

# Characterization and photodegradation mechanism of three Algerian wood species

Yasmina Ouadou<sup>1,2</sup> · Djamel Aliouche<sup>1</sup> · Marie-France Thevenon<sup>3</sup> · Mohamed Djillali<sup>4</sup>

Received: 5 September 2016 / Accepted: 30 January 2017 / Published online: 14 March 2017  
© The Japan Wood Research Society 2017

**Abstract** Aging is the irreversible change of mechanical, physical, and chemical properties of materials; the main objective of this work was to study the photochemical degradation and structural changes of three major Algerian wood species. For this, we evaluated the photodegradation mechanism for Maritime Pine (*Pinus pinaster*), zeen oak (*Quercus canariensis*), and afares oak (*Quercus afares*) by accelerated aging in a Xenon test chamber. Degradation of the samples was established by an initial color change (after 30 h exposure), followed by roughening and cracking (120 h exposure) as translated by scanning electron microscopy and Fourier transform infrared spectroscopy. The discoloration of irradiated wood samples was primarily related to the decomposition of lignin which is the key structure in wood photodegradation. As expected, a decrease in mechanical properties was observed; for all samples, the modulus of elasticity decreased after aging, indicating that the wood specimens loss some of their stiffness.

**Keywords** Zeen oak · Afares oak · Maritime pine · Photodegradation · UV accelerated aging

## Introduction

In Algeria, productive forests cover only a third of the national forest patrimony representing 4.1 million hectares with an afforestation rate of 16.4% in the north and only 1.7% if the arid Saharan regions are also considered. These afforestation rates are obviously insufficient to ensure the physical balance and biological balance. The predominant species are Aleppo pine (*Pinus halepensis*) located mainly in semi-arid areas, and the zeen oak (*Quercus canariensis*) and afares oak (*Quercus afares*) occupy the freshest areas in the cork oak forest. The maritime pine (*Pinus pinaster*) is present naturally in the northeast of the country. These wood species are the first group of so-called economic forests; they represent an annual opportunity of about 460,000 m<sup>3</sup> for timber industry. Nowadays, the local timber production has increased continuously from 1993 to 240,000 m<sup>3</sup>. Industrial round wood requirements which are currently 1.3 million m<sup>3</sup> are supported only up to about 18% by this local production; the rest is covered by imports [1, 2]. The characterization and preservation of the local wood are important not only for its suitable utilization but also for the Algerian market promotion that is necessary for wood derived from native plantations.

Wood is a natural polymer composite and an excellent building material with a high strength/density ratio. The specific formations of the wooden tissues imply significant mechanical and physical properties. Their low density is accompanied by desirable mechanical strength. With these advantages, wood is easy to process and widely used as structural engineering material. The combination of cellulose, hemicelluloses, and lignin naturally arranged into tubular structures forms a cylindrically layered composite. Besides these three main components, the extractives play important role in colouring the timber [3].

✉ Yasmina Ouadou  
ouadouyasmina@yahoo.fr

<sup>1</sup> Laboratory of Polymers Treatment and Forming, University M'Hamed Bougara, 35000 Bouverdes, Algeria

<sup>2</sup> Research Unit of Materials, Processes and Environment, Faculty of Science Engineering, M'Hamed Bougara University of Bouverdes, 35000 Bouverdes, Algeria

<sup>3</sup> Research Unit, BioWooEB, TAB-114/16, CIRAD, 34398 Montpellier Cedex 5, France

<sup>4</sup> National Center for Textile and Leather, Bouverdes, Algeria

Because of its organic nature, wood undergoes abiotic and biotic degradations that cause the gradual structure decay. The biotic degradation consists of microorganisms attacks. The abiotic degradations are usually surface phenomena and are influenced by the solar radiation, rainfall, heat, humidity content of the surrounding air, presence of oxygen, and air pollutants. These last degradations processes depend closely on the conditions where wood is used and stored. Aging of wood in natural conditions occurs in consequence of various external factors in the presence of air oxygen. These environmental factors such as solar irradiation, moisture, and temperature initiate weathering or oxidative degradation of wood products and the weathering behavior was affected by the wood species [4].

