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COLORIMETRIC AND FTIR ATR SPECTROSCOPY STUDIES OF DEGRADATIVE EFFECTS OF ULTRAVIOLET LIGHT ON THE SURFACE OF EXOTIC IPE (*TABEBUIA* SP.)WOOD

MAGDALENA ZBOROWSKA,[*] AGATA STACHOWIAK-WENCEK,[*]
BOGUSŁAWA WALISZEWSKA[*] and WŁODZIMIERZ PRĄDZYŃSKI[**]

[*]*Institute of Chemical Wood Technology, Poznan University of Life Science,*
WojskaPolskiego 38/42, Poznań, Poland
[**]*Institute of Wood Technology, Winiarska1, Poznań, Poland*
✉ *Corresponding author: Magdalena Zborowska, mzbor@up.poznan.pl*

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The objective of the study was to characterize the UV light resistance of one of the exotic wood species –ipe (*Tabebuia* sp) – commonly used in the furniture industry, using the colorimetric and infrared spectroscopy analyses. A softwood species, Scots pine (*Pinus sylvestris* L.), was also studied for comparison purposes. Based on the results obtained after 100 h of light irradiation, colour changes were found in the samples of both analysed species, but the extentand pattern of the changes differed significantly. It was observed that the ipe wood was less influenced by light in comparison with the pine wood. The total colour difference of the pine wood amounted to 14.26 and for the ipe wood to merely 1.05. The most significant changes were observed in the case of chromatic coordinate "b". Based on the infrared spectroscopic analysis, it was concluded that 340 UV irradiation yields the degradation of lignin structure. The infrared spectra gave an insight into the changes occurring in the range of carbonyl groups present in the structure of wood components and confirmed the resistance of carbohydrates to UV irradiation.

Keywords: discoloration, exotic ipe wood (*Tabebuia* sp.), pine wood (*Pinus sylvestris* L.), FTIR ATR spectroscopy, colorimetry

INTRODUCTION

In recent years, exotic wood species have gained increasing popularity. Due to their characteristics, such as e.g. wide diameters, attractive colour and structure, high durability and resistance to decay, these species are more and more frequently used in parquet, plywood and the furniture industry. The physical and mechanical properties mentioned above result mainly from the chemical composition of exotic wood, which varies significantly among species.[1-3] As a natural material, exotic wood is subject to different kinds of degradation processes.[4-7] While exposed to outdoor environment, wood undergoes a weathering process induced by factors such as moisture, sunlight, heat and cold temperature. In the course of weathering, the surface of wood evidently changes, primarily leading to an alteration of its colour, lightness and gloss.[8] For example, under the influence of atmospheric factors, the brown, brown-grey or deep brown colour of untreated ipe wood turns to a patinaor deepens. The extent of colour changes depends on the chemical composition of wood, which may determine a significantly different sensitivity to light. Lignin is responsible for absorbing 80 to 95% of the total UV light absorbed by wood, carbohydrates 5 to 20% and extractives about 2%.[9]

Several researchers have studied the weathering of exotic wood.[10-12] However, to the authors' knowledge, there is still little information concerning the discoloration of exotic wood from the chemical point of view. It is well known that processes that occur during irradiation are complex physicochemical reactions,[13] which finally cause a decrease in the lignin content related to an increase of carbohydrates concentration. Light irradiation degrades the chromophore groups originally found in wood,[14] and leads to the formation of free radicals. The formed singlet oxygen is a source of peroxide, which causes the autoxidation of carbohydrates and the cleavage of aromatic components of wood.[15] The degradation of lignin and extractives, followed by oxidation processes, creates new chromophore chemical groups as well. It can be supposed that a number of these changes also depend on the concentration of lignin and extractives in wood. This dependence can be crucial especially in the case of exotic wood species, which sometimes include higher content of lignin and extractive substances in comparison with European species.[16,17] What is more, the substances extracted from exotic wood are more varied in comparison with those obtained from species growing in temperate zones. One of the methods used in the analysis of the structure and chemical processes occurring during light irradiation is infrared spectroscopy.[18-22] It is a well-known technique with a great potential for chemical characterization of materials. It is a very useful tool to identify various inorganic and organic compounds, based on their selective absorption of radiation in the infrared region. Fourier Transform Attenuated Total Reflectance (FTIR ATR) uses the phenomenon of absorbing infrared energy during reflection from a measured surface. This technique allows samples to be measured without their preparation.

