Cost Action FP1006
Bringing new functions to wood
through surface modification

Programme and Book of Abstracts

1st Workshop

Basics for Chemistry of
Wood Surface Modification

April 25-27, 2012
Kuchl/Salzburg, Austria

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Edited by: Stefanie Wieland and Thomas Schnabel
Salzburg University of Applied Sciences
HTB - Forest Products Technology & Timber Constructions
Campus Kuchl
Markt 136a
5431 Kuchl/Salzburg, Austria
www.fh-salzburg.ac.at

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Preface

In your hand you are holding the book of abstracts of the 1st Workshop *“Basics for Chemistry of Wood Surface Modification”* of the 1st COST Action FP1006 meeting on April 25-27, 2012, Kuchl, Austria. The idea for this workshop was initiated by the management committee of COST Action FP1006 and defined during the 1st Steering Committee Meeting on June 21, 2011, Kuchl, Austria.

The main objective of COST Action FP1006 *„Bringing new functions to wood through surface modification“* is to provide a scientific-based framework and knowledge for enhanced surface modification of wood and wood products towards higher functionalization and towards fulfilment of higher technical, economic and environmental standards. Such improvement is essential for a wider and more innovative usage of wood and wood based products.

The Austrian-Swiss physicist Wolfgang Pauli (1900-1958) said “God made the bulk; the surface was invented by the devil”. This expresses the special characteristics of surfaces, derived from the fact that a surface shares its border with the external world. Therefore, the surface properties of an object or a product have to be and are quite different depending upon their location. Consequently surfaces are the location for many phenomena occurring between a material and its environment, where all physical and chemical interactions and exchanges take place.
I believe that understanding the *“Basics for Chemistry of Wood Surface Modification”* in the frame of this 1st Workshop is a futher important step towards innovative wood surface modification techniques and improved knowledge for upcoming challenges leading to wood being the material of the 21st century.

One very good way to inform decision makers about new developments all over the world is to bring together scientists, researchers & developers from various disciplines in a meeting place for open discussions within the framework of a COST workshop. Thus, on behalf of the management committee of COST Action FP1006, I would like to thank all those people involved in organizing, reviewing and hosting the 1st Action FP1006 workshop.

I specially thank the authors and the keynote speakers Marie-France Thévenon, Philip Evans, Callum Hill and Holger Militz.

I gratefully acknowledge the help of the scientific advisiory committee in reviewing the abstacts and preparing the workshop program.

I express my sincere gratitude to the local organising committee and the Action Grant Holder, Ingrid Seidl, Gianluca Tondi and Thomas Schnabel for their help in preparing the book of abstacts and organizing the workshop.

I finally wish all participants two interesting and successful days.

Stefanie Wieland
Chair of COST Action FP1006

Fachhochschule
Salzburg University
of Applied Sciences

Workshop Organisation

Scientific Advisory Committee

Action Chair	Stefanie Wieland Salzburg University of Applied Sciences, Austria
Vice-Chair	Bartlomiej Mazela Poznan University of Life Sciences, Poland
WG1 Leader	Gerhard Grüll Holzforschung Austria, Austria
WG1 Vice leader	Holger Militz University Göttingen, Germany
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WG2 Vice leader	Graham Ormondroyd Bangor University, United Kingdom
WG3 Leader	Sergej Medved University of Ljubljana, Slovenia
WG3 Vice leader	Guido Hora Fraunhofer WKI, Germany

Local Organising Committee

Stefanie Wieland, Thomas Schnabel, Gianluca Tondi, Ingrid Seidl
Salzburg University of Applied Sciences, Austria

Workshop Venue

Salzburg University of Applied Sciences, Campus Kuchl
Markt 136a, A-5431 Kuchl/Salzburg

Cost Action FP1006
Bringing new functions to wood
through surface modification

Scientific Programme

1st Workshop

Basics for Chemistry of
Wood Surface Modification

April 25-27, 2012
Kuchl/Salzburg, Austria

Wednesday April 25, 2012

		Room
	08:00 – 08:30	E.16
	Registration at the Desk (Workshop place)	

	08:30 – 08:50	
	Opening Session **Kerstin Fink, Doris Walter,** **Alexander Petutschnigg:** Welcoming	

	08:50 – 10:00	
	Overview of the COST Action FP1006	
08:50	**Stefanie Wieland, Bartlomiej Mazela:** Bringing new function to wood through surface modification. COST Action FP1006	p. 14
09:10	**Gerhard Grüll, Holger Militz:** Wood surface modification and functionalization - Working Group 1	p. 15
09:20	**Electra Papadopoulou, Graham Ormondroyd:** Wood interface modification and interface interactions - Working Group 2	p. 16
09:30	**Sergej Medved, Guido Hora:** Process and Service life modelling - Working Group 3	p. 17
09:40	Presentation of Results of the Training Schools	

	10:00 – 10:30	
	Coffee Break	

	10:30 – 11:00	
	Philip Evans (Chairperson) – Session I	
	Keynote speaker	
10:30	**Holger Militz:** Surface modification versus woodmodification: properties and challenges	p. 18

	11:00 – 11:40	
	Session I – Wood Surface Modification and Functionalization (WG1)	
11:00	**Claudia Contrini, Emanuela Callone, Simona Maggini, Sabrina Palanti, Rosa Di Maggio:** Preparation and characterization of antimicrobial coatings for wood preservation	p. 19
11:20	**Gheorghe Dinescu, M.D. Ionita, M. Teodorescu, E. R. Ionita, C. Stancu:** Atmospheric pressure plasma sources suitable for modification of wood surfaces	p. 21

