COMPARATIVE STUDY OF WEATHERING BEHAVIOR OF FOUR FAST-GROWING EUCALYPTUS SPECIES

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For the correct use of eucalyptus woods in the manufacturing of solid products, it is necessary to define reliable quality parameters. This study aimed at characterizing the degradation of juvenile and mature woods of four eucalyptus species submitted to natural weathering. *Eucalyptus botryoides*, *Corymbia citriodora*, *Eucalyptus paniculata* and *Eucalyptus teretircornis* wood samples from mature forests located in Southern Brazil were studied. The following characterization techniques were used: colorimetric analysis (CIELAB method and UV-VIS spectroscopy), contact angle measurements and Janka hardness tests. Deterioration of the samples was evidenced by color change (graying), indicated by a decrease in the L^* and C^* levels. Based on hardness results, the weathering resistance of the wood species decreased in the following order: *Corymbia citriodora*, *Eucalyptus teretircornis*, *Eucalyptus paniculata* and *Eucalyptus botryoides*. Furthermore, the properties of mature wood varied less than those of juvenile wood.

Keywords: wood color, wood decay, Janka hardness, field test

INTRODUCTION

In recent decades, massive cultivation of several fast-growing species, mainly of the *Eucalyptus*, *Pinus*, *Acacia*, *Teak* and *Corymbia* genera, has been taking place throughout Brazil in order to fulfill the demand of the pulp and paper industry and charcoal sector. In such cases, the wood is subjected to procedures that do not add value to the material. Instead, this raw material could be used for manufacturing solid products, such as panels and planks for the construction sector, as well as frames, furniture, moldings, among others.

The wood employed in the manufacturing of solid items is often selected based on empirical criteria only, and it may sometimes behave inappropriately. Premature weathering, *i.e.* the accelerated loss of some of its main technological characteristics, may also occur. Therefore, detailed knowledge of the technological properties of a particular type of wood is advisable, so that reliable parameters may be proposed for estimating the lifetime of resulting products.

When the wood is used outdoors, the main cause of wood deterioration is the combined action of biotic and abiotic agents. The main non-biological agents are humidity, temperature, solar radiation and ozone content,[1] whereas fungi and insects are the main biotic agents. Degradation starts with oxidation of the chromophore groups of lignin, which is photo-initiated by the action of ultraviolet and visible components of sunlight.[2] This yields free radicals that gradually weaken the cell wall of the wood, eventually fragmenting the lignocellulosic matrix.[3,4] As a consequence, a large amount of water-soluble compounds is produced on the wood surface, especially carbonyl and carboxyl groups, which are leached by the action of rain and wind.[5,6] Thereafter, combined repeated photodegradation and leaching cycles produce new surfaces, which are more susceptible to fungal attack. Colonization by fungi is dependent on the pH and temperature of the substrate, as well as the fungal species involved.[7]

The initial deterioration of wood due to weathering is usually identified by discoloration[8] and production of cracks.[9] After colonization by biological agents, weight loss attributed to the degradation of lignin and wood sugars occurs.[10] From a technological point of view, deterioration is characterized by an increase in surface roughness,[11] a decrease in glass transition temperature,[12] graying of the color,[13] specular gloss loss,[14] along with loss of mechanical properties[10] and efficiency in the application of paints and varnishes.[15]

Although the wood deterioration mechanism due to weathering has been widely discussed, it is not yet fully understood. In addition to lignin, other wood constituents, such as extractives, also play an important role in the deterioration, mainly owing to their antioxidant properties.[6] It is also important to assess the effect of factors such as species and age on the weathering resistance of wood. Therefore, this work investigates the resistance to natural weathering of juvenile and mature woods of four eucalyptus species.

EXPERIMENTAL

Raw material selection and field tests

In this study, five trees for each of the following species were selected: *Eucalyptus botryoides*, *Corymbia citriodora*, *Eucalyptus paniculata* and *Eucalyptus tereticornis*. At the time of felling, the trees were *c.a.* 60 years old. The trees belonged to a homogeneous forest in the city of Charqueadas, in the south of Brazil. From each felled tree, a 1.5 m long baseline log was obtained at a height of 10 cm from the ground. The logs were transformed into 8 cm thick central planks, which were then subjected to outdoor drying for about three months. Other samples (dimensions: 1 cm × 1 cm × 20 cm) were taken following the longitudinal axis of the planks, being the largest dimension oriented in the longitudinal direction. These samples were taken from regions near the pith or the bark of the planks in order to obtain juvenile or mature woods, respectively. Four samples from juvenile and mature woods of each species were used, comprising a total of 160 samples. The samples were then stored in a climatic chamber at 65% RH and 20 °C to reach 12% moisture content.