The aim of this study was to investigate photodiscoloration and photodegradation of an exotic wood species – ipe (*Tabebuia* sp.). For comparison purposes, a softwood European species, Scots pine (*Pinus sylvestris* L.), was also studied to detect differences in colour changes and degradation.

EXPERIMENTAL

The investigated material was exotic ipe hardwood (*Tabebuia* sp.) from South America. According to the literature,[23] the average density of ipe wood exceeds 1000kg/m^3 and, in spite of this, it has good dimensional stability. What is more, good mechanical and technical properties are connected with the high density of this wood. The choice of ipe wood was determined bythe increasing interest in this species shown by producers of furniture and wood base products. In the countries where ipe is harvested, it is used to make structural elements meeting a broad range of strength requirements (e.g. railway sleepers, docks, port reinforcements, bridge pillars). However, knowledge on the resistance of this species to irradiation is inaccessible.

The popularity of pine wood has led to extensive research, including on colour changes. Therefore, this is a rewarding, well-recognised comparison material. Changes of ipe and pine hues were monitored by measuring the colour by the colorimetric method and characterisingthe chemical and structural changes based on infrared spectroscopy.

Preparation of samples

Samples with dimensions of 40 × 15 × 5 mm (±1 mm) (long. × tang. × rad.) were prepared from the same boards. They were polished with sandpaper (400 P) prior to the investigation, after cutting. We used sets of 3 samples with a cross section of 10 mm in diameter and with 3 fixed measurement points.Pine samples were cut from softwood. The pine and ipe samples included both earlywood and latewood.

Chemical analysis of wood composition

Chemical analysis of the ipe and pine composition included determiningthe extractive substances according to T 204 cm-97 standard procedures (ethanol was used for extraction). For lignin quantification, acid-insoluble lignin was used according to T 222 om-02 standard. Pentosans were determined according to T 223 cm-01standard procedure. The analysis of the cellulose content was conducted according to the Seifert method.[23] Every determination was repeated three times for each sample.

Light irradiation of samples

Atlas Company apparatus equipped with 8 fluorescent UV lamps (40W) was used in the experiment. The distance between the UV light source and the sample surface was set to about 4.0 cm. Trial conditions were as follows: a UVA 340 ultraviolet lamp, wavelength of light falling onto the surface 290-400 nm, temperature BST (Black Standard Thermometer) = 38 °C, the value of light irradiation measured on the tested samples was established at the level of 0.5 W/m^2, irradiation was carried out under air atmosphere.

Colour change assessment

The colour coordinates (Lab) of tested samples were recorded before and after 1, 5, 10, 25, 50 and 100 hours of irradiation using the Datacolor 600 spectrophotometer. The colour change in the CIE Lab system was calculated according to the following formula:

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2}$$

where: ΔE – colour difference, L – achromatic coordinate of colour – brightness, L=100 white, L=0 black,a, b – chromatic coordinates of colour.

The measurement of colour coordinates L*, a*, b* of the ipe and pine wood surface before and after irradiation was done in the same accurately marked places.

The colour coordinates of the ipe and pine surface before and after irradiation were referred to thewhitestandard (L = 96.29, a = -0.34, b = 1.25). Table 1 presents the characteristics of the control samples of the examined species before light treatment.

Measurement of FTIR ATR spectra

After 100 h of UV light treatments, the ipe and pine samples were analysed by a Fourier Transform Attenuated Total Reflectance Alpha spectrometer produced by Bruker Optics GmbH. The spectral range was measured between 4000 cm^{-1} and 600 cm^{-1}. The spectral resolution of the spectrophotometer was 4 cm^{-1}, each spectrum was computed as the average of 32 successive measurements in order to minimize the measurement error. Five measurements were performed on each sample.

RESULTS AND DISCUSSION

Chemical analysis

The results of the chemical analysis of the ipe and pine wood are illustrated in Fig. 1. The concentration of extractive substances in the compared species differs and a higher value was found for the exotic wood. Another constituent of wood, lignin, which includes chromophore groups similarly to extractives, reaches high values in both investigated species, but a substantially higher concentration was noted for the exotic wood. Lignin is known as the most effective absorber of light irradiation. It can be supposed that a high content of lignin influences the resistance of the investigated exotic wood in an important way. The chemical analysis also detected differences in the percentage of short carbohydrates, such as pentosans. The concentration of cellulose fluctuated at a similar level in the compared wood species. The carbohydrate components of wood are less sensitive to photodegradation than lignin or extractive substances. They can also influence colour changes, but only to a limited extent.