Wednesday April 25, 2012

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	Emma-Rose Coad, Zarah Walsh, Oren A. Scherman: Confocal microscopy and raman imaging for the assessment of cell wall impregnation	p. 23
	Vjekoslav Živković, Josip Miklečić: Surface properties of Croatian heat treated wood floorings	p. 25
	Anna-Kaisa Anttila, Anna Maria Pirttilä, Hely Häggman, Riitta Julkunen-Tiitto: Plant polyphenolics as antimicrobial agents preventing wood decay	p. 27

	12:00 – 13:00	
	Lunch	

	13:00 – 14:40	
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13:00	**Martin Arnold:** Options to tailor wood surface properties	p. 29
13:20	**Simona Maggini, Elisabetta Feci, Sabrina Palanti, Rosa Di Maggio:** (i/o) alkoxysilane/3-butynoate-substituted Zirconium-oxocluster copolymers as coatings for wood preservation	p. 32
13:40	**Carsten Mai, Zefang Xiao, Yanjun Xie:** Modification of solid wood with glutaraldehyde to improve outside weathering performance	p. 35
14:00	**Marco Petrič, Franc Budija, Arnaud Cheumani-Yona, Borut Kričej, Andreja Kutnar, Matjaž Pavlič, Pavli Pori, Črtomir Tavzes:** Overview of possible uses of liquefied lignocellulosic biomass for surface finishing of wood	p. 37
14:20	**Elisa Cappelletto, Rosa Di Maggio:** Surface modification of wood with functionalized alkoxisilanes	p. 40

	14:40 – 15:10	
	Coffee Break and Poster Presentation	

Wednesday April 25, 2012

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	Keynote speaker	
15:10	**Callum Hill:** Surface Modification for bonding of wood surfaces – An overview	p. 42

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15:40	**Wolfgang Gindl-Altmutter, Michael Obersriebnig:** Wood adhesive interactions at cellular level by means of a new position-resolved micromechanical assay	p. 45
16:00	**Sergej Medved, Vladimir Jambreković, Milanka Djiporović-Momčilović:** Quality of wood based panel surface and its impact on surfacing with melamine impregnated paper	p. 47

	16:20 – 16:40	
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	Jörn Rathke, Martin Weigl, Ulrich Müller: Double cantilever I-beam test (DCIB) - characterization of adhesive bonding and wood raw material properties of particleboards	p. 49
	Olli Paajanen, Matti Kairi: Thermomechanical modification effect in contact drying of veneer	p. 52
	Ilaria Santoni, Benedetto Pizzo: Wood surface modification for mussel imitation with protein adhesive	p. 54
	Róbert Németh, József Ábrahám, Szabolcs Komán and László Tolvaj: Colour change of different wood surface due to reactions with different glues and during service life with and without indoor sun radiation	p. 57
	João Ferra, Jorge Martins, Nuno Costa, Cristina Coelho, João Pereira, Paulo Cruz and Luisa Carvalho: Study of the bonding performance of UF/PVAc formulations with low formaldehyde emission	p. 60

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17:30	**Jürgen Leßlhumer, Judith Sinic, Martin Reif, Andreas Haider, Diethard Cascorbi:** Surface modification of WPC products to improve bonding strength	p. 65
17:50	**Judith Sinic, Martin Weigl:** Atmospheric plasma treatment of natural fibres	p. 67
18:10	**Magnus Wålinder, Dennis Jones:** Some experiences and tools for the assessment of surface and adhesion characteristics of wood	p. 69

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Thursday April 26, 2012

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	Keynote speaker	
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09:40	**Milan Šernek:** Reactivation of inactivated wood surfaces	p. 79

10:00 – 10:30
Coffee Break and Poster Presentation

10:30 – 12:00
Visit of the Laboratory and production area

12:00 – 13:30
Lunch

	13:30 – 14:00	
	Sergej Medved (Chairperson) - Session III	
	Keynote speaker	
13:30	**Marie-France Thévenon:** Wood protection using tannin-boron associations	p. 81

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	14:00 – 15:00	
	Session III	
14:00	**Lone Ross Gobakken, Olav A. Høibø:** Factors influencing mould growth and modeling of aesthetic service life	p. 83
14:20	**Boris Forsthuber, Gerhard Grüll:** The effects of HALS compounds in the prevention of photo-degradation of acrylic clearcoats and wooden surfaces	p. 86
14:40	**Jakub Sandak, Anna Sandak, Dusan Pauliny, Sandro Bonfa, Simone Meglioli:** Multi sensor approach for monitoring of the changes to wood surface exposed to natural and artificial weathering	p. 88

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	Carmen-Mihaela Popescu, Bogdan C. Simionescu: Evaluation of the weathering behaviour of natural and synthetic protective coatings for wood	p. 92
	Emilia-Adela Salca, Gavril Budau: Review upon the colour stability of black alder veneers under sunlight influence	p. 93
	Maria-Cristina Popescu, Carmen-Mihaela Popescu: The study of structural changes of Tilia Cordata wood induced by exposure to accelerated UV/Vis-light	p. 96
	Markus Hauptmann, Hedwig Hanea, Marcus Müller, Ulrich Müller, Christian Hansmann: The use of the CIEDE 2000 colour difference equation for quality assessment of high quality hardwood	p. 97

Thursday April 26, 2012

15:30 – 16:00
Coffee Break and Poster Presentation

16:00 – 16:10
Further steps and information

16:10 – 16:30
Closing

from 19:00
Banquet

Friday April 27, 2012 **(COST FP1006 mebers only)**

		Room
	08:30 – 10:00	
	Working Group Meetings	
08:30	Working Group 1 Meeting	E 0.13
08:30	Working Group 2 Meeting	E 0.17
08:30	Working Group 3 Meeting	E 0.15

	10:00 – 10:30	
	Working Group Meeting	
10:00	General discussion of the Working Groups	E 0.17