The ultraviolet light (UV light) effect of solar radiation is one of the most effective parameters amongst all environmental factors that contribute to the weathering process of wood [5]. These combined effects lead to decomposition of the surface layers, to color changes, aesthetical value, and at long term resulted in a checkered gray surface [6].

The most sensitive molecule is the lignin macromolecule, because it is good absorber of ultraviolet light. Chemical analyses showed that the deterioration of light irradiated wood is primarily related to the decomposition of lignin [7–9]. When stored outdoor and exposed to direct sunlight, wood material undergoes chemical degradation caused by UV radiation due to its lignin content. The direct investigation of photodegradation caused by sunlight is difficult. Exposure to direct sunlight is not repeatable under the same conditions. Rainfall, air humidity, and temperature changes are uncontrollable parameters. It means that the irradiation time and intensity (the most important parameters) are not exactly known during outdoor solar radiation. Therefore, the effect of light irradiation is mostly investigated using artificial light sources. Wood exposed to solar radiation is subjected to surface degradation by the initial color changes and then mechanical breakdown occurs [10].

Photodegradation as well as oxidation processes can be simulated with artificial aging methods like the lightfastness (xenotest), UV irradiation, in a Q-panel laboratory Ultraviolet testing (QUV), accelerated weathering tester, and thermal treatment, respectively [11–14].

The main objective of our work was to study the effects of wood aging by UV radiation for three species (maritime pine, zeen oak, and afares oak) in terms of photodegradation mechanism. For this purpose, the aging mechanism of wood has been discussed after artificial aging in a Xenon arc chamber, which is a kind of simulated aging. These tests allowed us to study the mechanical behavior and structural changes of the wood surface samples before and after aging. Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM) were used to display changes between aged and non-aged wood. Mechanical

tests (tensile strength, strain, and modulus of elasticity) were also carried out to assess the mechanical behavior of the aged samples.

## Materials and methods

### Materials

The materials studied were randomly collected from three species of wood from the north-east Algeria. The cut was made on trees of 40–50 cm in diameter; samples were debited as trunks of 150 cm height, and then cut into slices of 50 cm thick. The wood species tested were as follows:

Zeen oak (*Q. canariensis*), age  $\approx$ 90 years.

Afares oak (*Q. afares*), age  $\approx$ 130 years.

Maritime pine (*P. pinaster*), age  $\approx$ 80 years.

For each wood species, a batch of washers is unrolled in sheets and sapwood specimens of  $(0.15 \times 4 \times 14 \text{ cm}^3)$ , T, R, and L) are cut out for the accelerated UV aging tests.

### Accelerated aging tests

The accelerated aging of the wood samples was studied on a Xenotest apparatus Heraeus Atlas 150 S equipped with a 1500 W xenon arc lamp. Seven infrared (IR) and ultraviolet (UV) filters are used to simulate the total sunlight spectrum through a prism ( $380 < \lambda < 750 \text{ nm}$ ); the radiation energy generated is about  $1030 \text{ W/m}^2$ . The samples ( $0.15 \times 4 \times 14 \text{ cm}^3$ ) were stabilized until constant mass in a conditioned room [ $20^\circ\text{C}$  and 65% relative humidity (RH)], positioned in rotating frames of the xenon lamp, and then irradiated in air. The wood specimens were exposed at a distance of 10 cm from the light source. The temperature and humidity were controlled at  $22\text{--}24^\circ\text{C}$  and 54–65% relative humidity during irradiation. Samples were exposed during various periods of time, ranging from 0 to 120 h. For all procedures, the tests are carried out in triplicate.

### Characterization methods

- Chemical composition: before characterization, the chemical composition of each wood species has been assessed; for this, sawdust was used. The dry mass consists mainly of three polymers which are: cellulose, lignin, and hemicelluloses. The ash (mineral residues) and extractives such as terpenes, tannins, and oils represent only a small fraction of the chemical composition. Sawdust raw materials were characterized according to the following standard methods: ash (TAPPI T211

om-93) [15], lignin (ASTM D1106-96 2007) [16], holo-cellulose, and  $\alpha$ -cellulose [17].

