Theses of PhD dissertation

Analysis of wood surface attributes, with special regard to the wettability of different wood species

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Introduction

Wood is a source of renewable raw materials and it's available in different quality and quantity around us. The different wood species are differentiated according to their origin: continent, climatic belt and country area also. Such differences can be the growth habit, color variant or the characteristics of machined wood. In case of wood as a structural material because of the material's diversity, those attributes which carry useful information for manufacturing industry, and their variability, even actually arise many open questions. During gluing and finishing wood surface, problems can be caused by the antecedent life of machined wood material: according to the machining method and storage conditions, etc.. It is a primary task to identify their causes for to overcome the errors. Despite of the modern technological background during wood gluing and finishing, the achieved quality of adhesion often shows up unsatisfactory, which causes difficulties.

Main topics of this scientific research concern processed and naturally/artificially aged wood surface properties. These properties are grouped around the time elapsed from the machining of wood surface, the surface roughness, and the chemical composition of the ageing wood surface – influencing the contact angle of wetting liquids, thus the adhesion as well.

Investigations - related to the upper topics - were made on two diffuse porous (beech ((*Fagus sylvatica* L.) and birch (*Betula pendula*)), a ring porous (sessile oak (*Quercus petraea*)), and pine (spruce (*Picea abies*)) wood species.

I. Research goals

Investigation of *the time elapsed from the machining of wood*, as technological parameter was performed by natural aging and artificial xenon radiation also.
The goal of the examinations was to reveal the effect of time elapsed from machining on surface free energy, from qualitative and quantitative aspects.

Wood surface roughness as a factor influencing the contact angle is a long time investigated parameter.
Since earlier researches on this subject mostly focused on examining a smaller scale of the surface roughness, due to the present research the surface roughness scale has been widened. The goal was to identify characteristic ranges of surface roughness (or grit sizes) and to understand the effects of the different roughness ranges on the contact angle of liquid.

In case of wood the third factor which has the most complex impact on wood surface wetting is *the quality and quantity of chemical components of wood* and especially the wetted surface. For to understand the relation between the chemical changes of wood components and surface free energy alteration during aging and artificial xenon radiation, simultaneously with artificial radiation investigation of chemical components was performed. During the radiation process the performed examinations were the following: FTIR, total phenolic and total soluble carbohydrate analysis.

II. Materials and methods

During the research the following examinations were performed:

- *wood surfaces sanded with different grit size* sandpaper: surface roughness measurements, contact angle measurements (distilled water), SEM images,
- *natural aged (indoor) surfaces:* contact angle measurements with distilled water,
- *artificial aged wood surfaces:* contact angle measurements (distilled water and diiodomethane), moisture content examinations, total phenolic and total soluble carbohydrate content measurements and FTIR measurements,

using the following wood samples:

- beech (*Fagus sylvatica* L.),
- birch (*Betula pendula*),
- sessile oak (*Quercus petraea*),
- and spruce (*Picea abies*).

Investigation of differently rough wood surfaces, with special regard to wettability

All wood surfaces were machined with Sandya 3S (SCM Group, Italy) contact sanding machine, parallel to the grain. After machining, sanding dust was removed from wood surfaces. Grit sizes of sandpapers used for machining were the following: 60, 80, 100, 120, 150, 180, 220, 240, 280, 320, 400, 500 and 600.
For investigation of contact angle dependence from surface roughness, contact angle measurements with PG-X goniometer (FIBRO SYSTEMS AG, Sweden) and surface roughness measurements with PERTHEN-Mahr S3P (PERTHEN, MAHR GmbH, Germany) PC controlled

stylus tip instrument were performed. SEM images were also taken with Hitachi S3400 (HITACHI Ltd., Japan) scanning electron microscope in order to visually investigate wood surfaces.

Surface roughness measurements

On each wood surface resulting from four different wood species and sanded with 13 different grit size sandpapers 10 surface roughness measurements were performed. Results of the surface roughness measurements were evaluated using the R_z (mean roughness depth) parameter.

Contact angle measurements

On each wood surface, resulting from four species sanded by different grit size sandpaper, 20 dynamic contact angle measurements were performed. Drop volume of the measuring liquid was 5 µl and the contact angle was measured 1 sec after the release of the droplet.