	10:30 – 12:30	
	Management Committee Meeting	E 0.15

	End of the meeting	
	Lunch	

Cost Action FP1006
Bringing new functions to wood
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Abstracts

1st Workshop

Basics for Chemistry of
Wood Surface Modification

April 25-27, 2012
Kuchl/Salzburg, Austria

Bringing new functions to wood through surface modification COST Action FP1006

Stefanie Wieland[1], **Bartlomiej Mazela**[2]

[1]Salzburg University of Applied Sciences, Markt 136a, 5431 Kuchl, Austria

stefanie.wieland@fh-salzburg.ac.at

[2]Poznan University of Life Sciences, 28 Wojska Polskiego str., PL-60637 Poznan, Poland

bartsimp@up.poznan.pl

Key words: Wood and Wood Based Products, Wood Surface Modification, New Functionalities,Mechanisms for Surface and Interface Modification, Interdisciplinarity, Environmentally-FriendlyTreatment, Service Life Modelling

ABSTRACT

Many product applications are determined by their special surface properties, and based on the physical, chemical and biological interchange of various molecules with the material surface. This is especially true for the use of wood and wood-based products due to special wood characteristics like anisotropy, UV-degradation etc. Thus, bringing new functions to wood through surface modification is necessary in order to enhance the quality of the existing wood products and to open the path to new applications, products or markets.

COST Action FP1006 aims to provide the scientific-based framework and knowledge required for enhanced surface modifications of wood and wood-based products relating to higher functionalization and towards the fulfilment of higher technical, economic and environmental standards.

The scientific program encompasses a broad spectrum of research disciplines and competences. To ensure the fulfilment of the objectives, the work within this Action is divided into the three areas of scientific focus which are stated below:

(a) Investigation of new surface modification and functionalization methods for wood and wood- based products to enhance existing properties and/or to create new properties and functionalities and/or new products.
(b) evaluation of wood interface modification methods and processes and investigation of the interface interactions
(c) investigation of adequate models for the description of the changes in material properties during the product life time

Based on the three areas of scientific focus, three Working Groups (WG) were formed: Wood surface modification and functionalization (WG1), Wood interface modification and interface interactions (WG2) and Process and Service life modeling (WG3).

Wood surface modification and functionalization (WG1)

Gerhard Grüll[1], Holger Militz[2]

[1]Holzforschung Austria, Austria

[1]Holzforschung Austria, Franz Grill Strasse 7, 1030 Vienna, Austria

g.gruell@holzforschung.at

[2]University Göttingen, Büsgenweg 4, 37077 Göttingen, Germany

hmilitz@gwdg.de

ABSTRACT

This area focuses on fundamental studies of wood interface modification which allows, for example eco-friendly self-binding or wood to wood binding. The focus will be set on studies of non-toxic interface modification methods for wood and wood products. Areas of interest will be e.g. the creation of bacterially generated adhesion, adhesion improvement by enzymatic pre-treatment, investigations into wood interface modification in order to create adhesion or adhesion improvement, interface modification through friction, heat and pressure, coupling agents, investigations concerning liquefied wood as a bonding agent or surface coating material. The possibility to improve the self-bonding properties e.g. joining of wood using linear friction welding processes will also be discussed.

In the last few years, several wood modification technologies (e.g. acetylation, furfurylation, resin treatments etc.) were developed and introduced on a practical scale. For a total modification of the entire wood dimensions, relatively high weight percent gain (WPG) and sophisticated technology are required. In the case of surface modification, the properties of polymers are maintained and lower amounts of chemicals are needed for the modification process. Materials with a polymer substrate and functional groups on the surfaces play an important role in biomedical and chemical applications.

A crucial pre-requisite for these materials is the possible linkage between the polymer substrate and the chemical reagents. Wood polymers show such functional molecule groups, and therefore wood could be a good polymer body for the modification step. Moreover, some wood species have natural bacteria resistance. Based on these considerations, surface modification should also be possible for the wood materials. When considering wood as a renewable material, the surface modification methods should also fulfil ecological demands, so that the wood products can maintain their reputation as natural materials. Therefore, surface modification methods using renewable ingredients and physical or chemical treatments (e. g. plasma treatment) will also be analysed.

The results might include new protective systems against abiotic and biotic degradation, as decay and fire, improved durability, improved UV stability, enhanced adhesion properties, increased dimensional stability and easier maintenance of wood and its products. Such properties could be advantageous for many wood-based products like parquet flooring, kitchen cabinets, furniture as well as panels for indoor and outdoor applications.

Wood interface modification and interface interactions (WG2)

Electra Papadopoulou[1], Graham Ormondroyd[2]

[1]Chimar Hellas S.A., Sofouli 88, GR 55131 Thessaloniki, Greece

papadopoulou@ari.gr

[2]Bangor University, Deniol Rd, LL57 2UW Bangor, United Kingdom

g.ormondroyd@bangor.ac.uk

ABSTRACT

This area focuses on fundamental studies of wood interface modification which allows, for example eco-friendly self-binding or wood to wood binding. The focus will be set on studies of non-toxic interface modification methods for wood and wood products. Areas of interest will be e.g. the creation of bacterially generated adhesion, adhesion improvement by enzymatic pre-treatment, investigations into wood interface modification in order to create adhesion or adhesion improvement, interface modification through friction, heat and pressure, coupling agents, investigations relating to liquefied wood as a bonding or surface coating material. An additional factor to be discussed is the improvement of the self-bonding properties e.g. joining of wood using linear friction welding processes.

One of the aims of this particular research is to enable scientists to gain more comprehensive knowledge of the interface modifications mechanisms and interactions. Interface analysis will be carried out (ESR spectroscopy, NIR spectroscopy, 13C CP/MAS NMR,...) in order to attain results on the effectiveness of the processes, long term performance, etc. The data will be used as input parameters and model validation for Working Group 3.

