The Role of Extractives and Wood Anatomy in the Wettability and Free Surface Energy of Hardwoods

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The main goal of this paper was to clarify to what extent extractives and wood structure determine the surface properties of hardwoods, mainly tropical. The role of wood extractives relative to properties, such as wettability and free surface energy, has been confirmed. The most significant seemed to be cyclohexane extractives. It was further found that in the case of tested tropical wood species, the extractives contents were high. Moreover the important role of axial parenchyma in wood wettability was established. It was established that multiple regression analysis could be useful in understanding wood properties as the result of the complex structure of wood. The obtained data is crucial from a practical point of view for its disclosure of those wood species that require surface modification prior to varnish coating.

Keywords: Tropical wood; Hardwoods; Wood extractives; Wood anatomy; Contact angle; Wettability; Free surface energy

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INTRODUCTION

Materials should be characterized in terms of their surface properties, as these determine their behavior in an aggressive environment (*e.g.*, water or organic solvents), consequently determining their susceptibility to degradation in those environments. The high hydrophilicity of lignocellulosic materials makes bioattacks more likely. In the manufacturing process, the wood flooring surfaces are usually coated with finishing chemical products (such as varnishes, oils, and waxes) to improve their surface properties, in particular to increase resistance to weathering and scratching, as well as to increase hardness. However, the surface adhesion of coatings can be problematic due to the basic properties of wood (Ghofrani *et al.* 2016). Wood wettability is one of these parameters that significantly affects the gluing as well as the coating process (Gindl *et al.* 2004; Akgül *et al.* 2012; Rathke and Sinn 2013; Qin *et al.* 2014). The surface characteristics of wood that affect glue bonding are quite complex (Christiansen 1991; Gardner 1996; Gérardin *et al.* 2007). Most past studies dealt with the influence of aging, drying, and extractives, *etc.*, on wood wettability. Gardner (1996) suggested that preferential molecular reorientation of the extractives will occur depending on the surrounding environmental conditions. Moreover, wood extractives are known to affect the wettability of wood surfaces (Gardner 1996; Maldas and Kamdem 1999). Gluing

difficulties have often been experienced with some tropical woods, such as kapur (*Dryobalanops* sp.), which has been used in adhesive joint composites.

Although the glue bond quality and durability can be affected in many ways, such as by the density, porosity, and surface smoothness of the adherent, the presence of the wood extractives including the inorganic components is one of the reasons for the bonding issues (de Cademartori *et al.* 2016). Boehme and Hora (1996) explained that the characteristic of wood most dictated by structure, moisture content, density, and extractives is the water absorption ability. They pointed out that so far little has been reported about the water sorption differences of native European and tropical wood species. So far, the influence of the anatomical elements on wood properties, especially dimensional stability, was investigated in several works. It was confirmed that the simple relation between the anatomical structure and wood shrinkage is hard to establish (Arévalo 2002).

Most of the studies that have focused on the wood wetting process used liquids with different polarities (Kúdela 2014). Woods from predominantly moderate climate zones were used in the tests, which resulted in confirming that polar and hydrophilic extractives might increase wetting and that nonpolar extractives might decrease wetting. Substantial work has been done to study the effect of extractive removal on the adhesion and wettability of tropical woods.

Extraction treatments are usually conducted using various combinations of solvents, temperature, and exposure times. In Chen's (1970) investigation, the machined wood surfaces of eight tropical species were treated with a 10% solution of sodium hydroxide, acetone, and alcohol-benzene, in that order. The extractive removal treatment improved wettability and increased the pH of the wood in all tested wood species.

Maldas and Kamdem (1998) observed decreased wettability in their research: wood extracted with an ethanol-toluene solvent exhibited a higher contact angle (lower wettability) compared to the un-extracted samples. They suggested that the high contact angle was due to the hydrophobic nature of the extracted wood surface promoted by the migration of hydrophobic extractives to the wood surface. They suggested also that the more hydrophobic extractives, such as waxes and long chain hydrocarbons, that are present in a wood species, the less water this species will absorb.

Nzoku and Kamdem (2004) investigated the influence of wood extractives on the sorption and wettability behavior of northern red oak, black cherry, and red pine using extractions in various combinations of solvents. It was determined that the contact angle decreased with increased extraction due to the removal of hydrophobic extractives. Still more detailed studies involving several species are required, especially to determine the significance of the influence of wood extractives on surface properties and how the contact angle is affected by extraneous wood substances, as the influence wood structure on wood surface properties has not been investigated in detail either.

The leading aim of the presented research is to study the impact of wetting phenomena on wood. This paper aims to clarify and confirm whether, and to what extent, extractives and wood structure determine the surface properties of tropical hardwoods. Subsequently, the aim of the study is to compare the differences in wettability of the wood species present in many wood floors manufactured in Europe. The obtained knowledge could have utility in the context of the wood finishing and wood gluing processes. The gathered data is also important from practical point of view as it discloses which wood species require surface modification prior to the finishing.

EXPERIMENTAL

Materials

The wood species used in this study are enumerated and described in Table 1.

