elmer Spectrum One FTIR instrument with a Universal ATR Diamond/ZnSe crystal with one reflection. Five accumulated spectra for each sample with a resolution of 16 cm^{-1} were obtained. Spectra were displayed in transmittance mode and limited to the region of interest: 1850 cm^{-1} to 900 cm^{-1} .

Compression strength

Some wood samples to which aromatic oil was applied, and their controls, were tested at the following compression strength: Compression strength parallel to grain with samples milled to $20 \times 20 \times 30$ mm taken from twenty pine and beech specimens each. The compression test was performed in accordance with American Society for Testing and Materials 143 (1996). Samples of the velocity of crosshead speed in the compression test at the time of breaking the machine is set up to break the force measured at 1.5 to 2 minutes.

RESULTS AND DISCUSSION

Color Change

The color changes of untreated and vegetable seed oil-treated Scots pine (*Pinus sylvestris* L.) samples for different time periods are showed in Fig. 4. The lowest values of ΔL^* , which is the most sensitive parameter of wood surface quality, were obtained for the untreated wood samples after 600 h of exposure. The negative lightness stability (ΔL^*) values occur during weathering because the surface becomes darker (Temiz *et al.* 2007). Other vegetable oil treatments caused fewer changes in the lightness (ΔL^*) than the control samples. The test samples composed of linseed oil-treated wood samples showed positive ΔL^* values, thus indicating that the wood surface became lighter (Fig.1). Except for control and linseed oil-treated samples, the lightness values for all samples decreased during first 200 h and increased afterwards to values comparable or higher than the initial L^* values (Nzokou 2004).

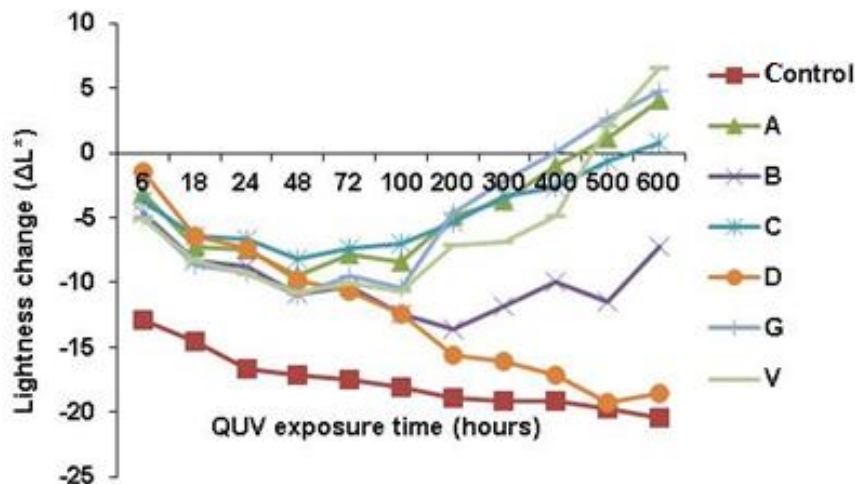


Fig. 1. Lightness change of weathered Scots pine (*Pinus sylvestris* L.) samples (A = Parsley seed oil; B = Pomegranate seed oil; C = *Nigella sativa* oil; D = Linseed oil; G = Canola oil; V = Sesame oil; M = Soybean oil; and K = Control)

Positive values of Δa^* and Δb^* indicate an increase in yellow color and a tendency of the wood surface to turn a reddish color. Negative values of Δa^* and Δb^* indicate an increase in the color blue, causing the surface to be perceived as a greenish color, as can be seen in Fig. 2 and 3. (Temiz *et al.* 2007). The change in chromacity coordinates Δa^* and Δb^* (Fig. 2 and 3) shows an increase during 100 hours and a decrease afterwards for all wood samples except for control sample. This is due to the sample surface becoming reddish and yellowish during the first phase of weathering process, and progressively greenish and bluish with extended exposure to artificial weathering (Nzokou 2004).

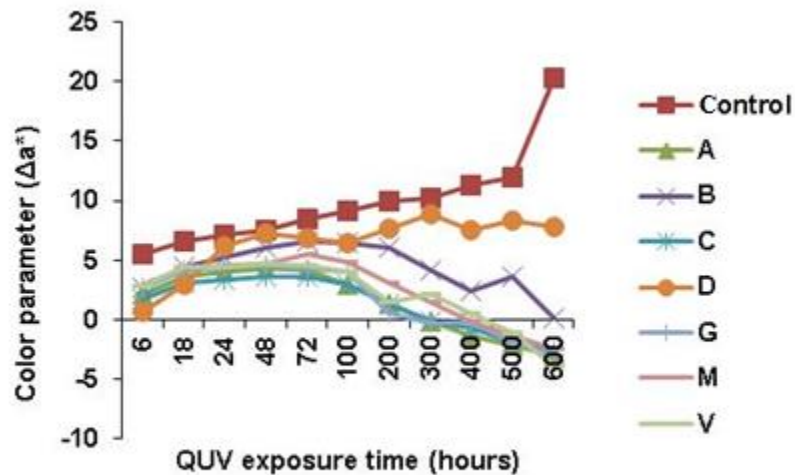


Fig. 2. Color parameter change (Δa^*) of weathered Scots pine (*Pinus sylvestris* L.) samples (A = Parsley seed oil; B = Pomegranate seed oil; C = *Nigella sativa* oil; D = Linseed oil; G = Canola oil; V = Sesame oil; M = Soybean oil; and K = Control)

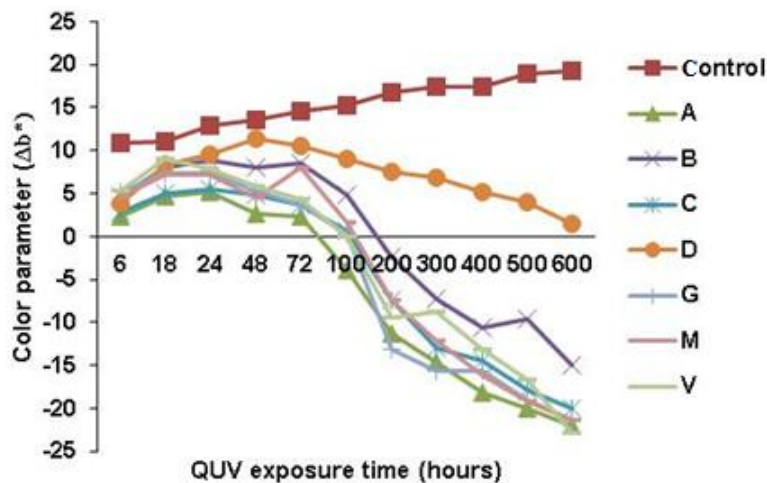


Fig. 3. Color parameter change (Δb^*) of weathered Scots pine (*Pinus sylvestris* L.) samples (A = Parsley seed oil; B = Pomegranate seed oil; C = *Nigella sativa* oil; D = Linseed oil; G = Canola oil; V = Sesame oil; M = Soybean oil; and K = Control)

The smallest change in color (ΔE^*) was determined for the pomegranate seed oil-treated wood samples (B group), probably because of the chemical breakdown of lignin and wood extractives (Feist 1988). All vegetable oil-treated sample groups exhibited lower color changes than the control group after 600 h of exposure.