The results might include enhanced adhesion properties for adhesives, paint, varnishes or the wood itself. Other potential findings are increased surface density, dimensional stability and easier maintenance of wood and its products. Products with these qualities will be of importance in numerous applications.

Such properties are useful for many wood-based products like parquet flooring, kitchen cabinets, furniture as well as panels for indoor and outdoor applications.

Process and Service life modeling (WG3)

Sergej Medved[1], Guido Hora[2]

[1]University of Ljubljana, Biotechnical Faculty, Department of Wood Science and Technology,
Rozna dolina, Cesta VIII/34, 1000 Ljubljana, Slovenia

sergej.medved@bf.uni–lj.si

[2]Fraunhofer WKI, Bienroder Weg 54e, 38108 Braunschweig, Germany

guido.hora@wki.fraunhofer.de

ABSTRACT

Understanding of the impact of different environmental conditions on the quality of material is essential for the prediction of product performance during its life cycle. When analyzing different materials and modification methods, the knowledge obtained by fundamental research and which is later used for the development of models, will not only help to simulate the changes in material properties but also in the optimization of existing surface modification techniques and materials, the development of new ones and also in saving time and money on the modification methods found. The developed models will also be a useful tool for the description of changes induced by the material itself and its behaviour under changing climatic and environmental conditions.

Test methods for estimating material properties are necessary, particularly with regard to the development of new surface modification processes. For example, artificial weathering tests (e.g. light, moisture, temperature and acid) have a great potential for the evaluation of changes in material properties during exposure time. The techniques of artificial weathering would be also supported by the investigation of effects of natural weathering and changes in climate conditions on material properties. One of the parameters that will be described and covered in this topic is an assessment of the chemical and physical degradation factors of polymeric modified surface layers.

The existent dosage-response functions of various materials (e. g. plastics) from other fields of research should be modified for the usage of the modified material properties. Also, an approach to use the probabilistic theory (e.g. Markov Chain) may have a great potential for the accurate modelling and simulation, provided that an adequate design of experiment is engineered.

The experimental validation of the model will contribute to its optimization. Moreover, the models will allow methods for computer simulations of the changes in material properties during the natural weathering to be developed, which are important for the estimation of the service life time of products. Due to the complexity of the interaction of the material and the environmental influences, a multi-disciplinary composition of the scientists (e. g. polymer science, environmental science, wood research) of this Cost Action is necessary.

Surface modification versus wood modification: properties and challenges

Holger Militz

University Göttingen, Büsgenweg 4, 37077 Göttingen, Germany

hmilitz@gwdg.de

ABSTRACT

It has taken many decades to develop new wood modification methods from laboratory scale to an industrial level. Already in the beginning of the 20th century researchers have shown, that wood cell wall polymers can be altered by some reactive chemicals, without destroying the integrity of the cell wall. Only the last years, due to environmental concerns about the toxicity of traditional wood preservatives and about the deforestation of tropical forests, some of these methods had been taken over by the industry and new products were introduced to the market. With most of these processes the wood is treated by elevated temperatures or by impregnating chemicals into deeper layers of the products, with the aim to change those wood properties, which cause problems in the daily use of a wooden product. Due to changing the water susceptible groups of the polymers, usually the modified substrates become more water resistant, and as a consequence, more dimensional stable and more resistant against biological degradation. With lumen filling treatment (waxes, some polymers), furthermore the hardness of a substrate can be increased. Examples for wood modification technology in Europe which entered the markets the last years are:

- thermally modified timber (approx. 200.000 m3 in several countries and with different processes),
- acetylation with acetic anhydride, (“Accoya” by Titan Wood, Netherlands),
- furfurylation with furfuryl alcohol (“Kebony”, Norway),
- Cross linking wood with DMDHEU and/or melamines (“Belmadur” by BASF, Germany),
- Treatment with waxes, parafins (several processes like “Dauerholz”, “Nat-Wood” etc.).

As said, most of the above processes aim in modifying the wooden products into deep layers to gain a durable and dimensional stable end product. However, for ease of technology and from economic reasons, it would be wishful to introduce processes which focus on just the surface of a product.
In this paper, the applicability of possible surface modification methods will be highlighted. The properties to be altered are UV-stability, moisture uptake behavior, surface integrity, surface hardness and biological resistance against surface degrading fungi. Challenges of surface modification technology will be discussed and compared to conventional wood modification systems.

Preparation and characterization of antimicrobial coatings for wood preservation

Claudia Contrini[1], **Emanuela Callone**[1], **Simona Maggini**[1], **Sabrina Palanti**[2],
Rosa Di Maggio[1]

[1]Department of Materials Engineering and Industrial Technologies, University of Trento,
Via Mesiano 77, 38123 Trento, Italy

claudia.contrini@ing.unitn.it

[2]IVALSA - Trees and Timber Institute, CNR - National Research Council, Via Madonna
del Piano 10, 50019 Sesto Fiorentino (FI), Italy

Key words: silica gel, antimicrobial coatings, wood preservation, copper, QAS

ABSTRACT

Contamination by microorganisms is of great concern in a variety of areas including medical devices, healthcare systems, water purification systems, food packaging and storage, household sanitation and also the wood industry. Wood is a widely used material, especially in the building and construction fields, because of its many technical-mechanical features. Its principal disadvantages are due to its organic constitution: it can be slowly destroyed by long-term impact of oxygen, light, water and it is a great source of nutrients for microorganism, fungi and insects, leading to its complete biological consumption [1].

The present project proposes two routes for the synthesis of silica based antimicrobial coatings for wood preservation: 1) preparation of silica matrix doped with copper or commercial antimicrobial compounds, 2) synthesis and introduction in the silica network of monomers containing a quaternary ammonium salt (QAS) moiety.