Table 1. Wood Species Used

Wood Name	Scientific Name	Plant Family	Origin	Special Features
Afzelia	*Afzelia* sp.	Caesalpiniaceae	Africa (Ghana)	Irregular fiber arrangement
Tatajuba	*Bagassa guianensis* Aubl.	Moraceae	South America (Brazil)	Irregular fiber arrangement
Sapele	*Entandophragma cylindricum* (Sprague) Sprague	Meliaceae	Africa (Ghana)	Irregular fiber arrangement
European beech	*Fagus sylvatica* L.	Fagaceae	Europe (Poland)	Wide wooden rays
Owangkol	*Guibourtia ehie* J. Leon.	Caesalpiniaceae	Africa (Ghana)	Irregular fiber arrangement
Courbaril	*Hymenea courbaril* L.	Fabaceae	South America (Brazil)	Irregular fiber arrangement, axial parenchyma in narrow bands
Merbau	*Intsia* sp.	Fabaceae	Asia (Burma)	Irregular fiber arrangement
Iroko	*Milicia excelsa* (Welw.) C.C. Berg.	Moraceae	Central Africa (Cameroon)	Axial parenchyma in wide bands, irregular fiber arrangement
Wenge	*Millettia laurentii* De Wild.	Fabaceae	Africa (Gabon)	Axial parenchyma in wide bands, irregular fiber arrangement
Opepe	*Nauclea diderrichii* (De Wild. & Th. Dur.) Merr.	Rubiaceae	Africa (Ghana)	Irregular fiber arrangement
African padouk	*Pterocarpus soyauxii* Toub.	Fabaceae	Africa (Gabon)	Axial parenchyma in narrow bands
European oak	*Quercus* sp.	Fagaceae	Europe (Poland)	Wide wooden rays
Light red meranti	*Shorea* sp.	Dipterocarpaceae	Asia (Indonesia)	Irregular fiber arrangement, axial parenchyma in narrow bands
Ipe	*Tabebuia* sp.	Bignoniaceae	South America (Brazil)	Irregular fiber arrangement
Teak	*Tectona grandis* L.	Lamiaceae	Asia (Burma)	Axial parenchyma in narrow bands

These species were selected to have a representative sample of hardwoods with a wide range of densities, types and amounts of extraneous substances, and different anatomical structures. European beech and European oak were used as references. The

selected species are widely used in flooring production in Europe. All test materials were heartwood, as it is more commercially usable than sapwood. Wood from each wood species was acquired from DLH Poland, Warsaw, Poland. Material was identified in the laboratory using macroscopic techniques.

The samples of each wood species were collected from one log; thus, differences in the tested properties caused by differences in wood anatomy were avoided. Each part was quarter-sawn to produce planks of approximately 4 cm thickness. They were then were air-dried in a room with relative humidity up to 50% and temperature of 21 °C for 6 months prior to testing. The defect-free planks were sawn and sized into samples for the contact angle measurements. Ten samples of each wood species were prepared, each with a radial and tangential cross-section of 8 mm × 10 mm and a length of 70 mm. Tangential and radial direction were chosen due to the fact that in finished wooden products (such as furniture, floors, *etc*.) they are the main surfaces. The radial-oriented or tangential-oriented surface of the wood block was cut with a sledge-microtome using a type 'R35' knife. According to Gardner (1996) and Liptakova *et al.* (1994), a wood surface microtomed parallel to the grain only shows roughness caused by the cellular structure of wood and only a negligibly small roughness caused by cutting. Furthermore, the wood surface is chemically heterogeneous and therefore does not comply with the requirements of the physicochemical theory of contact angle in a strict sense.

Methods

Extraction

Wood sawdust was extracted in adherence with the standards ASTM D110-84 (2013) and ASTM 1107-96 (2013), with modification to the solvents. Extraction was done with a Soxhlet extractor using a mixture of chloroform and ethanol (93:7, v/v), cyclohexane, and hot water. The solvents were used separately. The mixture of chloroform and ethanol was used as substitution of mixture of ethanol-toluene based on Antczak *et al.* (2006). The reason was toluene toxicity to human health (Tardif *et al.* 1992). All of the chemicals were analytical reagent grade products of Chempur, Poland.

Each wood sawdust sample was extracted over a period of 10 h using the Soxhlet equipment. The solvents were vaporized to a viscous solution in a rotary evaporator and then dried to produce dry mass.

Wettability and free surface energy measurement

Water contact angle is a measurement allowing the characterization of surface properties. A single measurement provides several important parameters: surface free energy, contact angle, and wetting coefficient or work of adhesion. The characterization of the surface properties allows for the prediction of interactions with wetting materials (lacquers or adhesives). The contact angle (θ) is a measure of the impact of wetting of the substrate by solution. The smaller value indicates better wettability of the material.