- The photochemical degradation of the specimens was followed first by visual aspect (discoloration). The structural changes were then studied by FTIR analysis and SEM, and mass loss and mechanical properties were also determined before and after aging.
- Infrared spectra were recorded using a Bruker Alpha FTIR spectrometer, with 40 scans in the analytical region of 4000–400  $\text{cm}^{-1}$ , with a 2  $\text{cm}^{-1}$  resolution. Powdered sawdust of untreated and irradiated samples was prepared in a KBr phase.
- In microscopic analysis, the samples microstructure was studied using Scanning Electron Microscope Stereoscan Leica 440 (acceleration voltage 300 V–30 kV). Before examination, the powder samples were coated with gold to make them conductive.
- The mass loss of the samples after irradiation was calculated from the following equation:

$$\text{ML} = \frac{m_b - m_a}{m_b} \times 100\%, \quad (1)$$

where ML is the percent mass loss,  $m_a$  (g) the sample mass after irradiation, and  $m_b$  (g) the mass before irradiation. ML represents average of ten assessments.

- Mechanical characteristics were measured on Zwick Roell ProLine Testing Machine 10 kN, equipped with testXpert applications software.

Mechanical tests were carried out on sheets ( $0.15 \times 4 \times 14 \text{ cm}^3$ ) of samples before and after 120 h exposure period. The ultimate tensile stress of wood was

**Table 1** Chemical composition (% dry matter) of wood materials

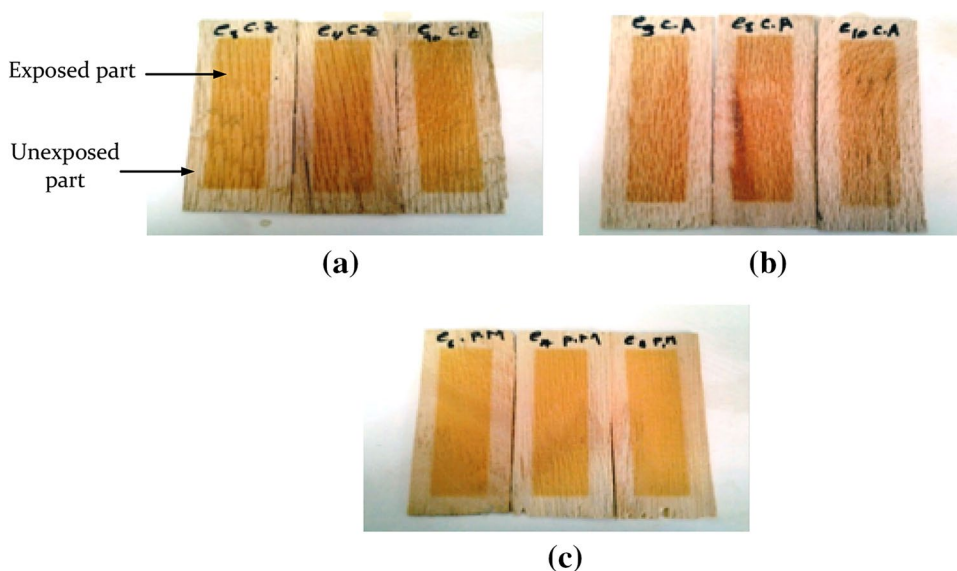
| Sample         | Zeen oak        | Afares oak      | Maritime pine   |
|----------------|-----------------|-----------------|-----------------|
| Cellulose      | 50.5 $\pm$ 0.08 | 54.2 $\pm$ 0.07 | 50.6 $\pm$ 0.05 |
| Hemicelluloses | 24.5 $\pm$ 0.03 | 23.4 $\pm$ 0.05 | 19.1 $\pm$ 0.01 |
| Lignin         | 22.6 $\pm$ 0.02 | 19.6 $\pm$ 0.3  | 27.1 $\pm$ 0.03 |
| Extractives    | 1.2 $\pm$ 0.4   | 1.7 $\pm$ 0.02  | 2.8 $\pm$ 0.4   |
| Ash            | 0.6 $\pm$ 0.1   | 0.9 $\pm$ 0.01  | 0.3 $\pm$ 0.03  |