Field tests were conducted in the city of Piratini, in the south of Brazil, whose climate is classified as Cfa by the Köeppen classification and its average temperature is 17.2 ºC. In decaying fields, samples were buried up to half of their length and four samples were organized in each square (side: 10 cm). The squares were separated by 30 cm, as shown in Figure 1. Samples were collected from the fields every 135 days, up to 540 days. After weathering, the wood samples were again conditioned in the same climatic chamber.

Characterization of samples

A CR-400 colorimeter (Konica Minolta), configured with a D65 source light and an angle of observation of 2°, was used to investigate color changes after weathering.

The colorimetric characterization was carried out in triplicate on both radial and tangential surfaces of each sample to determine the following parameters: brightness (L^*), green-red coordinate (a^*), yellow-blue coordinate (b^*), chroma (C^*) and hue angle (h). UV-Vis spectroscopy was also used for colorimetric characterization of the 540-day aged samples. Analysis was performed on a Shimadzu UV-Vis-NIR 3600 spectrophotometer, with diffuse reflectance in the 200-800 nm range.

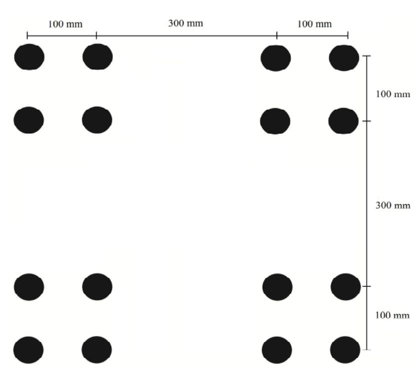

Figure 1: Layout of the samples distributed in the decay fields

Table 1
F and p values of multifactorial ANOVA applied to the colorimetric parameters of wood subjected to natural weathering

Parameter	Species	Type of wood	Exposure time	Anatomical face
L^*	5.45**	55.31**	59.79**	2.49^{NS}
a^*	10.16**	4.03*	265.58**	0.01^{NS}
b^*	2.89*	0.12^{NS}	252.67**	2.33^{NS}
C^*	4.13**	0.58^{NS}	297.94**	1.61^{NS}
h	2.11^{NS}	3.25^{NS}	17.07**	2.14^{NS}

L^* = brightness; a^* = green-red coordinate; b^* = blue-yellow coordinate; C^* = chroma; h = hue angle; *significant at 5% of probability of error; **significant at 1% of probability of error; ^{NS}not significant

Figure 2: Photos of the radial face of four eucalyptus samples for different exposure time

Figure 3: Photos of the tangential face of four eucalyptus samples for different exposure time

All color analyses were performed on the weather-exposed region, around 1 cm from the edge of the samples. Colorimetric data were subjected to ANOVA analysis to identify representative parameters related to wood degradation.

Surface wettability of the samples was assessed through contact angle measurements on a Data Physics goniometer. A 10-ml deionized water droplet was placed on the sample surface, and the kinetics of absorption of the drop was studied at four different contact times (0, 5, 10 and 15 s). Measurements were performed in triplicate for both radial and tangential planes of each sample, and the median value was reported in each case. The hardness of the tangential face of the samples was evaluated in accordance with the Janka method, using an EMIC universal testing machine (cross-head speed of 6 $mm.s^{-1}$).

RESULTS AND DISCUSSION

Colorimetric parameters obtained by the CIELAB method

Table 1 displays the results from the multi-factorial ANOVA analysis of the color data. The brightness (L^*) and green-red coordinate (a^*) were the most sensitive colorimetric parameters for monitoring the discoloration of wood subjected to field tests, being significantly affected by three of the four factors investigated (species, type of wood and exposure time).

The anatomical face did not present any significant variation in the color parameters of wood, similarly to previous studies that analyzed the color of other wood species, *in natura* and after natural ageing.[13] Qualitative visual observation of images of the samples (Figs. 2-3) suggests the same behavior, *i.e.* similar color for the radial and tangential faces.

Gradual graying of the samples over time was obvious. Although discoloration of the material is evident from the photographs shown in Figures 2 and 3, the assessment of the actual color based only on this is controversial. Indeed, Huang and coworkers[8] suggested the combined use of several criteria. Comparing the four eucalyptus species and the juvenile and mature woods, the color parameters selected through multifactor ANOVA (L^* and a^*) indicate similar average values over the exposure period (Fig. 4). It can be noted that discoloration occurred abruptly, and nearly leveled out after approximately 225 days of exposure.