Subsequent to microtoming, the wood blocks were placed into the contact angle measuring apparatus, and measurements were started promptly. The contact angle is defined as the angle within the droplet between the solid surface and a tangent, drawn on the drop-surface, passing through the triple-point atmosphere-liquid-solid (Zisman 1963). Contact angles of the expanding droplets, *i.e.*, advancing angles, were determined using a contact angle measuring device. The surface free energy values were determined using the Owens-Wendt method (Owens and Wendt 1969). This was performed on a Goniometer Haas Phoenix 300 (Surface Electro Optics, Suwon City, South Korea)

contact angle analyzer, equipped with microscopic lenses, a digital camera, and attached to a computer with software that provided an image of the drop on the tested wood surfaces. An image analysis system (Image XP, Surface Electro Optics, version 5.8, Suwon City, South Korea) calculated the contour of the drop from an image captured by means of a video camera. The re-distilled water and diiodomethane were used as reference liquids for the wettability and free surface energy calculations. Four contact angle measurements were taken on each of ten drops per liquid placed on ten microtomed wood samples. Based on the research of Liptáková and Kúdela (1994), the measurements of the contact angle were after 30 s from each drop of reference liquid dropped. In this study, two test liquids (polar and nonpolar) were used (Table 2), allowing the determination of surface free energy.

The surface free energy was calculated from the previously set contact angles for the measurement of reference liquids, based on the Fowkes method. The method consists of determining the contact angles for two measuring fluids (water and diiodomethane), and free surface energy (γ_S) is the sum of two components, dispersion (γ_s^d) and polar (γ_s^p) (Wolkenhauer *et al.* 2009).

Table 2. Data for Surface Tension and Components of the Test Liquids (Van Oss *et al.* 1998)

Liquid	Properties				
	Surface Tension	Dispersion	Polar	Acid	Base
	mJ/m^2				
Water (H_2O)	72.80	21.80	51.00	25.50	25.50
Diodomethane (CH_2I_2)	50.80	50.80	0.00	0.00	0.00

The calculation of surface free energy was based on the following formulas:

$$\gamma_s = \gamma_s^d + \gamma_s^p, \quad (1)$$

$$\left(\gamma_s^d\right)^{0,5} = \frac{\gamma_d\left(\cos\Theta_d + 1\right) - \sqrt{\frac{\gamma_d^p}{\gamma_w^p}}\gamma_w\left(\cos\Theta_w + 1\right)}{2\left(\sqrt{\gamma_d^d} - \sqrt{\gamma_d^p\frac{\gamma_w^d}{\gamma_w^p}}\right)}, \quad (2)$$

$$\left(\gamma_s^p\right)^{0,5} = \frac{\gamma_w\left(\cos\Theta_w + 1\right) - 2\sqrt{\gamma_s^d\gamma_w^d}}{2\sqrt{\gamma_w^p}}, \quad (3)$$

where γ_s is the experimentally determined wood surface free energy (mJ/m^2), γ_s^d is the dispersed component of surface free energy (mJ/m^2), γ_s^p is the polar component of surface free energy (mJ/m^2), γ_d is the surface tension of the diiodomethane (mJ/m^2), γ_d^d is the dispersed component of surface free energy of diiodomethane (mJ/m^2), γ_d^p is the polar component of surface free energy of diiodomethane (mJ/m^2), γ_w is the surface energy (surface tension) of water (mJ/m^2), γ_w^d is the dispersed component of surface free energy of water (mJ/m^2), γ_w^p is the polar component of surface tension of water (mJ/m^2), Θ_d is the contact angle (°) between the tested surface and diiodomethane, and Θ_w is the contact angle between the tested surface and water (°).

Density determination

The density determination was performed in accordance with the ASTM D2395 (2002) standard.

Determination of proportion of anatomical parameters

Before the microscopic measurements were performed, the wood specimens were soaked for three months in a mixture of water, glycerol, and 96% ethanol to soften the wooden tissue (volume ratio 1:1:1) (Boruszewski *et al.* 2017). A sledge microtome (Reichert, Vienna, Austria) was used to cut samples in slices of 10- to 30-µm thickness each. Microscopic preparations were stained with 5% safranin solution in ethyl alcohol (96%). Anatomical parameters were measured using an image transverse and tangential cross-section. Images of the wood were captured using an Olympus BX40 light microscope (Olympus Corporation, Tokyo, Japan). The proportion of vessels, parenchyma, and rays and fibers were measured by the image processing software WinCELL (Regent Instrument Inc., version 2016a, Québec, Canada).

Statistical procedure and modelling data

The statistical analysis of the test results was conducted using Statistica v.10 software (StatSoft, Inc., Tulsa, OK, USA). The data were analyzed and the mean ± standard deviation, the coefficient of variation, a bar graph of results were provided. To compare and to determine the significance of differences between the data, t tests were used.

Moreover, the effects of different concentrations of extractives on the wood surface properties were determined. Multiple regression analyses were used to evaluate the relationships between the contact angle and the principle variables (extractive content and anatomical parameters). Before multiple regressions, simple correlations were calculated to identify the sources of multiple correlations. This allowed the determination of which variables remained independent.

To indicate the most important extraneous substances for the wood surface properties (contact angle) based on the obtained results, two models of regression were determined:

1. The dependence of surface properties of the wood on extractives soluble in a mixture of chloroform, cyclohexane, and hot water.
2. The dependence of surface properties of the wood on extractives soluble in a mixture of chloroform and cyclohexane, hot water, and anatomical parameters.

For each regression, a coefficient of determination (R^2) was established. To define the importance of each included independent variable, the beta coefficients were determined. These coefficients were calculated for each regression model and they cannot be compared.