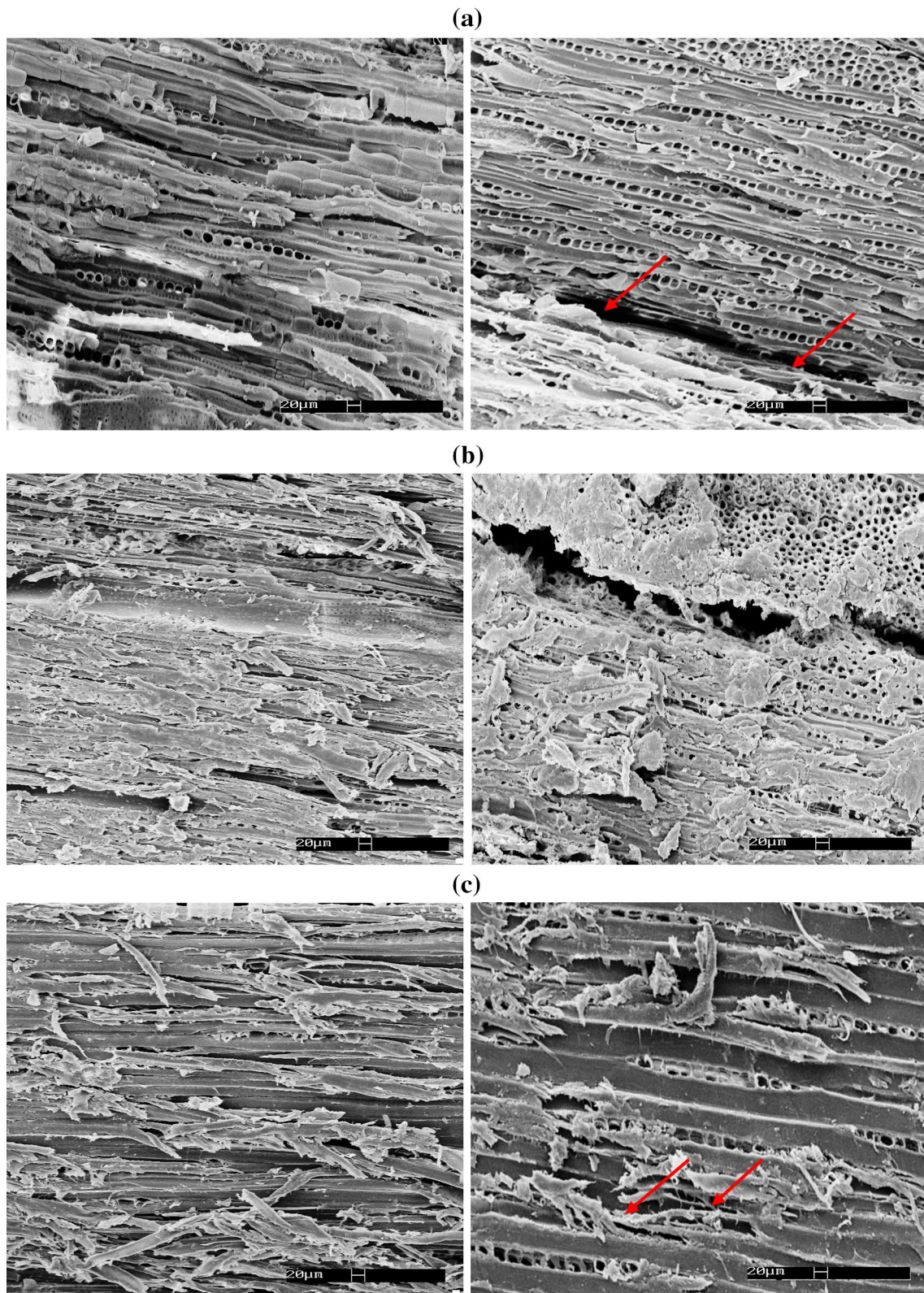
specified by measuring the breaking load applied statically along the longitudinal axis of the test piece. The maximum stress applied was 80 MPa. Ten tests were averaged for each wood species.