Thus, it is possible to identify two distinct stages of deterioration in the samples. Similar to previous studies, the first stage is expected to occur due to photo-oxidation and depolymerization reactions of the chromophoric groups of lignin and extractive compounds (phenolic compounds and terpenes), which promote the absorption of solar rays (in the visible light and ultraviolet regions),[4,5] with the subsequent leaching of degraded components due to rain and wind, revealing new wood surfaces.[6] The second stage (after 225 days) can be attributed to colonization of the newly formed surfaces by wood-destroying fungi, which is a function of the physicochemical characteristics of the wood, the kind of derogatory fungus and the exposure environment.[7] Although it is known that there is fungal colonization before 225 days of exposure, the fungal action is clearly more intense after the weakening of the wood structure caused by the abiotic agents mentioned. To further understand the mechanisms related to wood decay attributed to natural weathering, it would be necessary to identify and quantify the biological agents involved in each degradation stage.

The darkening of wood (L^* decrease) is associated with the formation of quinones, which result from lignin degradation.[16] The decrease in the red pigment (a^* decrease) is associated with reactions related to wood extractives. Mitsui and coworkers[17] also found decreased levels of a^*, which were attributed to photodegradation and subsequent leaching of extractive compounds of the Japanese cedar wood (*Cupressus japonica*).

In the current study, it was not possible to identify greater susceptibility/resistance among the four eucalyptus species based on the L^* and a^* values, as shown in Figure 4. However, comparing fresh and 540 days decayed samples, mature and juvenile woods presented 72 and 77% of a^* variation, respectively. Therefore, based on that, mature woods were more resistant to discoloration than juvenile woods (Fig. 4).

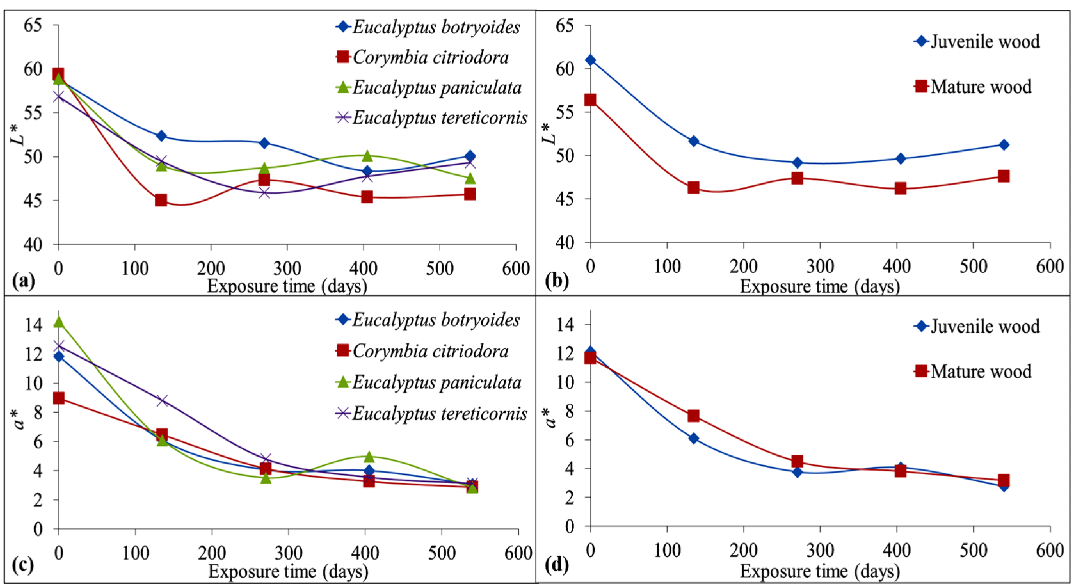

Figure 4: Variation of brightness (a-b) and green-red coordinate (c-d) with exposure time