RESULTS AND DISCUSSION

Differences between Wood Species

The results of anatomical characteristics and extractives content are shown in Table 3. The obtained results indicated high variation in the anatomical characteristics among the tested wood species. The highest variability was observed in the case of axial parenchyma content (the coefficient of variability was 75%). The percentage proportion

of axial parenchyma ranged from 3.5% in ipe to 55.6% in wenge (axial parenchyma present in the form of wide and tangential bands). The variability of vessels, rays, and fibers proportion was lower (the coefficients of variability were respectively 47%, 39% and 19%).

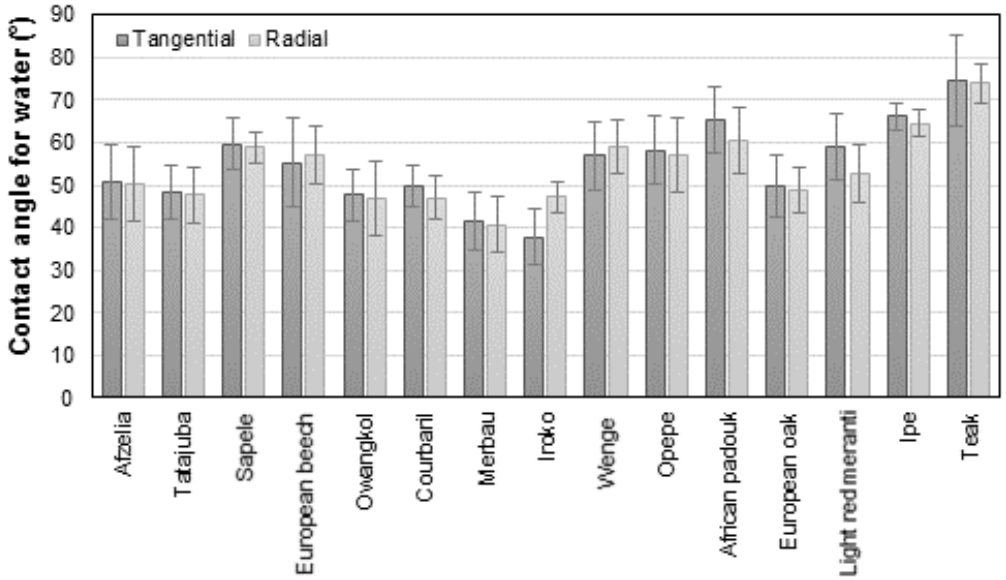
Table 3. Extractives Substances, Quantitative Anatomical Parameters, and Wood Density of Tested Wood Species (means and standard deviation in parenthesis)

Wood	Extractives Soluble in:			Anatomical Parameters (Proportion)				Density
	Chloroform-ethanol	Cyclo-hexane	Hot Water	Vessels	Axial Paren-chyma	Rays	Fibers	
	%			%				kg/m^3
Afzelia	3.62 (0.41)	0.50 (0.07)	7.99 (0.31)	12.2 (2.3)	23.6 (3,5)	16.1 (1.9)	64.2 (2.5)	725 (15)
Tatajuba	3.03 (0.33)	0.34 (0.05)	11.22 (2.09)	19.5 (3.6)	14.8 (2.1)	17.6 (1.5)	75.0 (1.9)	900 (19)
Sapele	1.91 (0.22)	1.04 (0.13)	6.07 (1.12)	11.5 (2.1)	23.6 (2.9)	16.1 (2.0)	67.8 (2.7)	637 (18)
European beech	1.44 (0.17)	0.23 (0.05)	4.24 (0.79)	25.0 (3.8)	5.2 (1.5)	10.5 (1.3)	69.9 (2.2)	686 (17)
Owangkol	1.29 (0.23)	0.30 (0.06)	5.93 (1.21)	7.9 (1.8)	4.2 (0.8)	18.4 (2.6)	83.6 (2.5)	974 (29)
Courbaril	6.04 (0.66)	0.31 (0.05)	12.02 (2.71)	7.8 (1.4)	15.8 (3,6)	11.7 (1.9)	79.4 (1.3)	949 (35)
Merbau	3.09 (0.44)	0.71 (0.10)	17.29 (3.65)	19.9 (4.1)	22.2 (5,0)	13.7 (2.2)	57.4 (0.6)	845 (24)
Iroko	8.90 (1.02)	0.94 (0.11)	6.47 (1.64)	20.0 (2.9)	34.2 (5.0)	25.6 (3.4)	45.8 (1.2)	521 (16)
Wenge	2.28 (0.27)	0.22 (0.04)	4.33 (0.92)	7.5 (1.1)	55.6 (6.2)	17.5 (0.5)	36.9 (0.1)	823 (20)
Opepe	2.58 (0.31)	0.27 (0.37)	4.19 (1.14)	22.7 (4.2)	8.1 (1.6)	34.9 (4,1)	69.3 (0.9)	696 (15)
African padouk	12.80 (1.40)	2.71 (0.04)	5.73 (1.06)	6.5 (1.5)	21.2 (3.8)	9.0 (1,0)	73.2 (2.0)	651 (38)
European oak	2.17 (0.26)	0.17 (0.18)	11.21 (2.09)	27.0 (5.7)	15.2 (2.9)	21.1 (2,6)	58.0 (3.8)	650 (22)
Light red meranti	1.82 (0.24)	1.40 (0.41)	2.92 (0.54)	26.7 (4.2)	4.6 (1.3)	16.7 (2,9)	68.2 (3.0)	499 (17)
Ipe	7.51 (0.89)	3.22 (0.41)	12.63 (3.54)	30.3 (4.1)	3.5 (1,1)	9.8 (1,3)	65.1 (3.0)	923 (15)
Teak	8.72 (1.04)	4.76 (0.39)	4.33 (0.76)	28.4 (5.4)	21.9 (3.9)	19.8 (3,9)	66.1 (0.6)	745 (20)