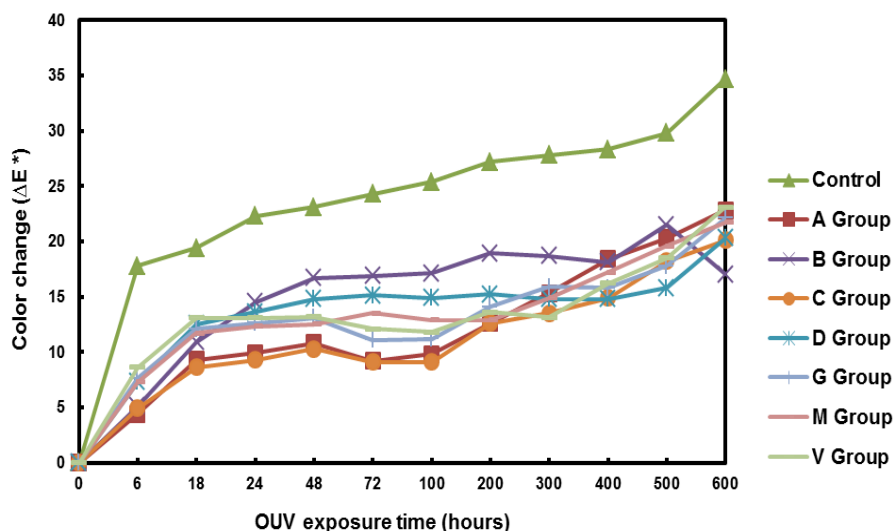


Fig. 4. Color change of weathered Scots pine (*Pinus sylvestris* L.) samples (A = Parsley seed oil; B = Pomegranate seed oil; C = *Nigella sativa* oil; D = Linseed oil; G = Canola oil; V = Sesame oil; M = Soybean oil; and K = Control)

The color changes (ΔE^*) increased quickly within the first 100 h of exposure and had a slight increase after 100 h of weathering (Table 1). When the control samples are compared with all the test samples, it is shown that all vegetable oil treatments prevented color change. When the samples exposed to continuous artificial weathering are compared within the group itself, it is determined that the pomegranate seed oil-treated wood samples (B group) had the lowest color change, followed by the nigella seed oil- (C group) and linseed oil- (D group) treated wood samples. The color change performances of parsley seed, canola, sesame, and soy oil-treated wood samples (A, G, V, and M groups) were very similar after 600 h of artificial weathering (Fig. 4).

The changes in the IR spectra of the wood surfaces demonstrate that UV light modified the chemical structure of wood. The absorption of UV light induced lignin degradation and the photooxidation of $-\text{CH}_2-$ or $-\text{CH}(\text{OH})-$ groups. These reactions are combined with the color changing of wood surfaces (Müller *et al.* 2003). The color of the wood changes to yellow or brown because of the chemical breakdown (photooxidation) of lignin and wood extractives. In addition, the water spray in artificial weathering will leach the water-soluble chemicals from the wood surface during exposure (George *et al.* 2005; Williams 2005). It was already determined that vegetable oil treatments would show less discoloration compared with control samples after artificial weathering. This can be attributed to the formation of complexes between oils and the guaiacyl unit of lignin. It is notable that the vegetable oil treated wood samples differed from control samples with respect to the FTIR-ATR spectra vibration in the region of 1220 to 1270 cm^{-1} (Figs. 6-13). The vegetable oil pretreatments for wood were effective at

photostabilizing lignin, the component of wood that is most susceptible to photodegradation (Evans *et al.* 2002; Temiz *et al.* 2007).

Surface Roughness

Results for the surface roughness of pine wood are shown in Table 2. Oxidized surfaces exhibit higher oxygen content than carbon content, compared to untreated surfaces, thus indicating that weathered wood surfaces contain cellulose with carbonyl groups, whereas the former lignin content was degraded and leached away by water (Feist and Hon 1984; Temiz *et al.* 2005; Nzokou *et al.* 2011). As a result of weathering, most of the solubilized lignin degradation products on the untreated wood (control) are washed out by water spray (Fig. 13). But as can be seen in IR spectra figures, vegetable oil-treated wood (especially the pomegranate seed and linseed oil-treated) samples are protected from lignin degradation during weathering time. The control wood surfaces after UV irradiation and water spray contained several checks, splits, and cracks (Fig. 5). The surface roughness values (R_a and R_z) of pretreated and untreated samples, which indicate the weathering effects, are listed in Table 2. Generally, the surface roughness values of vegetable oil-treated pine wood samples decreased over the irradiation time when compared with the surface roughness values of the control samples. In addition, it was concluded that the surfaces of the pomegranate seed and linseed oil-treated wood samples (B and D groups) were rougher than those of other test groups. However, the roughness of wood is a complex phenomenon because wood is an anisotropic and heterogeneous material, and several factors, such as anatomical differences, growing characteristics, and the machining properties, should be considered in evaluating the surface roughness of wood (Aydin and Colakoglu 2005).

Table 2. Changes in the Surface Roughness after 600 h of Artificial Weathering

Sample Groups	Before QUV Test					After QUV Test				
	R_a	SD	R_z	SD	HG	R_a	SD	R_z	SD	HG
Control (K)	3.3	0.1	28.9	3.9	A	10.6	0.4	64.4	4.4	B
A group	2.4	0.3	23.9	4.4	C	4.5	0.1	36.5	3.4	C
B group	2.6	0.2	22.1	2.8	D	4.7	0.4	40.6	4.8	D
C group	2.9	1.0	24.5	4.8	E	4.6	1.0	36.1	4.9	E
D group	2.5	0.5	20.8	4.9	F	5.4	0.2	41.6	2.6	F
G group	2.4	0.1	22.9	2.2	G	4.7	1.2	37.7	6.4	G
M group	3.2	0.4	29.8	1.1	H	4.6	0.6	37.8	6.6	H
V group	2.2	0.3	20.5	3.9	L	4.4	0.8	36.5	5.6	L

*SD: Standard Deviations. *HG: Homogeneity Group
 *Means with the same letter are not significantly different at $P < 0.05$. Comparisons were done between before and weathering QUV test for each group.
 * A = Parsley seed oil; B = Pomegranate seed oil; C = *Nigella sativa* oil; D = Linseed oil; G = Canola oil; V = Sesame oil; M = Soybean oil; and K = Control

The data were statistically evaluated by multiple-way ANOVA to demonstrate the effect of vegetable oil-treated and untreated wood samples on surface roughness (SR).

Differences between before and after weathering time for each group were not statistically significant at the 0.05 confidence level except for control group. As can be seen from Table 2, the SR parameters after QUV test was found a little bit higher on vegetable oil treated wood than untreated wood (control).