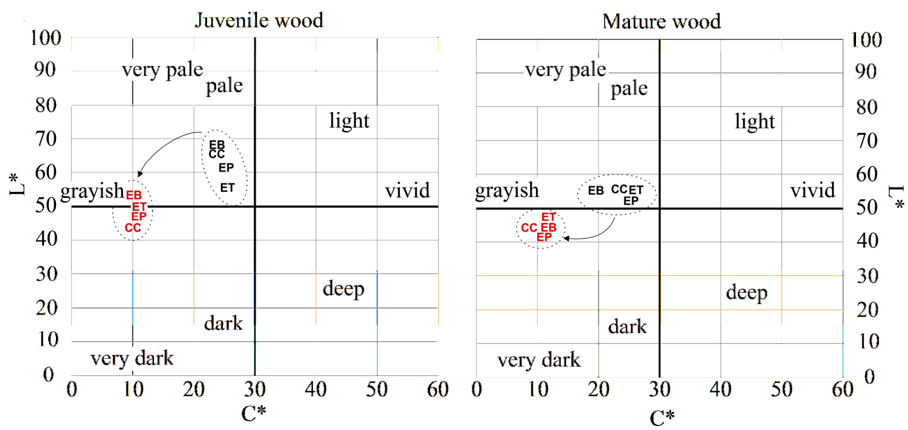

Figure 5: Chromaticity graphs for the studied juvenile and mature woods

Such behavior may be better appreciated using a chromaticity chart (Fig. 5), and it appears that although both mature and juvenile woods show color graying, indicated by the combined reduction in *L** and *C** levels, mature wood presented darker tones in all species, ratifying the findings related to Figures 2-4.

UV-VIS spectroscopy

The analysis of the graphs presented in Figure 6 confirms the similarity between the color of the radial and tangential faces throughout the wavelength range covered by the UV-VIS spectrum. The spectra clearly indicate differences between juvenile and mature logs among the four eucalyptus species, which are not allocated to certain isolated peaks. These differences were characterized by lower levels of reflectance for the mature wood, a result of its darker staining in comparison with juvenile wood.

Also based on Figure 6, the main UV-VIS spectra differences between fresh and decayed *Eucalyptus* woods are seen in two distinct regions of wavenumbers, within 250-400 nm and from 550 nm onwards. In the first region, the decayed wood absorbs less energy, and in the second, deterioration modifies the wood so that it absorbs more energy. Although extractives also usually have the ability to absorb light within 300-400 nm, it can be said based on the literature[18] that lignin may be the main component responsible for staining the wood, and its highest peak appears at 280 nm. Therefore, it appears appropriate to associate that first region to the degradation of lignin, which occurs due to the reaction of phenolic hydroxyl groups of their side chains with solar radiation, producing carbonyl and phenolic radical groups, which later turned into quinoid structures through demethylation or cleavage.[19]

The produced aromatic carbonyl groups appear around 330 nm, and the quinones at 360 nm.[19] Due to their proximity, these peaks appear combined into a single major peak in the spectroscopy. However, the quinoid structures and carbonyl groups produced during degradation alter the wood structure, darkening it and conferring a greater degree of reflectance in the 250-400 nm range. Thus, a first sign of differentiation between fresh and deteriorated wood may be the decrease in *L** levels.

A second differentiation region attributed to weathering, possibly due to reactions occurring in extractives, may be found based on the *a** parameter. This hypothesis is based on previous studies that reported the appearance of peaks near 650 nm related to the degradation of phenolic compounds.[20] Nevertheless, it is important to mention that the role of extractives in the natural weathering process is still unclear.[6,20] *C. citriodora* wood presented a different UV-VIS spectrum compared to *Eucalyptus* genus species. Comparing the differences in spectra between fresh and degraded wood and considering the above-mentioned studies, variation in the 200-400 nm range is perhaps due to the photodegradation of lignin.[18]