## Results and discussion

The results of the lignocellulosic compositions are shown in Table 1. Results are calculated as % w/w with respect to oven dried raw material. It seems that the wood chips of Afares oak contain more cellulose and less lignin than Zeen oak, while the Maritime pine present the highest lignin content and the lower ratio of hemicellulose. Amongst all constituents of wood samples, cellulose, hemicelluloses, and lignin, only lignin absorbs relatively strongly in the UV/visible region. Therefore, the light induced degradation of wood is mainly caused by photochemical reactions occurring in lignin. Wood discoloration has been associated with the formation of carbonyl groups and degradation of lignin [18]; this latter contains especially guaiacoxyl: the guaiacoxyl radical is formed by degradation of the guaiacyl chromophore group [10].

**Fig. 1** Discoloration of the inner part of wood specimens after 120 h UV aging: **a** zeen oak; **b** afares oak; **c** maritime pine

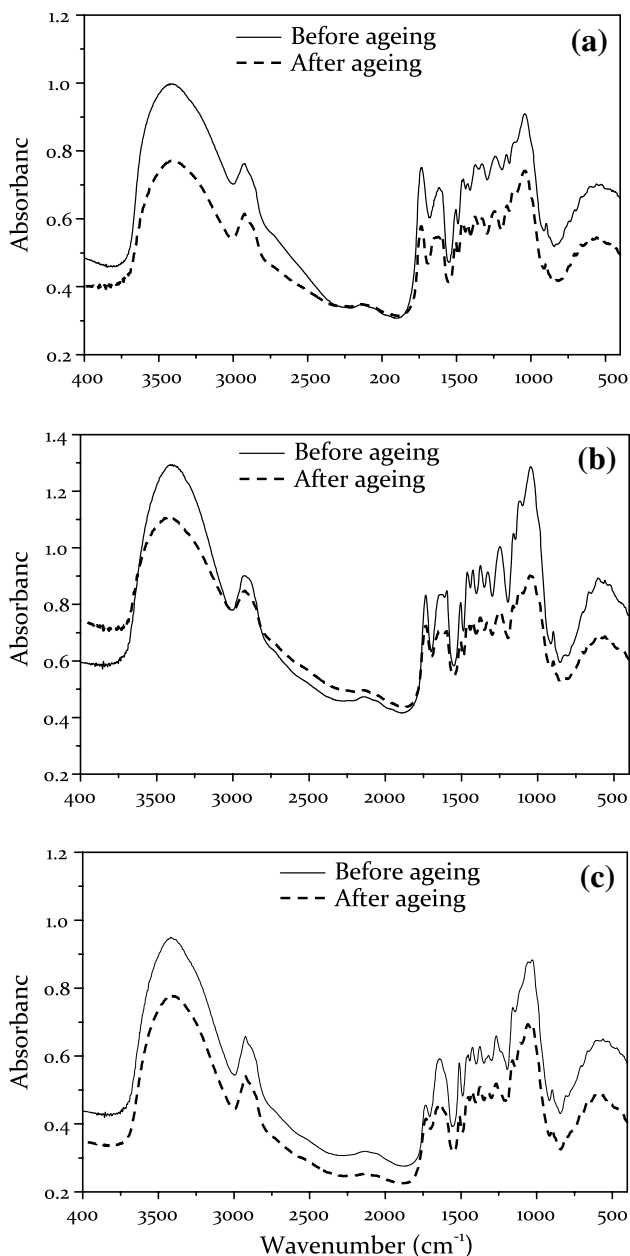




**Fig. 2** Microstructure of wood specimens before (*left*) and after (*right*) 120 h UV aging: **a** zeen oak; **b** afares oak; **c** maritime pine. *Arrows* show the micro-cracks in the wood structure

In this work, artificial accelerated aging was adopted to test surface light resistance of our wood species. Several methods and devices for artificial weathering have been developed to accelerate the testing of wood with the aim of increasing reproducibility. Xenon arc chamber match better to the solar spectrum than other devices with UV fluorescent lamps [19].