Untreated control samples displayed a high density of large cracks on the surfaces after outdoor weathering. In combination with the erosion of earlywood cells, these cracks produced a tangible surface roughness (Xie *et al.* 2008). In contrast, exposed front surfaces of Scots pine treated with vegetable oils developed fewer and smaller cracks, and this group of wood samples appeared smoother than the untreated ones, as can be seen in Fig. 5. Less cracking also occurred on the surface of the vegetable oil-treated wood samples compared with the untreated control samples; moreover, the vegetable oil-treated wood samples were less deformed, especially with regard to cupping, than the untreated samples (Fig. 5).

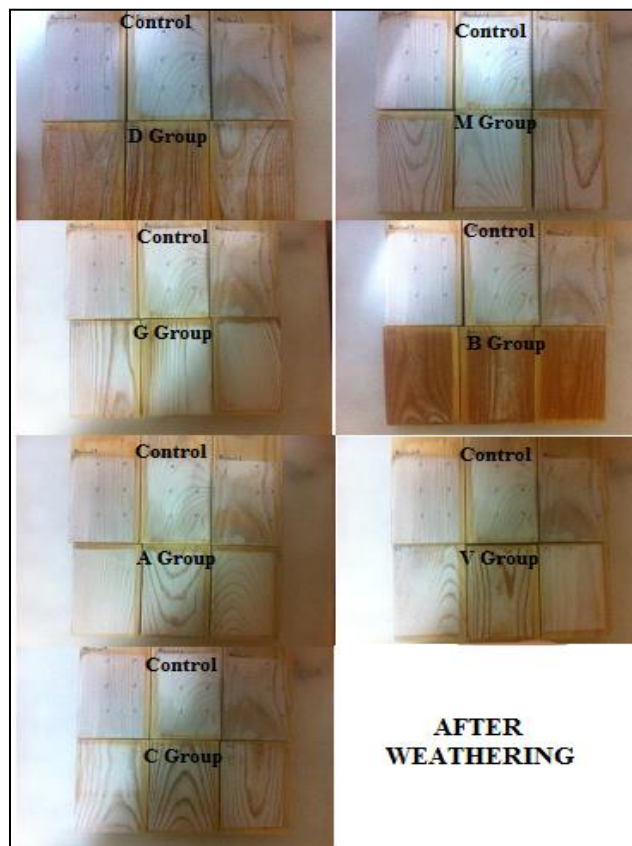


Fig. 5. Surface appearance of vegetable oil-treated and untreated Scots pine samples after 600 h of artificial weathering (A = Parsley seed oil; B = Pomegranate seed oil; C = *Nigella sativa* oil; D = Linseed oil; G = Canola oil; V = Sesame oil; M = Soybean oil; and K = Control).

Results show that when untreated samples were exposed to UV light and water spray cycles, in general fewer cracks developed than was the case with vegetable oil-treated samples exposed to the same cycle; this resulted in lower surface roughness values (R_a and R_z) than for untreated samples. The increase in roughness was attributed to

a stronger erosion of earlywood cells than of latewood cells (washboard effect) and due to crack and check formation. The increased waviness reflects a deformation of the wood samples as a whole (cupping, warping) (Feist and Hon 1984; Feist 1988). It thus follows that the surface roughness of weathered vegetable oil-treated wood samples can be attributed to a reduction in surface cracking and earlywood erosion.

Fourier Transform Infrared Spectroscopy (FTIR-ATR)

FTIR-ATR spectra of treated and untreated samples before and after weathering are shown in Figs. 6, 7, 8, 9, 10, 11, 12, and 13. Significant changes in the intensities of certain absorption bands are noticeable on the FTIR-ATR spectra between 900 cm^{-1} and 1850 cm^{-1} during 600 h of weathering. The assignments of characteristic absorption IR bands of wood samples in the fingerprint region are given in Table 3.

Table 3. Assignments of Absorption IR Spectral Bands in Wood

Fr (cm^{-1})	Group and Class	Assignments and Remarks
1720-40	C=O in unconjugated ketones aldehydes and carboxyl	C=O stretching
1645-60	C=O in para-OH substituted aryl ketones, quinines	Same
1600	C=C in aromatic ring in lignin	Aromatic skeletal vibrations
1510	Same	Same
1425	C=C in aromatic ring CH ₂ in carbohydrates	Same Same
1370	C-H in all components in wood	C-H deformation (bending)
1315	C-H in all components in wood	CH ₂ wagging
1267	CO in lignin and hemicellulose	Guaiacyl ring breathing with CO-stretching
1162-1086	C-O-C in cellulose	Antisym, Bridge oxygen stretching

The absorption at $1710\text{ to }1745\text{ cm}^{-1}$ is characteristic of the non-conjugated carbonyl group, which arises due to C=O stretching (xylan in hemicellulose) (Anderson *et al.* 1991; Temiz *et al.* 2007; Fabiyi *et al.* 2008; Fabiyi *et al.* 2011). The carbonyl absorption peak decreased on the weathered samples compared with the unweathered controls. The change in the band around $1710\text{ to }1745\text{ cm}^{-1}$ is due to the degradation of hemicelluloses. The change in this peak confirms the cleavage of the acetyl side chains in hemicelluloses (Kocaefe 2008; Yıldız *et al.* 2011b). The peak at $1710\text{ to }1740\text{ cm}^{-1}$ decreased significantly after 600 h for all oil-treated wood and control samples. Significant growth in this peak was seen in pomegranate seed oil-treated wood (1736

cm^{-1}) compared with other vegetable oils before weathering. The absorption at 1736 cm^{-1} shifted to 1732 cm^{-1} for pomegranate seed oil-treated wood, and this peak absorption decreased after weathering.

Some researchers have reported that the increase in the carbonyl absorption band at 1743 cm^{-1} is due to UV light degradation. However, a decrease was found for the carbonyl absorption band at 1710 to 1745 cm^{-1} in the present study. This is probably due to applied water on the sample surfaces that leached the carbonyl content formed by UV degradation. These findings have been shown in studies using both UV and water spray systems by several researchers (Nuopponen *et al.* 2004; Temiz *et al.* 2007; Zhang *et al.* 2009).

Changes in wood color reflect chemical changes in wood during photodegradation. The color change is attributed to the carbonyl group of conjugated ketones, aldehydes, and quinones resulting from the modification of lignin and other related compounds (Hergert 1971; Temiz *et al.* 2007; Müller *et al.* 2003; Pandey 2005). Also, UV photons can result in the formation of free radicals, and through the action of oxygen and water, a hydro peroxide can be formed. The presence of free radicals is thought to lead to discoloration reactions and an increase in the carbonyl peak (1740 to 1745 cm^{-1}) (Zhang *et al.* 2009).

It is expected that color change (ΔE) is highest when the carbonyl peak (1740 cm^{-1}) increases. Scots pine wood samples treated with pomegranate seed oil were analyzed for color change (Table 1). Although the absorption at 1740 cm^{-1} of Scots pine wood samples treated with pomegranate seed oil indicated the highest color change, the lowest color changes (ΔE) were determined to be probably due to the antioxidant properties of the pomegranate seed oil in this study. It is known that antioxidants protect wood against free radicals produced by UV photons (Müller *et al.* 2003).