In the former case, N-(2-aminoethyl)-3-aminopropyltriethoxysilane (DIAMO) was employed in the sol-gel preparation together with tetraethoxysilane (TEOS), in a ratio 1 to 1 to improve the Cu-doping of silica. The two amino groups of the DIAMO chelates copper ions and stabilise in this way its inclusion in the network. TEOS, as the basis of the silica network, is used also as matrix for doping with the commercial antimicrobial compounds. 2-Thiazol-4-yl-1H-benzoimidazole (IRGAGUARD®F3000) and 2,4,4'-trichloro-2'-hydroxy-diphenyl-ether (IRGAGUARD®B1000) were directly added during the sol-gel preparation in amount of 1% with respect to the silica. This value was selected on the basis of the compound activity. To test the stability of the prepared doped coating, the leaching was measured at different pH (4÷6) through two different techniques, spectrofluorimetric analysis for B1000 and F3000, and Inductively Coupled Plasma (ICP) analysis for copper (Cu^{2+}).
In the latter case, the QAS monomers were synthesized starting from triethoxypropyl-N-dimethylaniline or (2,3-epoxypropyl)-trimethylammonium salt, respectively, as precursors and then the siloxane products were hydrolyzed. The antimicrobial activity of the quaternary ammonium salts is known from literature [2]. However this activity was further investigated by modification of the QAS monomers through exchange reactions of the counter anion. The influence of the counter anions on other proprieties, such as the solubility, was also taken into consideration for the construction of the silica network.

Both bulk coating materials and coated wood (*Pinus sylvestris)* were characterized by infrared (FTIR) and nuclear magnetic resonance (^{1}H, ^{13}C and ^{29}Si NMR) spectroscopies. In particular, ^{29}Si MAS analysis was employed to determine the degree of condensation of the alkoxysilane.

The surface morphology of the coated wood samples was determined by scanning electron microscopy (SEM). The thickness of the coating and its penetration in wooden trachea was analysed as well. Wood samples coated with copper were further characterized with Electron Paramagnetic Resonance (EPR) at 77K using a finger Dewar.

Antimicrobial test are performing to evaluate the activity of these different types of coatings, against brown or white rot fungi, respectively *Coniophora puteana* and *Trametes versicolor*.

REFERENCES

[1] Donath S., Militz H. and Mai C. (2004) Wood modification with alkoxysilanes. Wood Sci. Technol. 38:555-566.

[2] Marini M., et al., (2007) Preparation and antibacterial activity of hybrid materials containing quaternary ammonium salts via sol-gel process. European Polymer J. 43:3621-3628

Atmospheric pressure plasma sources suitable for modification of wood surfaces

G. Dinescu*, M.D. Ionita, M. Teodorescu, E.R. Ionita, C. Stancu

National Institute for lasers, Plasma and Radiation Physics,
Atomistilor Str. 409, Magurele- Bucharest, 77125 Ilfov, Romania

*dinescug@infim.ro

Key words: wood surface modification, atmospheric pressure plasma, plasma sources

ABSTRACT

Wettability, adhesion, chemical stability, porosity and resistance to biological agents are important surface properties for many wood applications. Painting, coating, welding, anti-ageing treatments are examples of processing technologies which are controlled by the surface properties. Thus, the techniques related to modification of wood surfaces, aiming to extend their qualities beyond that of the natural wood received considerable attention. Plasmas have been used successfully in other fields, to increase wettability of polymers, to prepare biocompatible or biocidal surfaces, to activate surfaces for chemical grafting, in thin films technology, and it is also a current approach for wood surface modification [1-4]. In case of wood modification it was proved that plasma species (excited atoms, molecules, active radicals, electrons, ions) act on surface, change its chemical composition and topography, or contribute to its coating with thin films. Nevertheless, there are peculiarities that should be considered in order to make the plasma systems compatible with wood processing. In this contribution we discuss these peculiarities, some of the possible plasma sources that ensure that compatibility, and the limitations.

The most frequent problems associated to plasma processing of wood are related to adequacy of the existing plasma sources to this material, and to the size and/or complex shape of objects. The main requirements considered are the cold character of plasma, the access to the surfaces to be processed, the size acceptable for processing, and versatility. Beyond the basic research related to plasma interaction with the surface, in view of practical applications, the efficiency is important, as well.

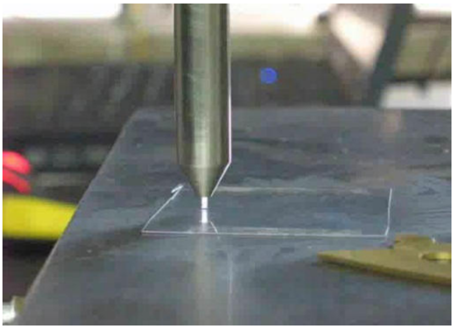

Figure 1. Atmospheric pressure axisymmetric plasma jet source

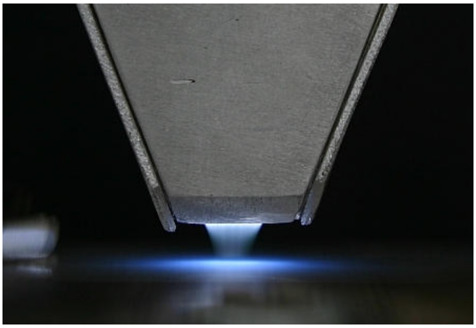

Figure 2. Atmospheric pressure planar plasma jet source

As concerning the cold character of plasma, the restriction in the selection of plasma sources is related to the stability of the wood against heat damage. Thus, cold (non-thermal) plasma sources should be considered. The cold processing is normally fulfilled at low pressure (less than 1 mbar): the low pressure sources are based mostly on glow discharges which are cold by their physical nature. Also, low pressure plasmas may have large volumes. These advantages are counterbalanced by a strong drawback: the vacuum technology inherently associated to low pressure processing is difficult with porous, vapor releasing materials, and expensive to scale-up for large objects.