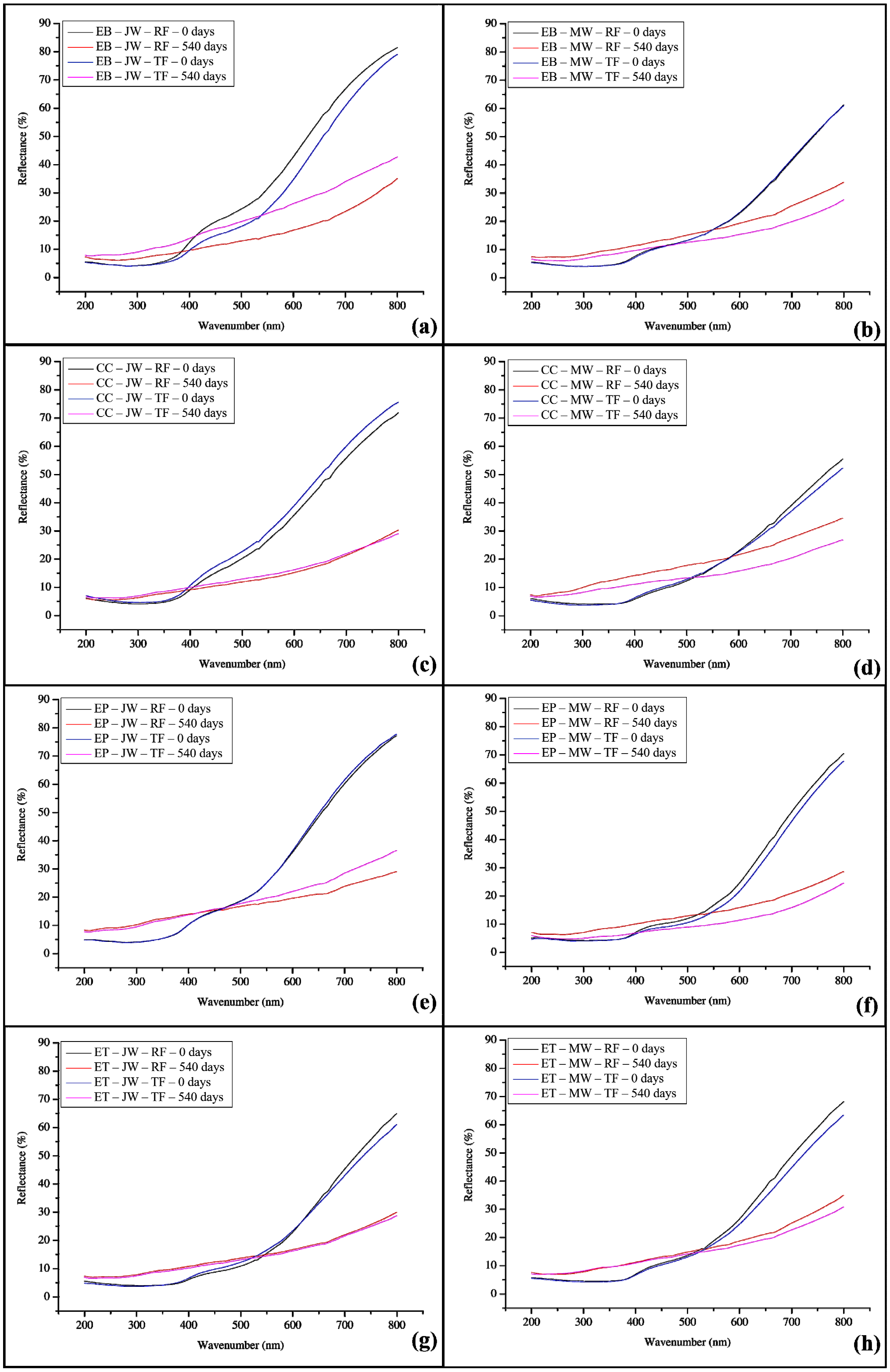

Figure 6: UV-VIS spectra obtained for both juvenile (JW on the left) and mature (MW on the right) of *Eucalyptus botryoides* (EB; a-b), *Corymbia citriodora* (CC; c-d), *Eucalyptus paniculata* (EP; e-f) and *Eucalyptus tereticornis* (ET; g-h) woods on their radial (RF) and tangential (TF) faces