The behavior of the band at 1630 to 1660 cm^{-1} is related to $-\text{C}=\text{O}$ (conjugated aryl ketones), unconjugated $\text{C}=\text{C}$, and water (Anderson 1991; Liu *et al.* 1994; Temiz *et al.* 2006). Pomegranate seed oil, *Nigella sativa* oil, and sesame oil treatments increased, while parsley seed oil, linseed oil, canola oil, and soybean oil treatments reduced, the changes in absorption in the region of 1630 to 1660 cm^{-1} . The decline and shift of the 1650 cm^{-1} band reflects a decrease in absorbed water (Dubey 2010).

The changes in the band around 1508 cm^{-1} were assigned to guaiacyl nuclei in lignin. Guaiacyl nuclei are sensitive to the artificial degradation process (Colom *et al.* 2003). This peak usually appears at 1515 to 1500 cm^{-1} , depending on the ring substituent (Temiz *et al.* 2007). The bands peculiar to lignin at 1508 cm^{-1} disappeared or their intensity decreased after weathering. Temiz *et al.* (2007) reported that oil molecules were associated with lignin and were thus able to influence the absorbance. The increase in these bands is the result of the degradation of the aromatic rings of weathered wood. This is in agreement with the findings of previous studies (Pandey 2005; Temiz *et al.* 2007; Zhang *et al.* 2009). As shown in the figures (Figs. 6, 7, 8, 9, 10, 11, 12, and 13) absorbance at 1540 cm^{-1} was observed after weathering for all oil-treated wood, except for that treated with linseed oil. The reason for this is that the peak at 1510 cm^{-1} shifted to 1540 cm^{-1} (Lesar *et al.* 2011).

The peak of 1457 cm^{-1} , which is assigned to lignin (Huang *et al.* 2012), decreased significantly after weathering for all treatments. Among the wood-constituting polymers,

lignin is the most sensitive one to light (Pandey 2005). The observed increase of these peaks (1508 cm^{-1} and 1457 cm^{-1}) shows in figures that the chemical changes result in a decrease in water absorption and, consequently, an increase in dimensional stability (Sharratt *et al.* 2010; Huang *et al.* 2012). The behavior of these peaks was similar in previous studies (Temiz *et al.* 2006, 2007; Kapaca *et al.* 2011).

The absorbance band in the region of 1420 cm^{-1} is attributed to amorphous and crystalline cellulose (Colom *et al.* 2003). In this study, the FTIR-ATR peak of 1420 cm^{-1} was moderately shifted leftward to 1430 cm^{-1} , which is characteristic of crystalline cellulose, and it became wider with all oil-treated weathered samples. Colom *et al.* (2003) reported that the amorphous area of the cellulosic component was more affected than the crystalline area by the degradation process. Previous studies have shown that the behavior of the band at 1420 cm^{-1} is similar peaks on FTIR-ATR spectra (Colom *et al.* 2003; Temiz *et al.* 2007; Kapaca *et al.* 2011; Lionetto *et al.* 2012).

The change in the band around 1370 cm^{-1} is related to the mass loss of cellulose and hemicelluloses (Emandi *et al.* 2011). Also, according to other study the reduction of this band reflects wood that has become more hydrophobic due to a reduction in the free hydroxyl groups (Kocafe *et al.* 2008). In this study, the intensity of the absorption band at 1370 cm^{-1} was increased by parsley, pomegranate and soybean oils, while this peak was unaffected by linseed, *Nigella sativa*, canola, sesame oil treatments after weathering. Similar findings in this peak were also observed by Temiz *et al.* (2007) for linseed oil- and tall oil-treated wood.

The absorbance band in the region 1321 to 1317 cm^{-1} was assigned to different groups in cellulose (Kapaca *et al.* 2010; Fufa *et al.* 2012). Significant growth in this peak was seen in pomegranate seed oil-, *Nigella sativa* oil-, canola oil-, and sesame oil-treated wood after weathering. These changes can be explained as the result of an increase in the rate of crystalline cellulose and, at the same time, a decrease in the amorphous cellulose area (Colom 2003). The peak around 1156-cm^{-1} is characteristic of amorphous cellulose (Colom 2003). The intensities of the cellulose band around 1156 cm^{-1} were affected by weathering for all treatments. The amorphous area was more affected by the degradation process (Colom *et al.* 2003). The peak at 1100 cm^{-1} is associated with cellulose (Kapaca *et al.* 2010), but the absorption at 1100 cm^{-1} was shifted to 1104 cm^{-1} for this study, and this peak absorption had a limited increase after weathering. However, the intensities of the absorption band at 1104 cm^{-1} were significantly increased by the sesame seed oil treatments. This result indicated that the structure of the cellulose polymer was moderately degraded, except for in the wood treated with sesame seed oil, after weathering.

The peaks around 1029 to 1033 cm^{-1} can be attributed to C-O groups in primary alcohols of lignin (Matuana *et al.* 2011). Also according to Castro *et al.* (2011), a peak of 1030 cm^{-1} could indicate changes in these oxidized functions due to the weathering process. The peak at 1030 cm^{-1} for untreated and all vegetable oil-treated Scots pine wood was very wide and high, and it appeared as a small peak, which can be described as the peak for degradation products in the cases of parsley seed oil and sesame seed oil treatments after weathering. Other vegetable oil-treated wood samples were moderately affected after weathering.