The alternative solution is the use of atmospheric pressure plasma sources, allowing processing in the ambient. The difficulty here comes from the natural tendency of plasmas to become hot, non-homogeneous and small volume (columnar, filamentary) with the pressure increase. Still, these difficulties can be overcome: in Figure 1 and Figure 2 we present, as examples, two atmospheric pressure plasma sources [5] suitable for wood surface processing without thermal damage. The design differs by the discharge type: one uses a discharge with bare electrodes (DBE), the other a dielectric barrier discharge (DBE). Both sources are supplied with radiofrequency voltages (13.56 MHz) and work with argon gas at low power (5 to 50 W) levels. The DBE source generates an axial jet, while the DBE source generates a planar plasma jet. We show that both jets are rich in active species (OH, NH radicals, oxygen atoms, argon metastables) and can be injected with adequate precursors (hydrocarbonic gases, organosilicon gases, fluorinated gases) for thin films deposition. They can effectively modify surfaces, as it was proved with polymers [6, 7]. They are easily adapted for treatment of objects with complex 3D convex-concave surfaces, and can access to surface features like holes and channels. They are versatile and compliant with scanning procedures: in this way larger surfaces can be treated. Particularly, the planar DBD plasma jet source can be up-scaled for large area processing.

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Confocal microscopy and Raman imaging for assement of cell wall impregnation

Emma-Rose Coad*, Zarah Walsh, Oren A. Scherman

Melville Laboratory, University of Cambridge, Chemsitry Department, Cambridge CB2 1EW

*Erc40@cam.ac.uk

Key words: Dye, Confocal microscopy, Raman, cell wall, wood-polymer composite

ABSTRACT

Globally the demand for timber and other forest products is increasingly being met with wood from planted forest and this is set to continue.[1] Therefore the demand for high end timber products met by planted forest is increasing. Typically however planted forest produces less timber suitable for structural purposes due to relatively rapid growth of the trees when compared to primary forest. This presents an opportunity to develop a method of modifying native wood currently not suitable for construction to bring it up to these standards.

The method for modification in question here is impregnation of cut lumber with a designed mixture of monomeric material. This is then polymerized in situ to form a wood-polymer composite material. In order to form composite material suitable for structural purposes it is essential however that effective impregnation of the wood is achieved and in order for this to occur an understanding of the interactions between the polymer impregnate and the natural polymers is essential.

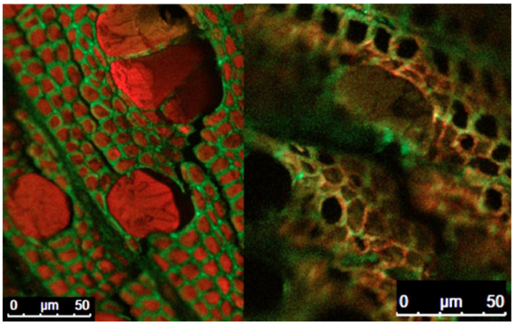

Figure 1: Confocal microscope images (courtesy of Z. Walsh) illustrating the difference in distribution of different dye molecules (Left) Non polymerisable dye molecule, (Right) Polymerisable dye molecule

The use of dyes for selective labeling of natural material is one which is commonly practiced in many area of biology in order to study the movement of specific molecules and how they interact in highly complex living systems. Here this approach was applied to the impregnation of cut lumber in an effort to understand the distribution of polymer through the wood's cellular structure.

It can clearly been seen in figure 1 that the distribution of dye (red colour) is highly sensitive to modification through changes in the chemistry of the dye. When a polymerisable pendant group is attached to the red dye molecule, dye can be found in the cell wall of the wood (green), right image figure 1. Without this polymerisable group however the cell wall is free of dye, left image figure 1. The presence of dye within the cell wall indicates that the dye molecule is small enough to enter the cell wall. The figure also shows that by changing the chemistry of the dye selectivity of the cell wall or impregnated polymer can be achieved.

Raman spectroscopy has been used by many to look at the distribution of lignin, cellulose and other natural wood constituents through sections of cut wood [2]. The technique has also been used to look at wood degradation for example in archaeological samples [3]. Here confocal Raman spectroscopy has been used to look at the distribution of synthetic polymeric material through the natural wooden matrix in an effort to understand the distribution of this material and interface interactions between the materials.

Through the use of these two techniques it is possible to probe the location of polymer through the impregnated wood structure and find selectivity in location on the basis of chemical modification.

Acknowledgement: Confocal Microscopy courtesy of Z. Walsh.

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Surface properties of Croatian heat treated wood floorings

Vjekoslav Živković*, Josip Miklečić#

University of Zagreb, Faculty of forestry, Department for wood technology, Svetosimunska 25, HR-10000 Zagreb, Croatia

*zivkovic@sumfak.hr

#miklecic@sumfak.hr

Key words: heat treated wood floorings, water and vapour permeability, light resistance, FTIR

ABSTRACT

Heat treated wood (HTW) can be successfully applied for floorings due to its better moisture resistance, increased dimensional stability, and uniform colour change to darker, brownish colours.
Material of ash (A), beech (B) and hornbeam (H) for parquet elements was treated at two temperature levels, 190 °C and 210 °C, and the properties were compared with native wood. The reduction in dimensional changes was expressed by volumetric shrinking and Anti Shrink Efficiency (ASE). Additionally, parquet elements, produced from HTW, were oil-impregnated and waxed, and subsequently tested for water vapor and liquid water permeability.