Recording the scanning electron microscope (SEM) images

To take SEM images samples sanded with different grit sizes (60, 220 and 500) were used with 20*20 mm surface. When recording the images (3D type, 100* magnification) 10 kV accelerating voltage were applied.

Investigation of artificially aged wood surfaces, with special regard to wettability

Artificially aged wood surfaces were sanded with grit size 150 before ageing.

Three types of samples were used for different measurements:

- type 1: for contact angle and moisture content examinations,
- type 2: for total phenol and total carbohydrate content measurements and
- type 3: for FTIR measurements.

Technological background of artificial ageing and determination of measurement periods

Artificial ageing of different wood species were performed with Original Hanau Suntest (HERAEUS, Germany) equipped with xenon bulb and built-in UV mirror. During artificial ageing temperature of wood surfaces did not exceed the predetermined 55±5°C.

The different measurements were performed in the following ageing periods:

0 h (control), 1 h, 3 h, 5 h, 8 h, 10 h, 15 h, 20 h, 30 h, 60 h, 96 h, 132 h, 174 h and 240 h, respectively.

Contact angle measurements of artificially aged wood surfaces

20-20 contact angle measurements were performed on each wood surface, in case of all ageing periods. For tests bi-distilled water (polar and disperse) and diiodomethane (disperse) (SIGMA-ALDRICH, USA) were used as test liquid.

Investigation of total phenolic and total soluble carbohydrate contents

To accomplish the total phenolic and total soluble carbohydrate contents the upper ~75-100 micrometer thick layer was collected from the different wood samples during ageing.

Alcoholic extraction

For extraction 4:1 methanol:water mix was used. Ultrasonic bath (BRANSON 3510, EMERSON, USA) (20 min) was applied after 5 ml extracting agent was mixed to the previously collected wood material (~0,05 g). The extract – produced in this manner – was centrifuged with MiniSpin (EPPENDORF, Germany) spinner for 10 minutes (13400 1/r RPM).

Determination of total phenolic content

Total phenolic content was calculated based on the Folin-Ciocalteu method (Singleton and Rossi, 1965). During the measurements Folin-Ciocalteu reagent (2,5 ml, ten-fold dilution) was mixed to the extract (0,5 ml) firstly. After 1 min application time 2 ml (concentration: 0,7M) Na_2CO_3 solution was blended to the mixture. The reaction mixture was warmed in a water bath (Memmert WNB 200, MEMMERT GmbH, Germany) at 50°C for 5 minutes. After warming, the solutions were cooled in cold water bath, until the temperature of solutions reached ~25°C. For determination of total phenol content spectrophotometer (Metertech SP 8001, METERTECH Inc., China) was used, at 760 nm wavelength and as standard, quercetin was used.

Determination of total soluble carbohydrate content

Total phenolic content was calculated based on method of Dubois et al (1956). Firstly to the extract (0,5 ml) phenol solution (0,5 ml; dilution: 5%) was mixed. After mixing to the solution 2,5 ml concentrated sulfuric acid, sealed test tubes was hold for 10 minutes at room temperature, followed by a second cooling for 20 min, at 25 °C temperature water bath. Total soluble carbohydrate content was measured by using spectrophotometer (Metertech SP 8001, METERTECH Inc., China) at 490 nm. During the total soluble carbohydrate content measurements glucose was used as standard.

Investigation of FTIR spectra

FTIR spectra were taken using DR-81 FTIR 6300 (JASCO, USA) spectrophotometer. The sample surfaces were sanded with grit size 150.

Each spectra was taken as result of 50 measurements, with 4 cm^{-1} resolution, using the *Spectra Manager* program of the measuring instrument. As background for the spectra aluminum plate was used. The spectral intensity was expressed in Kubelka-Munk unit of the FTIR instrument's software. The correction of the base line was performed choosing two predefined wave numbers (3800 cm^{-1} and 1900 cm^{-1}).

Investigation of naturally aged (indoor) wood surfaces with special regard to the wettability

Naturally aged wood surfaces were sanded with grit size 150 before ageing.