Figure 1 shows the discoloration effect of UV aging on wood samples. Photodegradation of the samples is

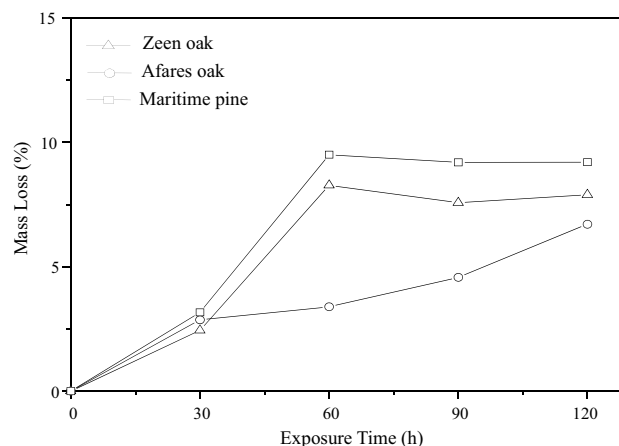


**Fig. 3** FTIR spectra of wood specimens before and after 120 h UV exposure: **a** zeen oak; **b** afares oak; **c** maritime pine

manifested by an initial color change, followed by roughening and cracking as shown by SEM microscopy. However, the processes of decomposition and crosslinking in wood include a wide variety of interrelated ionic, radical-chain, and molecular reactions. Scission of chemical bonds can take place leading to a production of radicals; this process is claimed to be responsible for yellowing of wood [20, 21]. The color change due to photodegradation is linearly dependent on the appearance of the carbonyl groups on the surface of the material but not the disappearance of the benzene ring of the lignin [22]. The decisive role in wood aging is performed by competitive chemical processes of decomposition and crosslinking of macromolecules in this natural polymer composite.

Figure 2 shows the SEM images of the samples structure before (pictures in left) and after (right pictures) UV irradiation. The action of light leads to formation of microscopic cracks or checks. Cells lose bond strength with adjacent cells near the wood surface because of the degradation of lignin. The observed changes can be then summarized as formation of micro-cracks and destruction of the various layers of the cell wall. Microscopic changes accompany the color changes and chemical changes of wood during degradation.

Spectroscopy was used for studying the chemical changes in wood caused by light irradiation. FTIR spectroscopy is used as a powerful technique nowadays. In case of wood, the fingerprint region is located between 800 and 1800  $\text{cm}^{-1}$ . Figure 3 shows the FTIR spectra of the wood samples before and after aging. The overall FTIR spectrum of both aged and crude wood polymers indicates that a number of spectral features appear to be sensitive to irradiation. All bands assigned only to lignin component, such as 1590, 1505, and 1465  $\text{cm}^{-1}$  for the afares and zeen oak woods in Fig. 3a and b, and 1505, 1630, and 1450  $\text{cm}^{-1}$  for maritime pine in Fig. 3c, decrease significantly as a



**Fig. 4** Variation of wood percent mass loss vs. UV time exposure

**Table 2** Mechanical parameters of wood species before and after accelerated UV aging

| Wood species  | UV <sup>a</sup> aging | Strength break $F$ (MPa) | Strain break $\sigma$ (%) | MOE <sup>b</sup> (MPa) | Density (g/cm <sup>3</sup> ) |
|---------------|-----------------------|--------------------------|---------------------------|------------------------|------------------------------|
| Zeen oak      | Before                | 43.2 ± 14.3              | 1.8 ± 0.9                 | 3964.2 ± 407.2         | 0.894 (0.075)                |
|               | After                 | 42.0 ± 16.5              | 3.2 ± 1.1                 | 3233.2 ± 369.2         |                              |
| Afares oak    | Before                | 64.3 ± 11.6              | 2.9 ± 0.5                 | 4155.0 ± 319.3         | 0.825 (0.059)                |
|               | After                 | 58.6 ± 13.5              | 4.1 ± 0.7                 | 3036.8 ± 439.7         |                              |
| Maritime pine | Before                | 77.1 ± 22.7              | 2.8 ± 0.7                 | 4948.1 ± 366.8         | 0.638 (0.026)                |
|               | After                 | 66.8 ± 20.1              | 3.9 ± 0.8                 | 3713.6 ± 389.3         |                              |

<sup>a</sup>Ultraviolet light<sup>b</sup>Module of elasticity

result of the irradiation process. This result indicates that the structure of the lignin of the three wood samples was degraded to a significant extent.