Shrinking coefficients of HTW were not reduced in comparison with native beech wood. However, the significant reduction in absolute water uptake resulted in ca 50 % lower EMC values and up to ca 60 % improved ASE values of HTW. Heat treatment only slightly reduced the density of all species tested, but significantly improved their biological durability. This biological resistance was drastically influenced by treatment temperatures above 190 °C. Surface treatment with flooring oil and wax further improved the hygroscopic properties of HTW parquet elements (figure 1) [1].

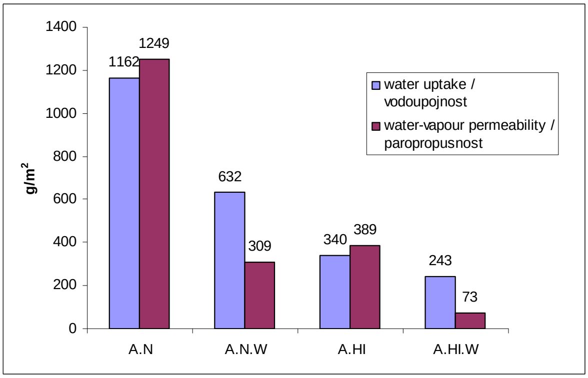

Figure 1: Liquid water and water-vapour permeability of ash wood according to EN 927-5 and EN 927-4 (A – ash, N – not modified, HI – heat treated at 210°C, W - waxed)

The effect of UV light through window glass on the changes in colour of surfaces of uncoated and clear-coated thermally modified wood, and on chemical changes of surfaces of uncoated

thermally modified and unmodified wood was monitored using QUV accelerated exposures. Discoloration of the uncoated wood samples and those treated with three commercial transparent coatings (two-component polyurethane varnish (PU), water-borne varnish (AQ), and nano-impregnation (I)) was measured spectrophotometrically using CIELAB parameters (L*, a*, b* and ΔE*). FTIR spectroscopy was used to study chemical changes caused by UV irradiation. Colour change (ΔE*) was recorded in all tested wood samples after exposure to UV light, and the smallest discoloration was recorded in wood samples coated with two-component polyurethane varnish. FTIR spectroscopy results show that thermal treatment and exposure to UV light modify the chemical structure of wood surface and that the thermally modified samples exposed to UV light show similar changes as unmodified samples exposed to UV light, but less pronounced [2].

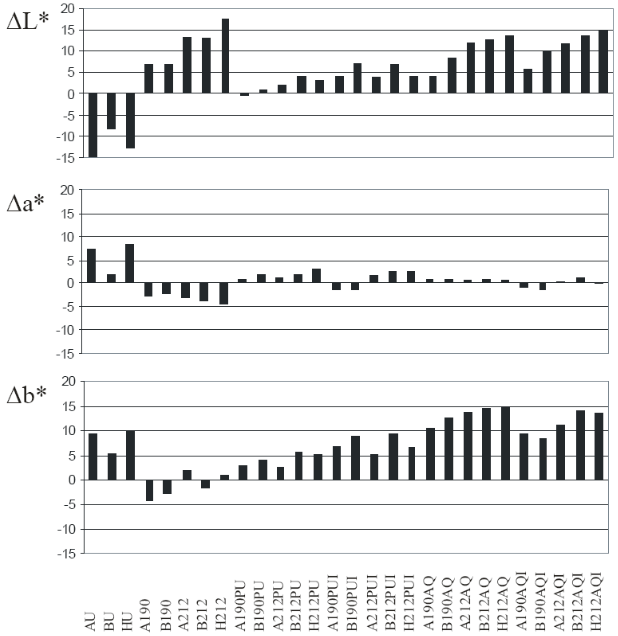

Figure 2: ΔL*, Δa* and Δb* values after 32 days of accelerated indoor sunlight exposure

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Plant polyphenolics as antimicrobial agents preventing wood decay

Anna-Kaisa Anttila[1*], Anna Maria Pirttilä[1], Hely Häggman[1], Riitta Julkunen-Tiitto[2#]

[1]Department of Biology, University of Oulu, P.O. Box 3000, 90014 Oulu, Finland

[*]annakaisa.anttila@gmail.com

[2]Department of Biology, University of Eastern Finland, P.O. Box 111, 80101 Joensuu, Finland

[#]riitta.julkunen-tiitto@uef.fi

Key words: Plant polyphenolics, wood preservation, decay fungi, growth inibition

ABSTRACT

Introduction

Wood has been used as a building material through the human history in many constructions having several problems beside its many advantages. One is decay of untreated wood material in presence of moisture and fungi. Recently, many traditionally used wood preservatives have been forbidden by EU legislation due to their toxicity to the environment. Thus new and more environmentally friendly preservatives are now needed.

Plants are able to protect themselves against rot with many means, including polyphenolic compounds. By extracting and using these compounds new and efficient, environmentally friendly wood preservatives could be prepared.

Polyphenolic compounds form one main secondary metabolite group in plants, and most of them have no direct function in essential plant operations such as growth and development. Many polyphenolic compounds are effective against bacteria, fungi and herbivores [2]. They are found in almost every plant part (bark, wood, leaves, fruits and roots). Especially the heartwood of many trees contains high concentrations of polyphenolics which helps preventing decay and serve thus as natural defense against a wide range of microbial infections in wood material [1, 3].

Most common decaying organisms are fungi. White-, brown- and soft-rot fungi are main groups of decaying fungi. Basidiomycete-genus white-rot and brown-rot fungi are the most efficient decaying species of wood among microorganisms in the environment. White-rot fungi use wood walls hemi cellulose, cellulose but mostly lignin for its nutrition leading the wood to become fiber-like corroded. White-rot fungi attack most likely deciduous trees. Unlike white-rot, brown-rot fungi use mainly cellulose and hemi cellulose shrinking the wood and breaking it into small brown cubes. Because brown-rot fungi prefer dead coniferous wood, timber and wooden structures, they are the most common cause of rot in building materials (e.g. [4]).