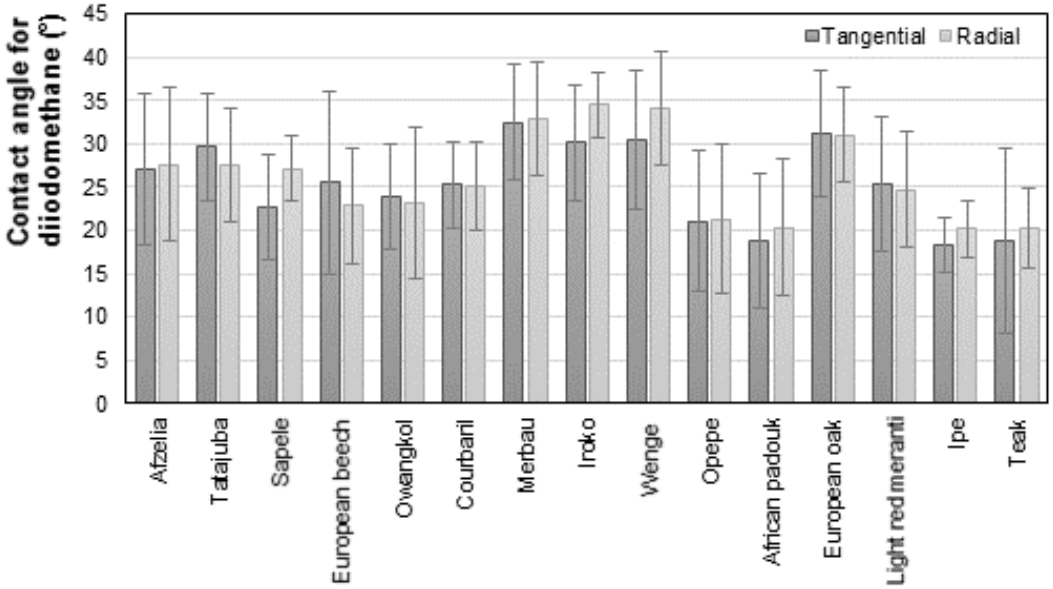
The extraneous substances exhibited high solubility during the course of study (Table 3) and high variability. Hot water extractives ranged from 2.92% in light red meranti to 17.29% in merbau. Organic solvent-soluble extractives reached lower results. The amount of extractives soluble in the mixture of chloroform-ethanol ranged from 1.29% in owankgol to 12.80% in African padouk. The amount of extractives soluble in cyclohexane ranged from 0.22% in wenge to 4.76% in teak and showed the highest variability (the coefficient of variability was 119%).

Contact Angles and Free Surface Energy of Tested Wood Species

As a result, it was observed that the drop, upon contact with the wood surface, simultaneously spread over the surface and soaked into the porous structure of the wood. The drop parameters, as well as the contact angle, changed. The average values of the measured contact angles and free surface energy of the tested wood species are given in Figs. 1 and 2.



a)



b)

Fig. 1. Mean values of the contact angle obtained for each tested wood species studied for: a) water, and b) diiodomethane

It was observed that for each wood species, the conducted contact angle test between the tested surface and the diiodomethane was lower. Such a result was expected, as diiodomethane is an apolar liquid of a lower surface free energy than distilled water. The tangential surfaces showed a higher contact angle for water in most of the cases (in case of contact angle for diiodomethane there such relation was not observed). However, there were no significant differences between the radial and tangential cross-sections in any of the tested wood species (t tests were used).

Iroko and wenge wood were the exceptions, which meant that in both cases, the radial cross-sections of the wood species showed a higher value of contact angle for water as well as diiodomethane. This relatively higher values could have been caused by wood structure. Both iroko and wenge are wood species with wide tangential parenchyma bands. Moreover, the percentage share of axial parenchyma in the wood structure is relatively high in both wood species. Other tested wood species did not have such wide tangential parenchyma bands. This type of tissue was present mainly in wooden rays. It confirmed that wood structure had an influence on the properties of the wood surfaces.