The evolution of the lignin loss is best followed by the band at 1505 cm<sup>-1</sup> of the three woods, assigned to the partial decomposition of lignin, the decrease in the intensity of this peak indicated degradation of lignin during the irradiation process. Other authors have investigated the difference FTIR spectra recorded for lignin from irradiated and non-irradiated wood [23, 24]. The decrease observed for this band is significantly larger in the case of maritime pine than in the case of oaks, after 120 h of treatment.

For the softwood, the decrease of the absorbance at 1740 cm<sup>-1</sup> assigned to C=O stretching vibration of acetyl or carboxylic acid groups was compensated by an increase in the same groups derived mainly from lignin. The behavior of the band at 1430 cm<sup>-1</sup>, which is characteristic of crystallized cellulose I, indicates that the amorphous area of the cellulosic component of both woods is more affected by the degradation process. Two great absorption decreases are apparent at 1236 and 1154 cm<sup>-1</sup>. The first decrease belongs to the asymmetric stretching of ether bond, while the second belongs to the symmetric stretching of ether bond, the aromatic C–H deformation, and to the glucose ring vibration. These absorption decreases indicate the ether splitting and the degradation of cellulose [25]. The observed changes can be then summarized as formation of micro-cracks and destruction of the various layers of the cell wall. The samples were withdrawn from the device after different irradiation times ranging from 30 to 120 h. A material lack is also observed; Fig. 4 shows the wood mass loss, expressed as a percentage loss, against UV time exposure. After the first 30 h of light irradiation by xenon lamp, the mass loss increases sharply, and then the rises stabilize gradually for Maritime pine and zeen oak. On the other hand, the afares oak mass loss seems to increase steadily throughout the entire exposure time.

The mechanical strength was used also as measure of the level of degradation in the wood specimens. We have

measured the tensile strength of the wood specimens before and after UV exposure of 120 h. Table 2 shows the mechanical characteristics of the wood samples. Based on the mechanical test results and although the ultimate strengths of the unexposed woods were higher than their aged wood counterparts, their Modulus of elasticity MOE was clearly higher. This behavior can be explained probably by micro-cracks in the irradiated wood samples, which have a much greater influence on the tensile strength than on the modulus [26, 27]. On the other hand, the decrease of MOE after aging indicates that the wood samples loss some of stiffness due to the lowered moisture content of samples involved by the degradation of hemicelluloses and lignin.

## Conclusion

The observed behavior for the three samples through degradation process in a Xenon test chamber shows significant differences after 120 h. Discoloration occurs for all samples due to photodegradation of lignin and extractives on wood surface during irradiation. The microstructure weakens mostly in areas with high hemicellulose and lignin content. From the measured mechanical properties, it appears that after irradiation the samples of the three species have dropped some stiffness because of the macromolecular chain breaking. However, it seems necessary to study the aging of wood at longer time intervals to be fixed on the mechanisms of degradation. Future activity is expected to concentrate on improving the protection strategy for the wood coating system.

**Acknowledgements** The authors would like to thank IBDM France (especially SEM team unit) and staff of the wood processing company (TRANSbois) in Algeria.