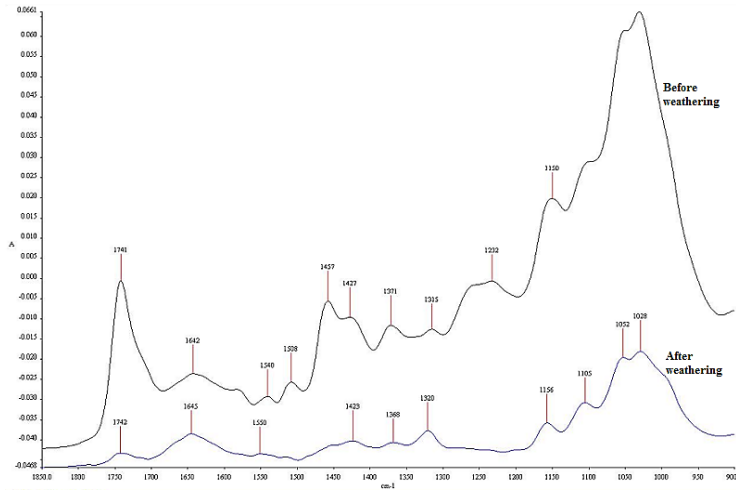


Fig. 6. FTIR-ATR spectra of the parsley seed oil (A) test group

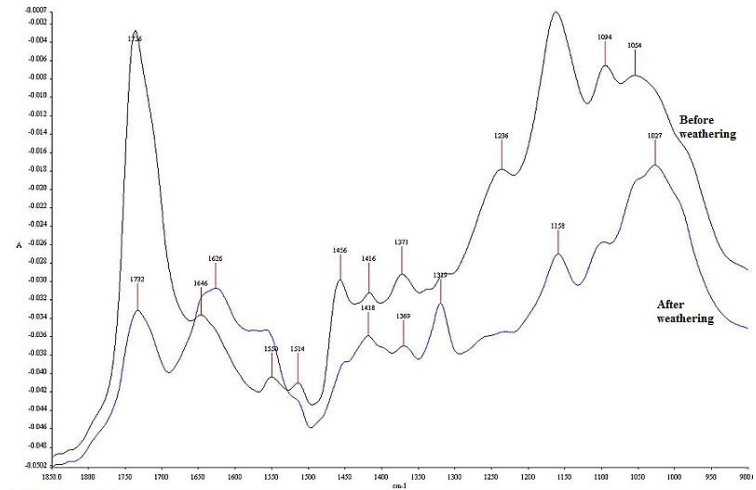


Fig. 7. FTIR-ATR spectra of pomegranate seed oil (B) test group

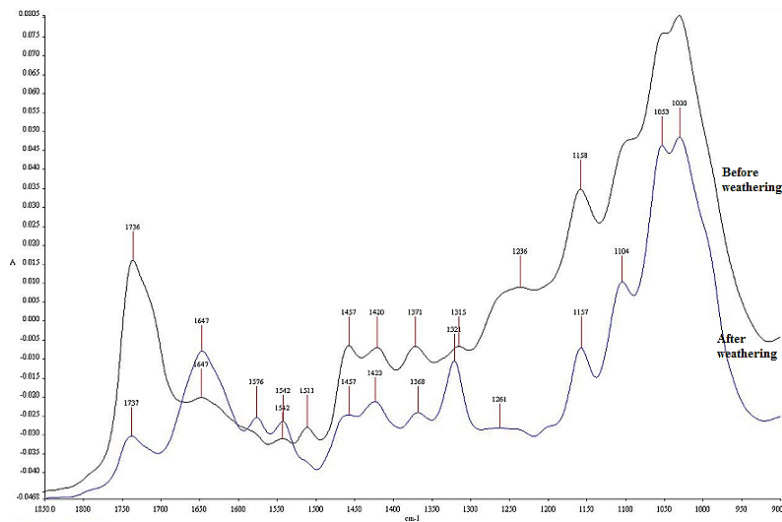


Fig. 8. FTIR-ATR spectra of the *Nigella sativa* oil (C) test group

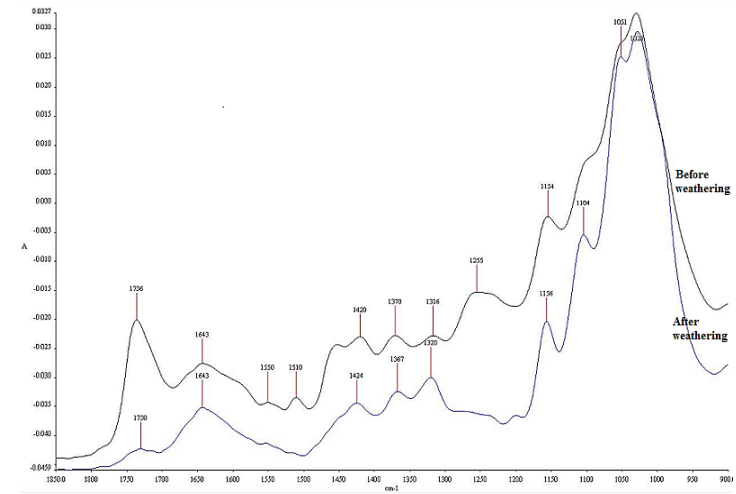


Fig. 9. FTIR-ATR spectra of the linseed oil (D) test group

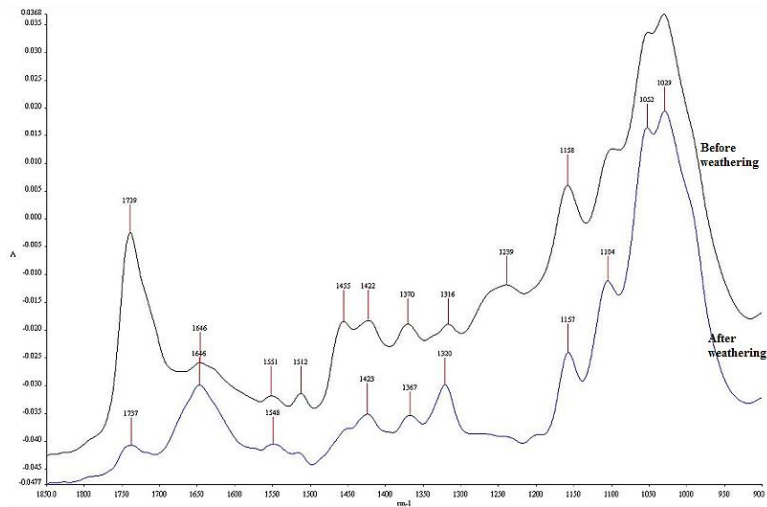


Fig. 10. FTIR-ATR spectra of the canola oil (G) test group

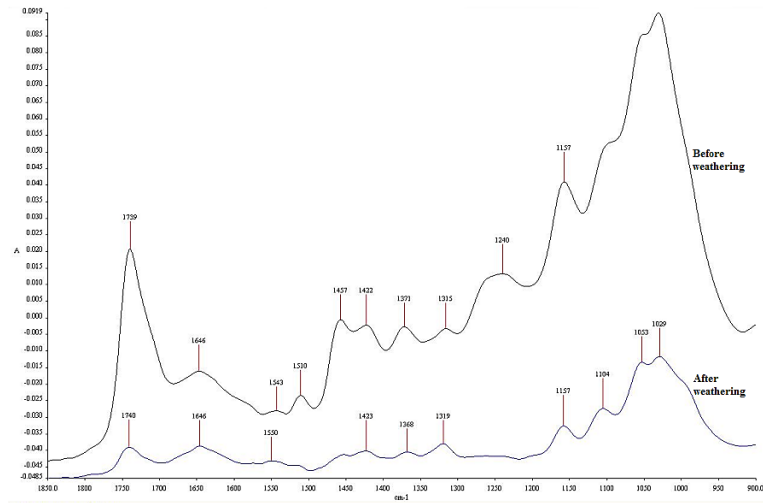


Fig. 11. FTIR-ATR spectra of the soybean oil (M) test group

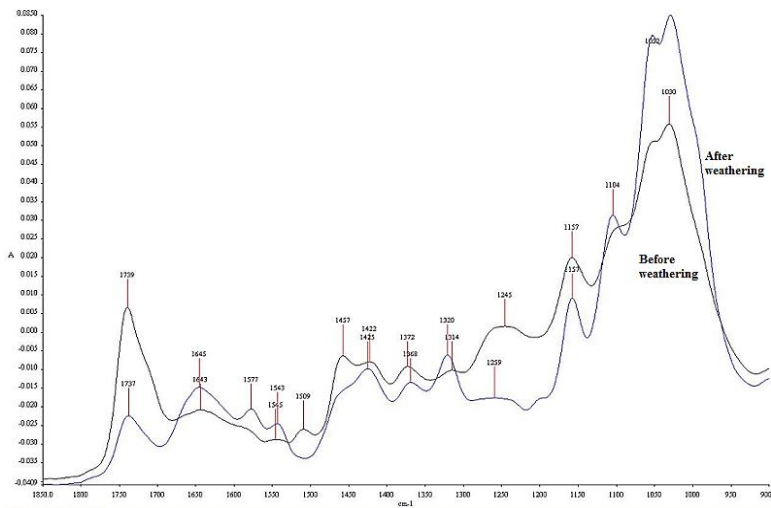


Fig. 12. FTIR-ATR spectra of the sesame oil (V) test group

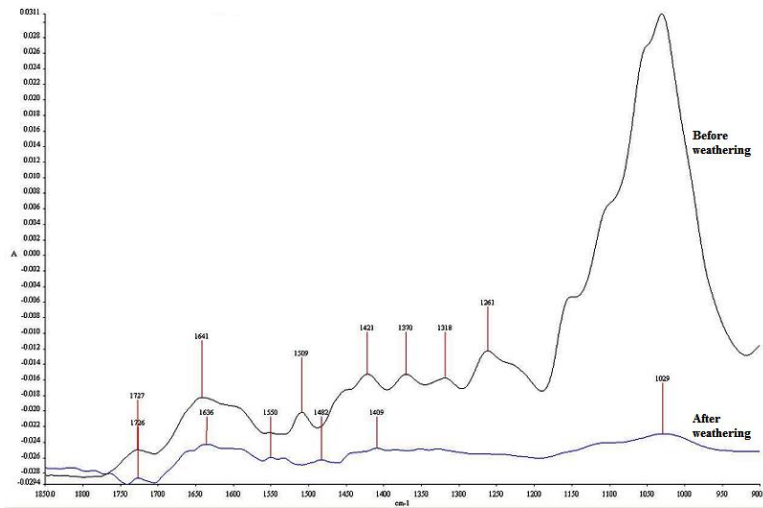


Fig. 13. FTIR-ATR spectra of control group

Compression Strength

In general, the vegetable oil treatments increased the mechanical properties of wood. The effects of vegetable oil treatments on mechanical properties were directly related to several key wood material factors and pretreatment, treatment, and post-treatment processing factors (Tomak 2011; Yıldız *et al.* 2011a). Non-toxic vegetable oils can form a protective layer on the surface of wood cells, which decreases the water uptake of wood. For this reason, such oils demonstrate great potential as wood preservatives (Tomak and Yıldız 2012).

Table 5. Compression Strength Values

Treatment	Mean CS before Weathering (kg/cm ³)	Mean CS after Weathering (kg/cm ³)	Duncan test*
Parsley seed oil	630 (18.8)	618 (17.6)	A
Pomegranate seed oil	721 (21.7)	717 (19.6)	B
<i>Nigella sativa</i> oil	681 (15.9)	674 (14.7)	C
Linseed oil	682 (17.9)	675 (16.9)	D
Canola oil	620 (18.5)	606 (15.5)	A
Sesame oil	650 (15.9)	638 (17.4)	E
Soybean oil	678 (16.7)	668 (15.6)	F
Control	611 (14.3)	588 (13.2)	A

* Values in parentheses are standard deviations. *CS: Compression Strength.
* Different letters indicate a significant difference among groups.

The data were statistically evaluated by one-way ANOVA to demonstrate the effect of vegetable oil-treated and untreated wood samples on compression strength after weathering (CS). Differences between control groups and parsley and sesame oil treated wood groups were not statistically significant at the 0.05 confidence level. But the compression strength of another vegetable oil treated wood groups was found to be a little higher than its control groups. Table 5 gives the compression strength values of different vegetable oils in treated and untreated samples before and after weathering exposure. Table 5 shows the increasing ratios in the compression strength values of treated test specimens compared with those in the control group. The highest value in compression strength was observed in Scots pine treated with pomegranate seed oil, at 721 kg/cm². The lowest compression strength value was seen in the V group, in which the Scots pine was treated with sesame oil. It was determined that there were significant differences among the compression strength values of Scots pine treated with different vegetable oils.