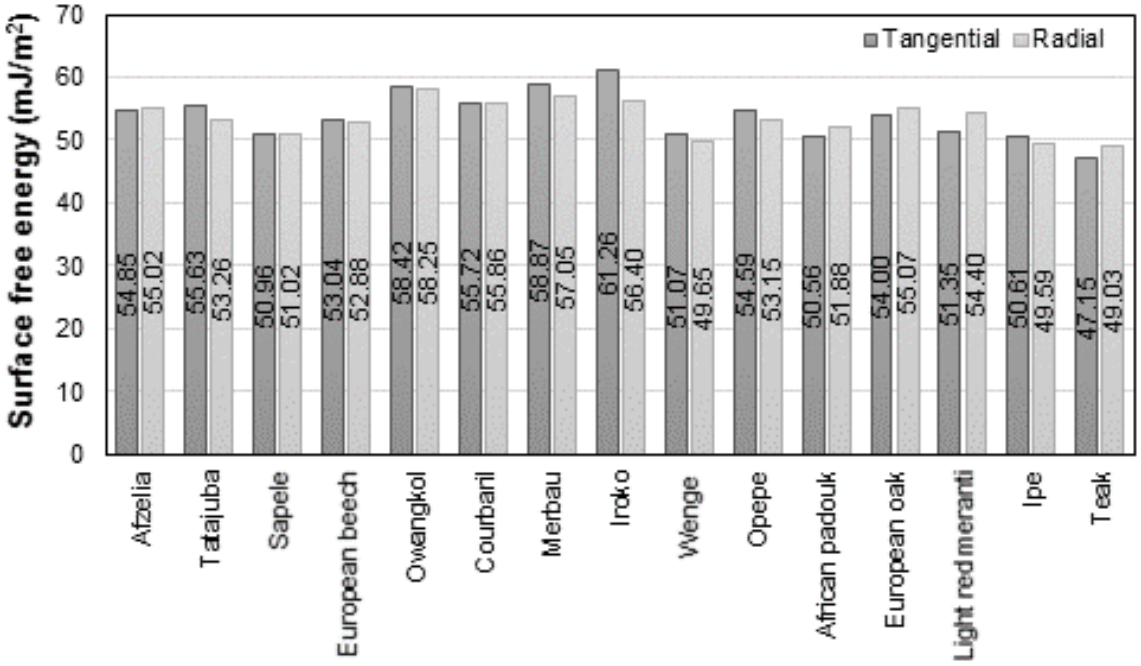


Fig. 2. Mean values of the surface free energy calculated for each tested wood species

The difference between the radial and tangential surface in terms of contact angle was confirmed by Amorim *et al.* (2013). The results indicated that the tangential face presented better wettability with water among the tested wood species. The highest value of contact angle for water was found in teak wood, with the relatively high content of extractives soluble in the chloroform-ethanol mixture and cyclohexane. A similar observation was made in the case of African padouk, with 12.8% chloroform-ethanol-extractives. The lowest average value of contact angle for water was found in merbau wood, with the highest content of extractives soluble in hot water (17.3%). Undoubtedly, due to the high content of hot water extractives (12.6%), and despite the high content of chloroform-ethanol extractives (7.51%) and cyclohexane extractives (3.22%), in the case of the ipe wood, the average contact angle for water was close to average values. A similar situation was detected for courbaril wood.

Considering all observations made, it could not be confirmed, using any statistical method, that any of the independent variables had a significant influence. This phenomenon is confirmed with former studies (Maldas and Kamdem 1999; Nzoku and Kamdem 2004). This was potentially the result of the complex chemical structure of the tested wood species. Thus, indicating the major factor, such as content particular extractives, was not possible. Furthermore, multiple regressions seem to be useful in explaining the differences between the wood species.

The results of the determination of surface free energy are given in Fig. 2. The average value of surface free energy in the tangential cross-section for all tested wood species was 53.9 mJ/m², and in the radial cross-section was 53.5 mJ/m². The surmise that there was no difference in surface properties between the radial and tangential cross-sections is confirmed in previous literature (Kúdela *et al.* 2015). However, according to Tokareva *et al.* (2007), the surface chemistry and wetting properties of the wood surfaces are directly dependent on the wood surface morphology resulting from the wood machining process used as a surface formation method, and these properties also vary greatly depending on, for instance, whether the cross-section, radial, or tangential section is being considered. This showed that studies in the area of surface free energy and contact angle are incomplete and that knowledge in this field of expertise should be followed up. Results of conducted tests indicated the wood species requiring special attention prior to surface finishing processes (for example using varnish coatings). These wood species are teak, and ipe that showed the lowest values of surface free energy.

Role of Extractives and Anatomy in Wood Wettability and Surface Free Energy

The standardized regression coefficients (Table 4) were applied to verify the main chemical and anatomical factors determining the tested surface properties. The larger the absolute values of the standardized regression coefficient, the greater its influence was on the dependent variables.

Table 4. Correlation Coefficients between Surface Properties, Extractives Content, and Anatomical Parameters