Colorimetric analysis

The values of colour changes and colour coordinates (ΔE*, ΔL*, Δa* and Δb*) of the ipe and pine wood during 100h of irradiation are presented in Fig. 2. The progress of discoloration after 1, 5, 10, 25, 50 and 100 hours of irradiation is laid out in Fig. 3. The analysis of the results leads to the conclusion that both samples of exotic and European wood darken after light irradiation, but the values of coordinate ΔL* for the pine wood changed to a greater extent in comparison with that of the ipe wood. The difference between ΔL* of non-irradiated samples and those irradiated for 100h amounted to 8.89 units for the pine and only 1.87 units for the ipe. In the case of the ipe wood, the most important changes took place after the first hours of light treatment. The changes detected on the surface of the pine had equal progress during the whole time of UV irradiation.

Table 1
Color characteristics of ipe and pine control samples

Wood species	Color coordinates		
	L	a	b
Ipe (*Tabebuia*sp)	-51.74	8.49	16.22
Pine (*Pinussylvestris* L.)	-14.10	4.83	21.88

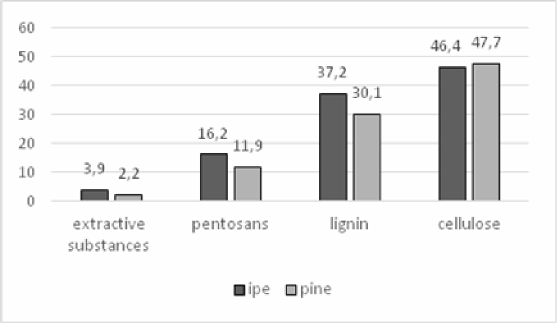

Figure 1: Chemical composition of ipe and pine control samples

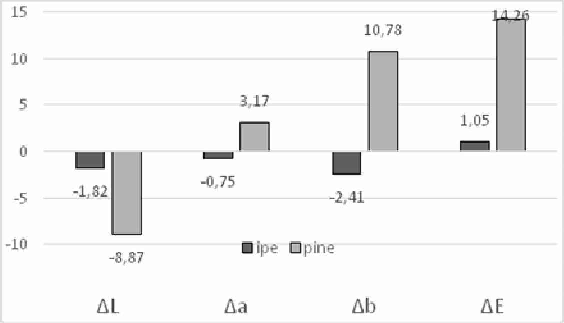

Figure 2: Changes of color and color coordinates (ΔL*, Δa*, Δb* and ΔE*) of ipe and pine wood samples caused by UV light after 100 hours of irradiation