Table 6 shows the decreasing ratios in compression strength values of treated test specimens compared with the non-treated control group (without impregnation) after weathering exposure.

Table 6. Decrease in Compression Strength Values in the Test and Control Sample Groups Due to Weathering Exposure

Treatment	Decrease in compression strength ratio (%)
Parsley seed oil	1.90
Pomegranate seed oil	0.60
<i>Nigella sativa</i> oil	1.02
Linseed oil	1.03
Canola oil	2.30
Sesame oil	1.80
Soybean oil	1.50
Control	3.80

The weathering of wood surfaces by the combined action of light and water results in surface darkening and leads to the formation of macroscopic to microscopic intercellular and intracellular cracks or checks. Cell wall bonds near the wood surface lose their strength (Feist 1988; Bengtsson and Stark 2007). The decrease in compression strength values of test groups treated with vegetable oils was lower than that of the control group. The decrease in the control group was not found to be significant.

CONCLUSIONS

1. In terms of color stabilization, surface roughness, chemical change, and compression strength, the best overall surface protection against weathering were obtained from pomegranate seed oil treatment.
2. All vegetable oil treatments showed fewer color changes compared with the untreated specimens after 600 h of exposure in a weathering test cycle. After weathering, pomegranate seed oil treatment provided the least color change compared with the other pretreatments.
3. FTIR-ATR spectroscopy was used to examine the lignin and carboxyl groups in the wood samples that were untreated or treated with vegetable oils exposed to an artificial QUV with water spray. The change in the intensity of peaks at 1508 to 1510 cm^{-1} and 1710 to 1745 cm^{-1} confirmed the lignin degradation.
4. Changes in surface roughness values during weathering occurred due to photodegradation and the leaching of lignin from exposed wood surfaces. Accordingly, the ability of the vegetable oil treatment to protect lignin from photodegradation may explain why the changes in surface roughness values during artificial weathering were significantly lower than those of untreated controls.
5. The artificial weathering process negatively affected the compression strength of untreated controls more than that of samples treated with vegetable oil. This showed that the samples treated with vegetable oil were more resistant to the artificial weathering process.

6. Future study should focus on the durability properties of vegetable oil-treated hardwood and softwood using impregnation method against weathering and biological destructive in outdoor exposure.