Variables	Θ_{wT}	Θ_{wR}	Θ_{dT}	Θ_{dR}	γ_{sT}	γ_{sR}	C-E	Cyc	HW	V	P	R	F	D
Θ_{wT}	1.00	**	*	**	**	ns	ns	**	**	ns	ns	ns	ns	ns
Θ_{wR}	0.75	1.00	ns	ns	*	**	ns	*	ns	ns	ns	ns	ns	ns
Θ_{dT}	-0.67	-0.41	1.00	**	ns	ns	*	ns	*	ns	ns	ns	ns	ns
Θ_{dR}	-0.80	-0.54	0.78	1.00	*	ns	ns	**	*	ns	ns	ns	ns	ns
γ_{sT}	-0.94	-0.67	0.45	0.62	1.00	ns	ns	*	**	ns	ns	ns	ns	ns
γ_{sR}	-0.48	-0.91	0.20	0.19	0.46	1.00	ns	ns	ns	ns	ns	ns	ns	ns
C-E	0.46	0.32	-0.61	-0.39	-0.34	-0.19	1.00	*	ns	ns	ns	ns	ns	ns
Cyc	0.81	0.72	-0.57	-0.75	-0.73	-0.46	0.66	1.00	ns	ns	ns	ns	ns	ns
HW	-0.82	-0.50	0.60	0.64	0.82	0.34	-0.09	-0.43	1.00	ns	ns	ns	ns	ns
V	0.14	0.16	0.18	-0.38	-0.13	0.02	-0.51	0.14	-0.12	1.00	ns	ns	ns	ns
P	0.36	0.48	-0.06	0.04	-0.39	-0.59	0.08	0.02	-0.41	-0.32	1.00	ns	**	ns
R	0.25	0.21	-0.09	-0.30	-0.12	-0.08	-0.34	-0.13	-0.31	0.47	0.40	1.00	*	ns
F	-0.45	-0.58	-0.06	0.21	0.47	0.57	0.26	-0.12	0.48	-0.35	-0.78	-0.71	1.00	ns
D	-0.09	-0.18	0.15	0.24	0.05	0.17	-0.14	-0.31	0.56	-0.44	-0.03	-0.20	0.31	1.00

Note: γ_s - experimentally determined surface free energy (surface tension), Θ_d - contact angle for diiodomethane, Θ_w - contact angle for water, last letter: $_R$ - radial surface, $_T$ - tangential surface; C-E - extractives soluble in mixture of chloroform and ethanol, Cyc- extractives soluble in cyclohexane, HW - extractives soluble in hot water; V - proportion of vessels on transverse surface, P - proportion of axial parenchyma on transverse surface, R - proportion of rays area on tangential surface, F - proportion of fibers on transverse surface; *- statistical significant value at p-level < 0.05; ** - statistical significant value at p-level < 0.01; ns - not significant at 0.05 level.

As density is widely acknowledged to reflect many wood properties (Hernández 2007; Schulgasser and Witztum 2015), it was expected to influence the contact angle and free surface energy of the tested wood species. However, it appeared that wood density was not an important indicator determining surface wood properties. As demonstrated in Table 4, the calculated correlation coefficients were relatively low (below 24%). Significant correlations were determined for extractive contents that indicated a high role in wettability and free surface energy. The nature of the relation (positive or negative) depended on the group of extractives. Polar extractives (HW) had a positive influence on wettability with dispersion liquid and free surface energy and a negative relationship with wettability with water. The extractives that were soluble in nonpolar extractives (C-E, Cyc) had the opposite relationships.

Thus, to simplify the data analysis, and due to the weak relationship between wood surface properties, vessels proportion, and wood density, in subsequent analyses, wood density was not included.

Table 5. Multiple Regression Equation Models of the Relations between Properties of Wood Surface and Extractives

Multiple Regression Equation Model	R^2	p
Θ_{wT} = 56.81* - 0.73 C-E + 6.99 Cyc* - 0.97 HW* (-0.26) (0.79) (-0.42)	0.81	0.011
Θ_{wR} = 51.38* - 0.82 C-E + 7.96 Cyc* - 0.82 HW (-0.29) (0.92) (-0.14)	0.78	0.017
Θ_{dT} = 24.42* - 0.68 C-E - 2.12 Cyc* + 0.37 HW (-0.16) (-0.52) (0.38)	0.76	0.106
Θ_{dR} = 22.48* - 0.75 C-E - 3.84 Cyc* + 0.49 HW* (-0.31) (-0.77) (0.53)	0.81	0.009
γ_{sT} = 52.80* - 0.41 C-E - 2.48 Cyc* + 0.30 HW (-0.37) (-0.78) (0.35)	0.72	0.055
γ_{sR} = 55.36* - 0.20 C-E - 2.35 Cyc* + 0.02 HW (-0.18) (-0.77) (0.02)	0.78	0.022

Note: γ_s - experimentally determined surface free energy (surface tension), Θ_d - contact angle for diiodomethane, Θ_w - contact angle for water, C-E - extractives soluble in mixture of chloroform and ethanol, Cyc - extractives soluble in cyclohexane, HW - extractives soluble in hot water; last letter: $_R$ - radial surface, $_T$ - tangential surface; in parentheses beta coefficient of regression is given; *- statistical significant value at p-level < 0.05.

The multiple regression models for the tested wood surface properties are presented in Tables 5 and 6. The retained models gave relatively high coefficients of determination. In the case of the models of the relations between the properties of wood surface and the extractives, the R^2 averaged from 0.72 to 0.81, suggesting an important role for extractives in wood wetting both with water and diiodomethane. The most important independent variable in those models was the cyclohexane extractives. Investigation of standardized regression coefficient showed that cyclohexane extractives accounted for approximately 52% to 92% (depending of the model) of the total variance. Thus, the wetting properties of teak, ipe, and African padouk could be easily explained. Those wood species contain the highest amount of cyclohexane extractives and showed the highest contact angle for water (polar) and the lowest contact angle for diiodomethane (dispersive). Moreover, these wood species showed relatively high content of chloroform-ethanol extractives. The important influence of cyclohexane extractives was emphasized when testing the dimensional stability of wood and the equilibrium moisture content (Hernández 2007; Jankowska *et al.* 2017). It was observed that the high content lowered shrinkage. Cyclohexane is a non-polar solvent and presumably not able to open up and penetrate cell walls. Instead, cyclohexane is expected to remove extractives located within the cell lumen and intercellular spaces (Hernández 2007). Removing hydrophobic extractives, such as waxes and sterols, seems to demand cyclohexane as an extraction solvent. The variability in the chloroform-ethanol and hot water extractives was an important factor, and in the case of merbau wood, the hot water extractive content was relatively high. Most likely, due to the polar character, this influenced the decreased contact angle for water and increased the contact angle for the non-polar liquid, diiodomethane.