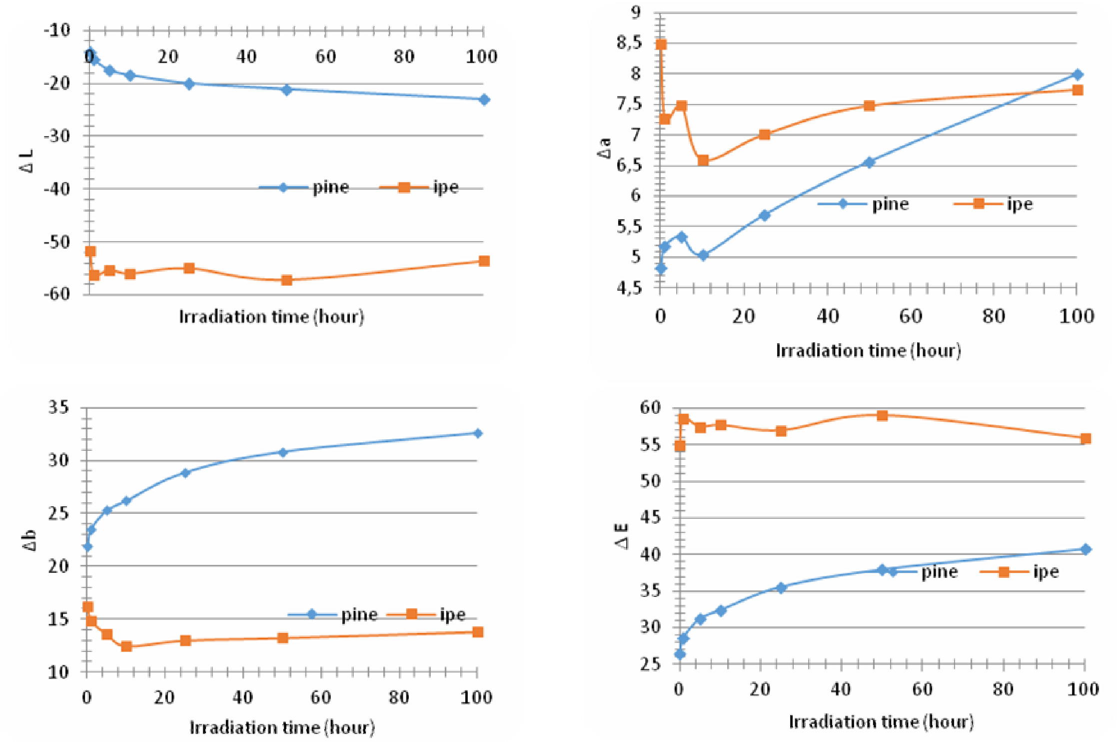

Figure 3: Changes of colour and colour coordinates (ΔL*, Δa*, Δb* and ΔE*) of pine wood samples caused by UV light irradiation after 0, 1, 5, 25, 50 and 100 hours of treatment

The analysis of changes in chromatic coordinate a* indicates that after 100 h of light treatment the pine wood was more reddish and the variation amounted to approx. 3 units. On the contrary, this coordinate changed to a smaller extent and in the opposite direction in the case of the ipe wood, as the samples became slightly less reddish (by 1 unit). Both for the ipe and the pine wood, the steepest variations were observed after 25 hours of the irradiation process. The analyses of the variation of chromatic coordinate "b" during light exposure of the samples reveal that the development trends of the compared wood species had again an opposite character. The surface of the pine wood was significantly yellower, while that of the ipe was less yellow after 100 h of irradiation. The most important yellowing of the ipe wood was remarked after 25 hours of UV irradiation. After that time, coordinate "b" was stable. According to the literature, the yellowing of wood is connected with changes in the lignin structure.[23,24] The concentration of this component in wood is probably not so influential. The lignin in the composition of exotic wood probably has a more resistant structure to UV irradiation. What is more, it is possible that this component is better protected by other components, for example by extractives, than in pine wood. Finally, the pine wood was less resistant (a higher Δb* value) to light compared to the ipe wood. Based on the evolution of colour coordinate ΔE* (total colour difference), it may be observed that the colour in the pine samples changed rapidly and continuously throughout the experiment. The value of ΔE* after 100 h of irradiation changed by approx. 14 units.A significantly different behaviour may be noticed in the case of the ipe wood. The total colour difference of the exotic wood amounted to only 1.04 units, which indicates greater resistance of this species to light irradiation. The obtained result suggests that a higher concentration of wood components, including chromophore groups, which are more sensitive to photodegradation, does not influence the decrease in the UV resistance of wood. Ipe wood, which is richer in lignin and extractive substances, is more resistant to light irradiation than pine wood. This phenomenon may be possibly explained by the different concentration of extractive substances in the analysed wood species. According to other authors,[1] extractive substances play an important role in the impact of UV irradiation on wood. A higher concentration of substances soluble in organic solvents, even though they include chromophores, guarantees lower sensitivity of wood to light irradiation.