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REFERENCES CITED

- Anderson, E. L., Pawlak, Z., Owen, N. L., and Feist W. C. (1991). "Infrared studies of wood weathering Part I: Softwoods," *Applied Spectroscopy* 45(4), 641-647.
- Aydin, I., and Colakoglu, G. (2005). "Effect of surface inactivation, high temperature drying and preservative treatment on surface roughness and colour of alder and beech wood," *Applied Surface Sci.* 252(2), 430-440.
- Barnes, H. M., and Lindsey, G. B. (2009). "Bending properties of wood treated with a new preservative system," *Biores. Technology* 100, 778-781.
- Bengtsson, M., and Stark, N. M. (2007). "Durability and mechanical properties of silane cross-linked wood thermoplastic composites," *Comp. Sci. and Techn.* 67(13), 2728-2738.
- Castro, K., Princi, E., Proietti, N., Manso, M., Capitani, D., Vicini, S., Madariaga, M. J., and Carvalho, D. L. M. (2011). "Assessment of the weathering effects on cellulose based materials through a multianalytical approach," *Nuclear Instruments and Methods in Physics Research B* 269, 1401-1410.
- Chang, S. T., and Chou, P.-L. (2000). "Photo discoloration inhibition of wood coated with UV-curable acrylic clear coatings and its elucidation," *Poly. Deg. and Stabil.* 69(3), 355-360.
- Chang, H.-T., Cheng, Y.-H., Wu, C.-L., Chang, S.-T., Chang, T.-T., and Su, Y.-C. (2008). "Antifungal activity of essential oil and its constituents from *Calocedrus macrolepis* var. *formosana* Florin leaf against plant pathogenic fungi," *Bioresour. Technol.* 99(14), 6266-6270.
- Chou, P.-L., Chang, H.-T., Yeh, T.- F., and Chang, S.-T. (2008). "Characterizing the conservation effect of clear coatings on photodegradation of wood," *Biores. Technol.* 99(5), 1073-1079.
- Colom, X., Carrillo, F., Nogues, F., and Garriga, P. (2003). "Structural analysis of photodegraded wood by means of FTIR spectroscopy," *Polym. Degrad. Stabil.* 80(3), 543-549.
- Corcione, C. E., and Frigione, M. (2012). "UV-cured polymer-boehmite nanocomposite as protective coating for wood elements," *Progress in Organic Coating.* 74, 781-787.
- Dawson, B. S. W., Singh, A. P., Kroese, H. W., Schwitzer, M. A., Gallagher, S., Riddiough, S. J., and Wu, S. (2008). "Enhancing exterior performance of clear coatings through photostabilization of wooden surfaces. Part 1: Treatment and characterization," *J. Coat. Res.* 5(2), 193-206.

- Decker, C., Masson, F., and Schwalm, R. (2004). "Weathering resistance of water based UV-cured polyurethane-acrylate coating," *Polym. Degrad. Stabil.* 83(2), 309-320.
- Dubey, K. M. (2010). "Improvements in stability, durability and mechanical properties of radiata pine wood after heat-treatment in a vegetable oil," Ph.D. Thesis, University of Canterbury, New Zealand, p. 80.
- Evans, P. D. (2009). "Review of the weathering and photostability of modified wood," *Wood Material Sci. Eng.* 4(1-2), 2-13.
- Evans, P. D., Wallis, A. F. A., and Owen, N. L. (2000). "Weathering of chemically modified wood surfaces," *Wood Sci. Technol.* 34(2), 151-165.
- Evans, P. D., Owen, N. L., Schmid, S., and Webster, R. D. (2002). "Weathering and photostability of benzoylated wood," *Polym. Degrad. Stabil.* 76(2), 291-303.
- Emandi, A., Vasiliu, C.I., Budrugaec, P., and Stamatina, I. (2011). "Quantitative investigation of wood composition by integrated FT-IR and thermogravimetric methods," *Cell. Chem. Technol.* 45(9-10), 579-584.
- Fabiyi, J. S., McDonald, G. A., Wolcott, M. P., and Griffiths, P. R. (2008). "Wood plastic composites weathering: Visual appearance and chemical changes," *Polym. Degrad. Stabil.* 93, 1405-1414.
- Fabiyi, J. S., McDonald, G. A., Morrell, J. J., and Freitag, C. (2011). "Effect of wood species on durability and chemical changes of fungal decayed wood plastic composites," *Composites: Part A* 42, 501-510.
- Feist, W. C. (1988). "Outdoor wood weathering and protection," in: *Archaeological Wood: Properties, Chemistry, and Preservation*, R. M. Rowell and B. R. James (eds.), Washington D.C., Chapter 11.
- Feist, W. C., and Hon, D. N.-S. (1984). "Chemistry of weathering and protection," in: *The Chemistry of Solid Wood*, R. M. Rowell (ed.), Advances in Chemistry Series 207, Washington, DC: American Chemical Society, Chapter 11.
- Forsthuber, B., and Gröll, G. (2010). "The effect of HALS in the prevention of photo-degradation of acrylic clear topcoats and wooden surfaces," *Polym. Degrad. Stabil.* 95(5), 746-755.
- Forsthuber, B., Schaller, C., and Gröll, G. (2013). "Evaluation of the photo stabilizing efficiency of clear coatings comprising organic UV absorbers and mineral UV screeners on wood surfaces," *Wood Sci. Technol.* 47(2), 281-297.
- Fufa, M. S., Jelle, B. P., Hovde, P. J., and Rorvik, P. M. (2012). "Coated wooden claddings and the influence of nanoparticles on the weathering performance," *Progress in Organic Coatings* 75(1-2), 72-78.
- George, B., Suttie E., Merlin A., and Deglise, X. (2005). "Photodegradation and photostabilisation of wood-The state of the art," *Polym. Degrad. Stabil.* 88(2), 268-274.
- Hergert, H. (1971). "FTIR spectra," in: Sarkanen, K. U., and Ludwig, C. H., *Lignins: Occurrence, Formation, Structure, and Reaction*, New York: Wiley-Interscience, Chapter 7.
- Hill, S. C. A. (2011). "Wood modification: An update," *BioResources* 6(2), 918-919.
- Huang, X., Kocaefe, D., Kocaefe, Y., Boluk, Y., and Krause, C. (2012). "Structural analysis of heat-treated birch (*Betula papyrifera*) surface during artificial weathering," *Applied Surface Sci.* 264, 117-127.