Technological background of natural ageing and determination of measurement periods

Natural ageing of samples was performed between 2014.04.07. and 2014.05.20., during daylight and sunny periods, generally between 9 and 17 o'clock. Samples were exposed facing south; south – east, behind normal window glass.

The different measurements were performed in the following ageing periods: 0 h (control), 1 h, 3 h, 5 h, 8 h, 10 h, 15 h, 30 h, 60 h, 96 h, 174 h and 240 h.

Contact angle measurements of naturally aged wood surfaces

On each wood surface 20-20 contact angle measurements were performed, in case of all ageing periods. For tests bi-distilled water (polar and disperse) was used as test liquid.

Evaluation of different test results

Data processing and evaluation of different measurements was performed by using Microsoft Excel (2010) and STATISTICA (8) programs.

III. Theses

1. thesis

Within the investigated range of roughnesses, in case of investigated wood species three well distinguishable ranges of contact angle (of distilled water) have been identified on the curves, which correlate with the grit sizes, according to the equation:

$$y = b_5 * \left(\sin\left\{b_4 * \left(1 - e^{-\left(b_3*(x-b_2)\right)^{b_1}}\right)\right\}\right) + b_0 \text{ , where}$$

y: contact angle of distilled water [°]
x: grit size of sandpaper.

A sharply decreasing portion of the curve between 60 and 100 is followed by an equilibrated portion between 120 and 320 grit size, followed finally by a slightly increasing portion between 400 and 600.

2. thesis

The contact angle of distilled water after an initial (control value) increase decreases close to the initial value during both long term natural and artificial ageing. The monitored intense changes are caused by chemical changes. The changed polarity caused by the chemical changes of the surface influences negatively the wettability of the surface but in a later aged stage of the surface enhance it.

3. thesis

Based on contact angle measurements (performed with distilled water) on artificially aged surfaces the changes are different and more relevant than on naturally aged surfaces. On (240 h) naturally aged surfaces the contact angle values show a lower measure maximal difference than the artificially aged (240 h) surfaces. This difference is detectable after 50 hours ageing.

4. thesis

During long term artificial ageing (240 h) the polarity of wood surfaces increases, thus the contact angle of distilled water (polar and disperse) shows higher measure changes relative to the contact angle of diiodomethane (disperse). The surface free energy of artificially aged wood approaches the initial value after 60 hours of artificial ageing.

5. thesis

During artificial ageing with xenon bulb, in the upper wood surface layer (75-100 µm) the total soluble carbohydrate content was found to have increasing tendency. The extractable phenolics in the upper wood surface layer were detected in increasing quantity, but the tempo of the increase slows down during artificial ageing. During the 240 hours of artificial ageing, the total soluble carbohydrate content increases 6-8 times, whilst the total phenol content increases 15 times. Although the quantity of carbohydrates and phenolics is increasing, and the total increase of phenolics is higher than the total increase of carbohydrates, the carbohydrates have higher impact on contact angle evolution than the phenolics.

6. thesis

Based on the FTIR results of the research was concluded that the phenolics which are present on the surface and in the upper surface layer and have a major impact on the wettability of wood surfaces and on the values of contact angle, result from the degradation of lignin in case of investigated wood species: beech (*Fagus sylvatica* L.), birch (*Betula pendula*), sessile oak (*Quercus petraea*) and spruce (*Picea abies*).

IV. Future aims

A more punctual evaluation of the influence of surface roughness by checking the effect of eventual pollution with wood dust.

Investigation of possible chemical changes by FTIR occurring due to sanding procedure (on a large scale of grit sizes).

Investigation of the relation of wood density and the calculated surface energy. Differently dense but having mostly the similar extract content, machining and age relative to machining, wood samples are suggested for testing, in order to find the differences with regard to surface energy. Dynamic contact angle measurements are suggested to be also performed to evaluate the quality of absorption (t=30 sec).

V. Publications connected to the dissertation

Articles

Papp, É. A. – Csiha, Cs. (2017): Contact angle as function of surface roughness of different wood species. Surfaces and Interfaces 8 pp. 54-59.