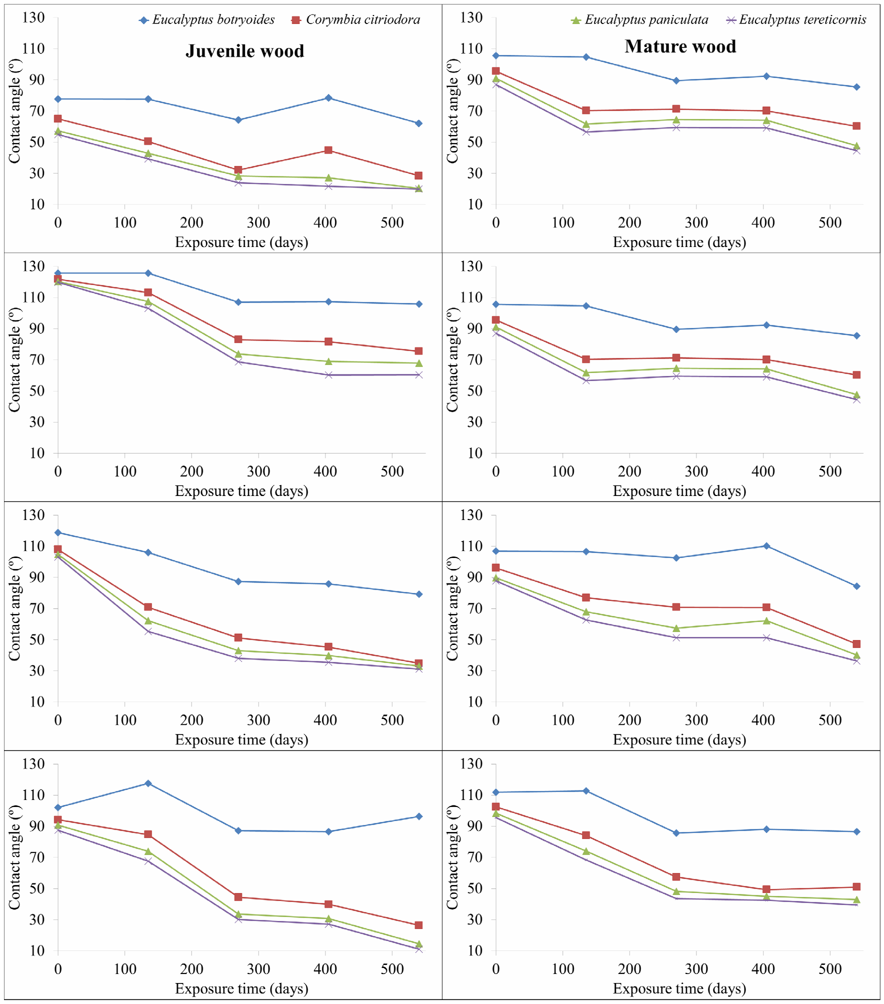

Figure 7: Variation in contact angle values obtained for the various eucalyptus samples (radial face)

The constitution of the lignin in the *C. citriodora* wood differs significantly from the lignins found in the other three *Eucaluptus* species examined, especially the larger amount of vanillic acid and lower amount of vanillin, syringaldehyde and acetovanillone.[21] However, reports on the chemical composition of their extractives, which could help justify these findings, are hard to find.

Variation of contact angle

The results of drop kinetics are compiled in Figures 7 and 8, which represent the average values for both radial and tangential faces of the wood, respectively. It can be noted that, regardless of the species and type of wood, degradation due to natural weathering resulted in a decrease of its hydrophobic character. The range of contact angles reported here is within those of other studies, such as Huang and coworkers,[9] who examined various species of hardwoods. Also, although the contact angle levels considerably decreased, they were still within the sensitivity range of the goniometer.

Although no clear differences were found among the four species of eucalyptus, nor between juvenile and mature woods, the median values obtained for the five samples (0, 145, 270, 405 and 540 days) of a particular case differed. For example, comparing the average initial (at 0 s) and final (at 15 s) contact angle values for the four eucalypts, *E. botryoides*, *C. citriodora*, *E. paniculata* and *E. tereticornis*, 48.6, 47.6, 43.8 and 48.5% are obtained, respectively, which do not present relation with other results presented in this manuscript.

Thus, considering the positive characteristics of this analysis, *i.e.* fast and easy data collection, contact angle measurement can be an efficient way to monitor depreciation of the surface due to natural weathering, even though it was not able to differentiate surface quality among distinct species or among ages of a particular species.