- Hyvönen, A., Piltonen, P., and Niinimäki, J. (2006). "Tall oil/water-emulsions as water repellents for Scots pine sapwood," *Holz als Roh-und Werkstoff* 64, 68-73.
- Kapaca, E., Cirule, D., Grinins, J., Bikovens, O., and Andersons, B. (2011). "Chemical changes of untreated and hydrothermally modified hardwood after artificial weathering," *Proceedings of the 7th meeting of the Nordic-Baltic Network in Wood Material Science & Engineering (WSE)*, 37-42.
- Kartal, S. N., Hwang, W.-J., Imamura, Y., and Sekine Y. (2006). "Effect of essential oil compounds and plant extracts on decay and termite resistance of wood," *Holz als Roh-und Werkstoff* 64(6), 455-461.
- Kocafe, D., Poncsak, S., and Boluk, Y. (2008). "Effect of thermal treatment on the chemical composition and mechanical properties of birch and aspen," *BioResources* 3(2), 517-537.
- Lesar, B., Pavlic, M., Petric, M., Skapin, A. S., and Humar, M. (2011). "Wax treatment of wood slows photodegradation," *Polymer Degradation and Stability* 96(7), 1271-1278.
- Lionetto, F., Sole, D. R., Cannoletta, D., Vasapollo, G., and Maffezzoli, A. (2012). "Monitoring wood degradation during weathering by cellulose crystallinity," *Materials* 5(10), 1910-1922.
- Lionetto, F., and Frigione, M. (2012). "Effect of novel consolidants on mechanical and absorption properties of deteriorated wood by insect attack," *J. Cultural Heritage* 13, 195-203.
- Liu, R., Ruddick, N. R. J., and Jin, L. (1994). "The influence of copper (II) chemicals on the weathering of treated wood, Part I. ACQ treatment of wood on weathering," The 25. IRG Annual Meeting; Stockholm.
- Matuana, L. M., Jin, S., and Stark, M. N. (2011). "Ultraviolet weathering of HDPE/wood-flour composites coextruded with a clear HDPE cap layer," *Polym. Degrad. Stabil.* 96(1), 91-106.
- Müller, U., Rätzsch, M., Schwanninger, M., Steiner, M., and Zöbl, H. (2003) "Yellowing and IR-changes of spruce wood as result of UV-irradiation," *J. Photochem. and Photobio. B: Biology* 69, 97-105.
- Nakayama, F. S., and Osbrink, W. L. (2010). "Evaluation of kukui oil (*Aleurites moluccana*) for controlling termites," *Ind. Crops Prod.* 31(2), 312-315.
- Nuopponen, M., Wikberg, H., Vuorinen, T., Sirkka, L. M., Jamsa, S., and Vitaniemi, P. (2004). "Heat-treated softwood exposed to weathering," *J. Appl. Poly. Sci.* 91(1), 2128-2134.
- Nzokou, P. (2004). "The influence of wood extractives on durability properties of hardwood and softwood species exposed to artificial weathering," ProQuest Dissertations and Theses, Doctorate Thesis, Michigan State University.
- Nzokou, P., Kamdem, D. P., and Temiz, A. (2011) "Effect of accelerated weathering on discoloration and roughness of finished ash wood surfaces in comparison with red oak and hard maple," *Progress in Organic Coating* 71(4), 350-354.
- Ozgenç, O., Hiziroglu, S., and Yıldız, U. C. (2012). "Weathering properties of wood species treated with different coating applications," *BioResources* 7(4), 4875-4888.

- Palanti, S., and Susco, D. (2004). "A new wood preservative based on heated oil treatment combined with triazole fungicides developed for above-ground conditions," *J. Intl. Biodeg. Biodeg.* 54(4), 337-342.
- Pandey, K. K. (2005). "Study of the effect of photo-irradiation on the surface chemistry of wood," *Polym. Degrad. Stabil.* 90(1), 9-20.
- Pandey, K. K., and Chandrashekar, N. (2006). "Photostability of wood surfaces esterified by benzoyl chloride," *J. Appl. Polymer Sci.* 99(5), 2367-2374.
- Saha, S., Kocaefe, D., Krause, C., and Larouche, T. (2011). "Effect of titania and zinc oxide particles on acrylic polyurethane," *Prog. Organic Coatings* 70(4), 170-177.
- Sharratt, V., Hill, C. A. S., Zaihan, J., and Kint, D. P. R. (2010). "Photodegradation and weathering effects on timber surface moisture profiles as studied using dynamic vapour sorption," *Polym. Degrad. Stabil.* 95, 2659-2662.
- Sen, S., and Yalçın, M. (2010). "Activity of commercial still waters from volatile oils production against wood decay fungi," *Maderas Ciencia Tecnol.* 12(2), 127-133.
- Temiz, A., Yıldız, U. C., Aydın, I., Eikenes, M., Alfredsen, G., and Çolakoğlu, G. (2005). "Surface roughness and color characteristics of wood treated with preservatives after accelerated weathering test," *Applied Surface Sci.* 250(1-4), 35-42.
- Temiz, A., Terziyev, N., Jacobsen, B., and Eikenes, M. (2006). "Weathering, water absorption and durability of silicon, acetylated, and heat-treated wood," *J. Applied Polym. Sci.* 102(5), 4506-4513.
- Temiz, A., Terziyev, N., Eikenes, M., and Hafren, J. (2007). "Effect of accelerated weathering on surface chemistry of modified wood," *Applied Surf. Sci.* 253(12), 5355-5362.
- Tomak, D. E. (2011). "The effect of oil heat treatment and emulsion techniques on decreasing the leachability of boron in wood," Ph.D. Thesis, Karadeniz Technical University, Forest Industrial Engineering, Trabzon, Turkey.
- Tomak, D. E., and Yıldız, U. C. (2012). "Applicability of vegetable oils as a wood preservative," *Artvin Coruh University Faculty of Forestry Journal* 13(1), 142-157.
- Treu, A., Militz, H., and Breyne, S. (2001). "Royal-treatment—Scientific background and practical application," *COST Action E22 Conference: Environmental Optimization of Wood Protection*; Reinbek, Germany.
- Van Acker, J., Nurmi, A., Gray, S., Militz, H., Hill, C., Kokko, H., and Rapp, A. (1999). "Decay resistance of resin treated wood," *The International Research Group on Wood Preservation 30th Annual Meeting*, Rosenheim, Germany, 6-11 June 1999.
- Williams, R. S. (2005). "Weathering of wood," *Handbook of Wood Chemistry and Wood Composites*, Forest Products Laboratory, USA, Chapter 7.
- Xie, Y., Krause, A., Militz, H., and Mai, C. (2008). "Weathering of uncoated and coated wood treated with methylated 1,3-dimethylol-4,5-dihydroxyethyleneurea (mDMDHEU)," *Holz Roh Werkst.* 66(6), 455-464.
- Yamaguchi, T., Fujita, K., and Sakai, K. (1999). "Biological activity of extracts from *Cupressus lusitanica* culture," *J. Wood Sci.* 45(2), 170-173.
- Yang, X. F., Vang, C., Tallman, D. E., Bierwagen, G. P., Croll, S. G., and Rohlik, S. (2001). "Weathering degradation of a polyurethane coating," *Polym. Degrad. Stabil.* 74(2), 341-351.

- Yıldız, S., Yıldız, U. C., and Gezer, E. D. (2011a). "Effect of some pre-treatments on copper content of refractory spruce wood treated with CBA-A," The International Research Group on Wood Preservation 40th Annual Meeting; Beijing, China.
- Yıldız, S., Yıldız, U. C., and Tomak, E. D. (2011b). "The effects of natural weathering on the properties of heat-treated alder wood," *BioResources* 6(3), 2504-2521.
- Zhang, J., Kamdem, D. P., and Temiz, A. (2009). "Weathering of copper amine treated wood," *Applied Surface Sci.* 256(3), 842-846.

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