Table 6. Multiple Regression Equation Models of the Relations Between Properties of Wood Surface, Extractives Content, and Wood Anatomy Parameters

Multiple Regression Equation Model	R^2	p
Θ_{wT} = 53.97* - 1.54 C-E + 9.59 Cyc* - 0.83 HW + 0.20 P + 0.02 R + 0.25 F (-0.54) (1.11) (-0.36) (0.25) (0.29) (0.15)	0.86	0.074
Θ_{wR} = 55.31* - 1.78 C-E + 11.71 Cyc* - 0.38 HW + 0.34 P + 0.16 R + 0.17 F (-0.54) (0.96) (-0.23) (0.25) (0.29) (0.16)	0.91	0.018
Θ_{dT} = 20.55* + 0.11 C-E - 3.84 Cyc* + 0.31 HW - 0.22 P* - 0.29 R - 0.37 F* (0.07) (-0.85) (0.27) (0.60) (-0.42) (-0.75)	0.89	0.090
Θ_{dR} = 24.42* + 0.06 C-E - 4.83 Cyc* + 0.41 HW - 0.15 P - 0.31 R - 0.28 F (0.36) (-0.97) (0.32) (-0.58) (-0.40) (-0.56)	0.90	0.038
γ_{sT} = 52.59* + 0.65 C-E - 2.93 Cyc* + 0.23 HW - 0.14 P* - 0.09 R + 0.22 F (0.59) (-0.87) (0.27) (-0.60) (-0.42) (0.28)	0.84	0.112
γ_{sR} = 59.56* + 0.63 C-E- 3.64 Cyc* + 0.23 HW - 0.20 P* - 0.07 R + 0.25 F (0.54) (-1.05) (-0.26) (-0.73) (-0.73) (0.34)	0.84	0.106

Note: γ_S - experimentally determined surface free energy (surface tension), Θ_d - contact angle for diiodomethane, Θ_w - contact angle for water, C-E - extractives soluble in mixture of chloroform and ethanol, Cyc - extractives soluble in cyclohexene, HW - extractives soluble in hot water, V - percentage share of vessels on transverse surface, P - percentage share of axial parenchyma on transverse surface, R - percentage share of rays area on tangential surface; last letter: $_R$ - radial surface, $_T$ - tangential surface; in parentheses beta coefficient of regression is given; *- statistical significant value at p-level < 0.05.

The multiple regression equations describing the relations between the properties of the wood surface, extractives content, and wood anatomy parameters (Table 6) confirmed their strong relation (coefficient of determination R^2 in a range from 0.84 to 0.91). The very low level of the p values suggested that the obtained equations could be used for prediction. Those correlations were stronger than when only wood extractives were analyzed. This illustrated the important role of wood anatomy. This aspect was mentioned in previous studies, but detailed data are not shown (Boehme and Hora 1996; Tokareva *et al.* 2007). According to the results, the most important parameter was the axial parenchyma content. In the case of the contact angle for water, the correlations were positive. The important role of axial parenchyma results from the fact that most wood extractives are found largely in the parenchyma (Hillis 1971), especially the substances such as fats and waxes that act hydrophobic are present in parenchyma cells (Sjöström 1993). The variability in the share of the wood rays on the tangential surface was not high, and thus no significant role of parenchyma tissue in the wood rays was established. While the percentage proportion of axial parenchyma in the tested wood species ranged from 3.5% to 55.6%, the proportion of rays on the tangential surface ranged from 9.0% to 34.9%.

CONCLUSIONS

1. The role of wood extractives in the properties of the wood surface, namely contact angle for polar and dispersive liquids, was confirmed. The most significant appeared to be cyclohexane extractives. Moreover, it was found that in the case of tropical wood species, the content of extractives can be much higher than in the wood from moderate climate zone, which significantly affected the surface properties of wood.

2. The high variation in wood extractives among the tested wood species was defined. It was also established that there was high variation in the anatomical characteristics among the tested wood species. The highest variability was observed in the case of axial parenchyma content
3. The role of axial parenchyma in wood wettability was determined. It was found that the higher the content of axial parenchyma, the higher the contact angle that was reached, which was a result of the fact that wood extractives are mostly found in the parenchyma.
4. Multiple regression analyses can be useful in understanding wood properties as the results of the complex structure of wood. Thus, indicating the major factor (such as the content of particular extractives) is not possible.
5. Results of the tests indicated the wood species that require special attention prior to surface finishing processes (for example using varnish coatings). These wood species are teak, and ipe.

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