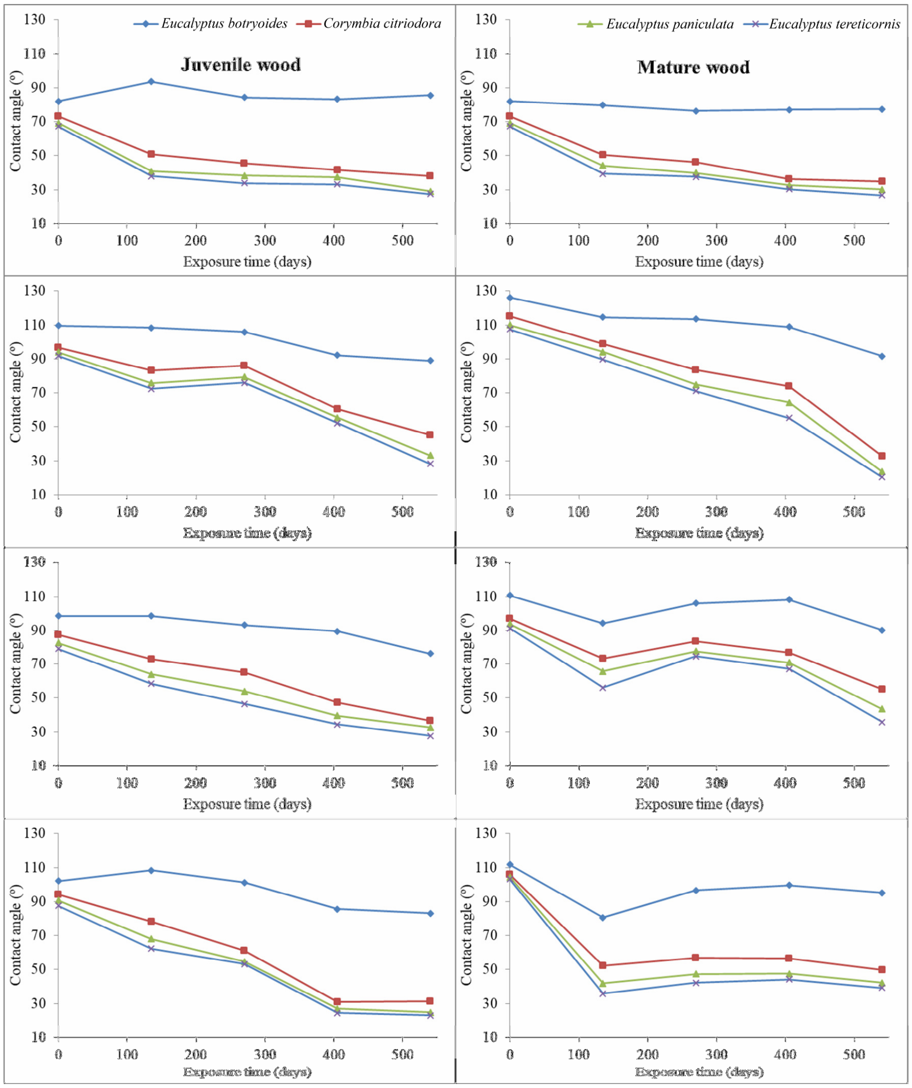

Figure 8: Variation in contact angle values obtained for the various eucalyptus samples (tangential face)

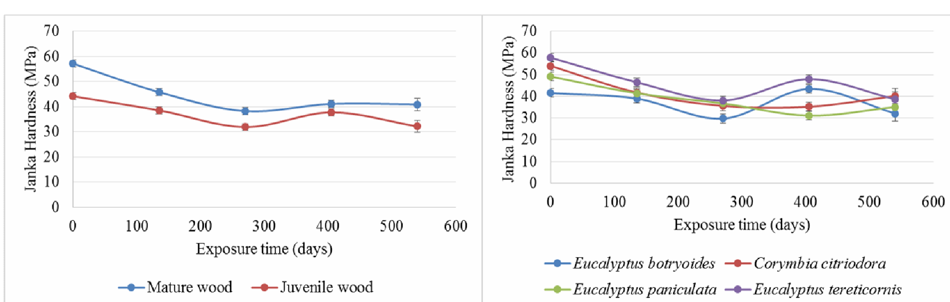

Figure 9: Variation of Janka hardness values of the samples with exposure time (tangential face)

Huang and coworkers[9] studied *Pinus banksiana*, *Populus tremuloides* and *Betula bapyrifera* woods submitted to artificial weathering and concluded that surface wettability of wood increases due to the formation of cracks during the decay process, which facilitate the flow of moisture into the interior of the wood cells. On the other hand, degradation of wood sugars yielded many hydroxyl groups, which increased the hydrophobic character of the surface.[22]

Janka hardness

The average values of Janka hardness for the four species of eucalyptus, juvenile and mature, are presented in Figure 9. A similar pattern to that observed for color decay is seen, again with two stages of depreciation of the surface of the material.

Similar to the wettability results, the Janka hardness levels showed a significant decrease for long exposure time. Also, the values were within the range of results reported in the literature,[23] validating the adjustments of the standardized procedure used for Janka hardness.

The mature wood showed greater resistance to natural weathering than juvenile wood, similar to the results of colorimetric characterization. Comparing wood species, it was found that *E. botryoides* and *E. paniculata* presented similar Janka hardness levels throughout the test period (540 days). However, fresh *E. tereticornis* wood presented Janka hardness greater than that of *C. citriodora* wood, and an opposite trend was found by the end of the exposure time. This is perhaps justified by their lignin composition, since woods with higher content of guaiacyl-syringyl lignin (typical of hardwoods) tend to have greater resistance to photobleaching, due to the lower rate of production of carbonyl and carboxyl groups during oxidation of its chromophoric groups.[5] Indeed, Santos and coworkers[21] reported that lignin extracted *via* the organosolv method from *C. citriodora* wood had lower lignin content, higher levels of phenolic compounds and higher S/G (syringyl lignin / guaiacyl-syringyl lignin) ratio than lignin extracted from *E. tereticornis* wood.