Papp, É. A. – Csiha, Cs. (2014): Tölgy fafelületek néhány paraméterének vizsgálata megmunkálás után. FAIPAR 62 (1) pp. 63-67. (*In Hungarian with English abstract)*

Proceedings

Papp, É. A. – Csiha, Cs. – Tolvaj, L. – Csóka, L. (2016): Investigation of artificial aged beech wood surfaces with FTIR spectroscopy. In: Proceedings of Eco-efficient resource Wood with Special Focus on Hardwoods (eds.: Teischinger, A. – Németh, R. – Rademacher, P. – Bak, M. – Fodor, F.), Sopron, Hungary, 8-9 September 2016. pp. 28-29.

Csiha, Cs. – *Papp, É. A.* (2014): Gyalult lucfenyő (Picea abies) felületi paraméterének vizsgálata mesterséges öregítés hatására. In: Az 5. Báthory-Brassai Konferencia tanulmánykötetei, Budapest, Magyarország, 21-22 Május 2014. pp. 417-421. (ISBN: 978-615-5460-38-8). (*In Hungarian)*

Csiha, Cs. – *Papp, É. A.* (2014): Surface tension measurement of differently rough sanded oak surfaces. In: International Conference on Processing Technologies: Proceedings of the 3rd Conference for the Forest and Bio-based Products Industries (PTF BPI 2014), Kuchl, Austria, 24-26 September 2014.

Papp, É. A. – Csiha, Cs. (2013): Surface analysis of sanded and planed wood surfaces. In: Proceedings of the 'Science for Sustainability' International Scientific Conference for PhD Students (eds.: Neményi, M. – Varga, L. – Facskó, F. – Lőrincz, I.), Győr, Hungary, 19-20 March 2013. (ISBN: 978-963-3341-03-2) pp. 22-27.

Csiha, Cs. – *Papp, É. A.* – Valent, J. (2012): Feature of contact angle of ageing Beech and Birch surfaces. In: The 5th Conference on Hardwood Research and Utilization in Europe 2012: Proceedings of the 'Hardwood Science and Technology' (eds.: Németh, R. – Teischinger, A.), Sopron, Hungary, 10-11 September 2012. (ISBN: 978-963-9883-97-0) pp. 41-49.

VI. Other publications

Articles

Horváth, N. – *Papp, É. A.* (2017): Nyárkutatás új szempontok figyelembevételével: Termőhely-specifikus faanyagtudományi vizsgálatok. ERDÉSZETI LAPOK 152 (1) pp. 2-5. (*In Hungarian)*

Papp, É. A. - Horváth, N. (2016): Nyár faanyagok anyagtudományi vizsgálataihoz szükséges hazai szakirodalom áttekintése, értékelése. FAIPAR 64 (2) pp. 22-28. (*In Hungarian with English abstract)*

Csiha, Cs. – *Papp, É. A.* – Valent, J. (2013): The feature of color alteration of bleached oak, beech and black locust surfaces during artificial xenon radiation. Wood Material Science And Engineering 8 (3) pp. 212-218.

Csiha, Cs. – Valent, J. – *Papp, É. A.* (2011): Hagyományos bevonatok teljesítmény mutatói. FAIPAR 59 (4) pp. 16-25. (*In Hungarian with English abstract)*

Proceedings

Csiha, Cs. – *Papp, É. A.* (2013): Investigation on bleaching Beech wood using environment friendly agent. In: Proceedings of the XXVIth International Conference Research for Furniture Industry (ed.: Szmardzewsky, J.), Poznan, Poland, 19-20 September 2013. pp. 7-15.

Csiha, Cs. – *Papp, É. A.* (2013): Bleached furniture surfaces – color stability under natural and artificial radiation. In: Process and service life modelling (eds.: van Acker, J. - van den Bulcke, J.), Ghent, Belgium, 17-19 April 2013. pp. 1-2.

Papp, É. A. – Csiha, Cs. – Valent, J. (2016): Colour change of some wood species during artificial xenon radiation. In: International Interdisciplinary Conference on Colour and Pattern Harmony: 5th Colour Specialists International Conference in Hungary (eds.: Ürmös, A. – Mihalik, G.), Budapest, Hungary, 12-13 June 2012. pp. 89-96.

VII. References

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