## References

- Messaoudene M, Tafer M, Loukkas A, Marchal R (2008) Propriétés physiques du bois de chêne zeen de la forêt des Aït Ghobri, Algérie (in French). *Bois For Trop* 298:37–48
- Haddad A, Lachenal D, Marechal A, Janin G, Labiod M (2009) Delignification of aleppo pine wood *Pinus halepensis* Mill by soda-anthraquinone process: pulp and paper characteristics. *Cellulose Chem Technol* 43:287–294
- Ashby MF, Gibson LJ, Wegst U, Olive R (1995) The mechanical properties of natural materials. I. Material property charts. *Proc R Soc Lond Ser A Math Phys Eng Sci* 450(1938):123–140
- Biblis EJ (2000) Effect of weathering on surface quality and structural properties of six species of untreated commercial plywood siding after 6 years of exposure in Alabama. *For Prod J* 50:47–50
- Ayadi N, Lejeune F, Charrier F, Charrier B, Marlin A (2003) Color stability of heat-treated wood during artificial weathering. *Holz Roh Werkstoff* 61:221–226
- Unger A, Schniewind AP, Unger W (2001) Wood properties in conservation of wood artifacts. A handbook. Springer, Berlin, pp 23–42
- Hon DN-S (2001) Weathering and photochemistry of wood. In: Hon DN-S, Shiraishi N (eds) *Wood and cellulosic chemistry*, 2nd edn, revised and expanded. Marcel Dekker, New York, pp 513–546
- Pandey KK, (2005) Study of the effect of photo-irradiation on the surface chemistry of wood. *Polym Degrad Stab* 90:9–20
- Popescu CM, Popescu MC, Vasil C (2011) Structural analysis of photodegraded lime wood by means of FT-IR and 2D IR correlation spectroscopy. *Int J Biol Macromol* 48:667–675
- George B, Suttie E, Merlin A, Deglise X (2005) Photodegradation and photostabilisation of wood—the state of the art. *Polym Degrad Stab* 88:268–274
- Chang HT, Chang ST (2001) Correlation between softwood discoloration induced by accelerated lightfastness testing and by indoor exposure. *Polym Degrad Stab* 72:361–365
- Nagarajappa GB, Pandey KK (2015) UV resistance and dimensional stability of wood modified with isopropenyl acetate. *J Photochem Photobiol B Biol* 155:20–27
- Matsuo M, Yokoyama M, Umemura K, Sugiyama J, Kawai S, Gril J, Kubodera S, Mitsutani T, Ozaki H, Sakamoto M, Imamura M (2011) Aging of wood: analysis of color changes during natural aging and heat treatment. *Holzforsch* 65:361–368
- Miklečić J, Kasa A, Jirous-Rajković V (2012) Colour changes of modified oak wood in indoor environment. *Eur J Wood Wood Prod* 70:385–387
- T 211 om-02 (2002) Standard test method for ash in wood, pulp, paper and paperboard. TAPPI Standards Norcross, GA
- ASTM D1106-96 (2007) Standard test method for acid-insoluble lignin in wood. ASTM International, West Conshohocken
- Rowell RM, Pettersen R, Tshabalala MA (2005) Cell wall chemistry. In: Rowell RM (ed) *Handbook of wood chemistry and wood composites*. CRC Press, Boca Raton, pp 64–66
- Liu Y, Shao L, Gao J, Guo H, Chen Y, Cheng Q, Via BK (2015) Surface photo-discoloration and degradation of dyed wood veneer exposed to different wavelengths of artificial light. *Appl Surf Sci* 331:353–361
- Arnold M, Sell J, Feist WC (1991) Wood weathering in fluorescent ultraviolet and xenon arc chambers. *For Prod J* 4:40–44
- Alexopoulos J (1992) Accelerated aging and outdoor weathering of aspen wafer board. *For Prod J* 42:15–22
- Mitsui K, Tsuchikawa S (2005) Low atmospheric temperature dependence on photodegradation of wood. *J Photochem Photobiol B Biol* 81:84–88
- Cui W, Kamdem D P, Rypstra T (2004) Diffuse reflectance infrared fourier transform spectroscopy drift and color changes of artificial weathered wood. *Wood Fiber Sci* 36(3):291–301
- Temiz A, Terziev N, Eikenes M, Hafren J (2007) Effect of accelerated weathering on surface chemistry of modified wood. *Appl Surf Sci* 253:5355–5362
- Müller U, Rätzsch M, Schwanninger M, Steiner M, Zöbl H (2003) Yellowing and IR-changes of spruce wood as result of UV-irradiation. *J Photochem Photobiol B Biol* 69:97–105
- Colom X, Carrillo F, Noguès F, Garriga P (2003) Structural analysis of photodegraded wood by means of FTIR spectroscopy. *Polym Degrad Stab* 80:543–549
- Sonderegger W, Niemz P (2004) The influence of compression failure on the bending, impact bending and tensile strength of spruce wood and the evaluation of non-destructive methods for early detection. *Holz Roh Werkstoff* 62:335–342
- Benini KCCC, Voorwald HJC, Cioffi MOH (2011) Mechanical properties of HIPS/sugarcane bagasse fiber composites after accelerated weathering. *Proc Eng* 10:3246–3251