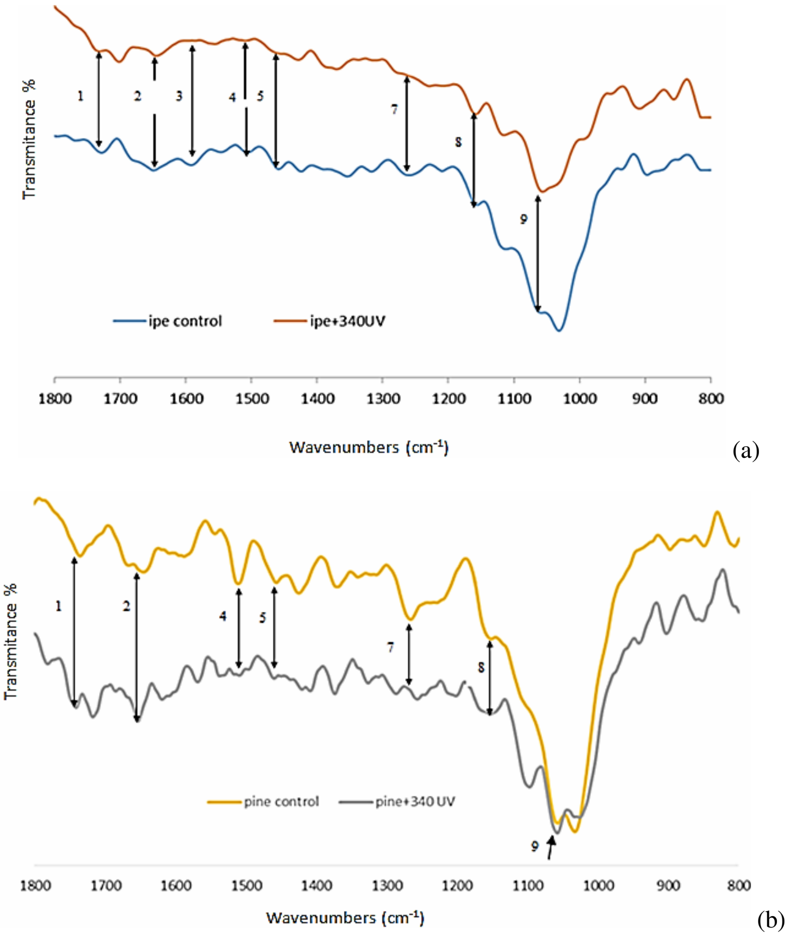

Figure 4: FTIR ATR spectra of ipe (a) and pine (b) wood before and after 100 h of photo-irradiation

Infrared spectroscopy analysis

The FTIR ATR spectra of the photo-irradiated ipe and pine wood are shown in Fig. 4. After light treatment, the intensities of the absorption bands related to lignin at 1592 (3), 1507 (4), 1467 (5), and 1269 cm^{-1} (7) decreased rapidly after 100h of exposure. The mentioned evolution was observed in the case of both the ipe and the pine wood. The changes indicate that the content of lignin decreased, probably due to depolymerisation and other degradation processes. This phenomenon confirms the finding of earlier publications,[1,24] claiming that the lignin structure is particularly susceptible to photodegradation. Based on the spectroscopy results, it can be suspected that even though the concentration and the probable structure of this component in pine and ipe wood are different (Fig. 1),its susceptibility to photodegradation is similar in the compared species. It means that in spite of quantity and quality differences in lignin,the changes in its structure have comparable progress. A specific evolvementin the ipe lignin structure can be observed in the ranges related to the C=O group: 1650 (2) (conjugated C=O in lignin) and 1738-1698 cm^{-1}(1) (non-conjugated in hemicellulose). It was established that the evolution of the spectra of pine wood before and after light irradiation in the range related to the C=O group was identical to those observed in the case of the ipe wood. However, the intensity of the bands was enhanced. The indicated changes were accompanied by the formation of new carbonyl groups,[11,26] which stem from the oxidation of cellulose and lignin.[27] By contrast, the intensity of the peaks at 1160 (8) and 1057 cm^{-1}(9) associated with carbohydrate components of wood increased visibly after irradiation both in the case of the ipe and pine wood. Stronger absorption at this band has been extensively discussed[11,19] and may be explained by a marked increase in the carbohydrate content related to lignin, which was partly degraded.

CONCLUSION

Based on the results obtained after 100h of light irradiation, it was stated that colour changes occurred in both types of samples, but the extent and pattern of changes were significantly different. Greater discoloration was observed in the case of the pine wood. For example, the difference between ΔL^* of non-irradiated samples and of those irradiated for 100 h amounted to 8.89 units for the pine and only 1.87 units for the ipe. Moreover, after the light treatment the pine wood surface was more reddish and yellowish, while for the ipe it was opposite. The photochemical stability of the compared wood species is different and exotic wood turned out to be substantially more resistant, even though it is richer in chromophore groups.

Based on the infrared spectroscopy analysis, it was concluded that 340 UV irradiation yields the degradation of lignin structure, possibly leading to a decrease of its content and changes in the carbonyl group. It is difficult to conclude which wood species of those analysed here is more or less influenced by light. Infrared spectra tests conducted with the ATR sampling technique provide general information on the chemical changes occurring during irradiation, as for example they can indicate degradation of lignin or changes of selected functional groups. Therefore, the analysis of FTIR ATR spectra should be supported by other techniques, such as XPS or UV-Vis reflectance spectra.

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Standard procedures
T 204 cm-97 Solvent extractives of wood and pulp
T 222 om-02 Acid-insoluble lignin in wood and pulp
T 223 cm-01 Pentosans in wood and pulp