Thus, other studies support the Janka hardness results obtained in this study, indicating that, although fresh *C. citriodora* wood shows lighter color, it is more resistant to photo-oxidation than *E. tereticornis* wood due to its content and composition of lignin. In addition, although the main components of wood (cellulose, hemicellulose, lignin and extractives) are susceptible to photobleaching, lignin is primarily responsible for its discoloration.[4]

CONCLUSION

The different techniques used in the present study for the characterization of wood subjected to natural weathering yielded similar results, so it can be concluded that the material was satisfactorily characterized. Regarding colorimetric properties, the brightness (L^*) and green-red coordinate (a^*) were the most efficient and sensitive parameters for monitoring the depreciation of the surface of the samples. Mature wood showed greater resistance to degradation than juvenile wood, as characterized by its darker grayscale and higher level of Janka hardness. In the UV-VIS spectra, the 200-400 nm range was attributed to the degradation of lignin and extractives, associated with a decrease in L^*, whereas the range of wavelengths beyond 550 nm was attributed to the degradation of wood extractives, with an associated variation in a^*. The contact angle technique proved efficient to characterize wood deterioration, even though this technique was not able to differentiate among species or types of woods within a single species. Based on the Janka hardness results, the analyzed eucalyptus species showed decreasing resistance to natural weathering in the following order: *C. citriodora*, *E. tereticornis*, *E. paniculata* and *E. botryoides*.

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REFERENCES

[1] X. Colom, F. Carrillo, F. Nogues and P. Garriga, *Polym. Degrad. Stabil.*, **80**, 543 (2003).
[2] B. George, E. Suttie, A. Merlin and X. Deglise, *Polym. Degrad. Stabil.*, **88**, 268 (2005).
[3] M. L. Kuo and N. Hu, *Holzforschung*, **45**, 347 (1995).
[4] P. D. Evans, N. L. Owen, S. Schmid and R. D. Webster, *Polym. Degrad. Stabil.*, **76**, 291 (2002).
[5] K. K. Pandey, *Polym. Degrad. Stabil.*, **90**, 9 (2005).
[6] T. C. Chang, H. T. Chang, C. L. Wu, H. Y. Lin and S. T. Chang, *Polym. Degrad. Stabil.*, **95**, 1518 (2010).
[7] D. R. Negrão, T. A. F. Silva Júnior, S. Passos Jr., C. A. Sansígolo, M. T. A. Minhoni *et al.*, *Int. Biodeterior. Biodegrad.*, **89**, 95 (2014).

[8] X. Huang, D. Kocaefe, Y. Kocaefe, Y. Boluk and A. Pichette, *Appl. Surf. Sci.*, **258**, 5360 (2012).
[9] X. Huang, D. Kocaefe, Y. Kocaefe, Y. Boluk and A. Pichette, *Wood Sci. Technol.*, **46**, 1215 (2012).
[10] B. D. Mattos, P. H. G. Cademartori, T. V. Lourençon, D. A. Gatto and W. L. E. Magalhaes, *Int. Biodeterior. Biodegrad.*, **93**, 210 (2014).
[11] E. A. Dunningham, D. V. Plackett and A. P. Singh, *Eur. J. Wood Wood Prod.*, **50**, 135 (1992).
[12] R. Garcia, M. C. Triboulot, A. Merlin and X. Deglise, *Wood Sci. Technol.*, **34**, 99 (2000).
[13] B. D. Mattos, P. H. G. Cademartori, T. V. Lourençon and D. A. Gatto, *Int. Wood Prod. J.*, **5**, 33 (2013).
[14] E. Baysal, S. Degirmentepe and H. Simsek, *Maderas: Cienc. Tecnol.*, **16**, 355 (2014).
[15] K. Pandey and K. Srinivas, *Eur. J. Wood Wood Prod.*, **73**, 111 (2015).
[16] L. Tolvaj and O. Faix, *Holzforschung*, **49**, 397 (1995).
[17] K. Mitsui, A. Murata and L. Tolvaj, *Eur. J. Wood Wood Prod.*, **62**, 164 (2004).
[18] M. Zborowska, A. Stachowiak-Wencek, M. Nowaczyk-Organista, B. Waliszewska and W. Prądzyński, *Bioresources*, **10**, 2057 (2015).
[19] J. A. Schmidt and C. Heitner, *J. Wood Chem. Technol.*, **13**, 309 (1993).
[20] S. Yildiz, E. D. Tomak, U. C. Yildiz and D. Ustaomer, *Polym. Degrad. Stabil.*, **98**, 1419 (2013).
[21] P. S. B. Santos, P. H. G. Cademartori, R. Prado, D. A. Gatto and J. Labidi, *Wood Sci. Technol.*, **48**, 873 (2014).
[22] M. Kishino and T. Nakano, *Holzforschung*, **58**, 552 (2004).
[23] S. Korkut, *Build. Environ.*, **43**, 422 (2008).