Material and methods

8 plant derived polyphenolic fractions were tested against 15 decay fungal species (8 brown-rot, 3 white-rot and 4 soft-rot fungi) to study their ability to inhibit fungal growth. The experiments were performed in 24-well plates in malt broth liquid cultures. 8 different concentrations were used to find out the effective concentration of the fractions against each fungal species. Fungal hyphae pieces were set to liquid media and grown in dark and in a shaker for 8-9 days. Fresh weights of the fungal hyphae were measured after the incubation time.

Results

According to the experiment 4 out of 8 polyphenolic fractions inhibited the fungal growth excellently in rather low concentrations (Table 1.). Generally these polyphenolic fractions seemed to inhibit brown-rot but not white-rot. The results obtained for the soft-rot varied between the species.

Table 1. The lowest concentration (mg/ml) of plant polyphenolic fractions introducing inhibition of fungal growth.

Polyphenol fraction/ Fungus species	**1.**	**2.**	**3.**	**4.**	**5.**	**6.**	**7.**	**8.**
C.puteana	0.25	0.25	0.25	0.25	0.25	0.25	1.5	0.25
G.sepiarium	1.75	>2	>2	>2	2	>2	>2	>2
G.trabeum	0.75	0.75	0.75	1.25	1.25	2	>2	>2
L.cyathiformis	0.5	0.5	0.25	0.25	1.5	2	>2	>2
N.lepideus	0.25	0.25	0.25	0.5	0.5	1	>2	>2
P.placenta	0.25	0.25	0.25	0.5	0.25	1.25	>2	>2
S.himantioides	0.25	0.25	0.25	0.25	0.25	0.75	1.25	>2
S.lacrymans	0.25	0.25	0.25	0.25	0.25	0.25	0.5	>2
H.lateritium	>2	>2	>2	>2	>2	>2	>2	>2
P.candolieana	1.25	1.25	1.25	0.5	0.5	0.25	1.75	>2
T.versicolor	>2	>2	>2	>2	>2	>2	>2	>2
H.grisea	0.5	0.5	0.5	0.5	0.25	0.5	>2	>2
L.mutabilis	>2	>2	>2	1.5	>2	>2	>2	1.75
P.setifera	1.5	>2	>2	1.5	2	>2	>2	>2
T.spiralis	0.5	0.25	0.25	0.5	0.25	0.25	1	>2

Conclusions

Our results indicate the at least 4 of these tested 8 plant derived polyphenolic fractions could be suitable as wood preservatives because of their good antifungal properties in liquid culture tested. Only rather low content of polyphenolics were needed that makes their use cheap and sustainable. More experiments will be needed to find out the effectiveness of these fractions in impregnated wood in native (outdoors) conditions.

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Options to tailor wood surface properties

Martin Arnold

Empa, Swiss Federal Laboratories for Materials Science and Technology,
Applied Wood Materials, Überlandstr. 129, CH-8600 Dübendorf, Switzerland

martin.arnold@empa.ch

Key words: biological surface modification, chemical surface modification, surface machining, wood

ABSTRACT

While some use attributes of wooden components or products are determined by the bulk properties of the material (e.g. mechanical properties, swelling/shrinkage), many aspects are more related to surface properties (e.g. haptics, aesthetics, adhesion, photodegradation). This is because interaction with the environment or other materials (gases, fluids or solids) mainly takes place at the surface. However, due to the cellular porous structure of wood, the concept of wood surfaces has usually to be extended to a surface layer, which includes both surface and bulk phenomena.

As a consequence, many processes for modern, high-value applications of solid wood and wood particles - such as adhesive bonding, coating or compounding - depend on defined properties of the involved surfaces. However, wood surfaces in their natural state are frequently not fully compatible with subsequent treatments. Therefore, pre-treatments are applied to control inherent or to achieve designed properties of wood surfaces for a superior performance.

Table 1: Options for wood surface functionalisation

	Types of wood surface functionalisation		
	mechanical	biological	chemical
Main modes of action	Change of structural surface properties, affecting wetting behavior and physical/mechanical interlocking of subsequent surface treatment	Change of visual, structural and chemical surface properties	Change of chemical surface functionality, frequently with the goal to achieve chemical bonds with subsequent treatments
Examples of available techniques	- Machining operations (e.g. planing, sanding [1]) - Surface densification	- ‘Bioincising’ [3] - Enzymatic treatment (e.g. with Laccase [4]) - Spalting	- Adhesion promoters (e.g. HMR primer [6, 7]) - Bulk modifications (e.g. thermal treatment) - Grafting with photoinitiators [2] - Hydrophobation [5] - Plasma

A wide range of different mechanical, biological or chemical methods may be used for wood surface modification and functionalisation, which all have their specific advantages and limitations. The Wood Laboratory of Empa has been involved in a number of different attempts in this area. The objective of this presentation is to give an overview over these activities based on selected examples (Table 1).

Example: The type of machining operations can have a profound effect on the subsequent application and performance of wood coatings [1] in so far that the amount of induced cell damage in the surface layer and the resulting surface roughness will lead to differences in wettability and coating adhesion (Figure 1).

Id	Planing		Sanding		Plot
	Type	Condition	Type	Condition	symbol
S1	conventional	sharp	none		△
S2	planing	blunt			○
S3	conventional	sharp	grit 80	sharp	▲
S4	planing	blunt			●
S5	+ sanding	sharp		blunt	▲
S6		blunt			●
S7	planing with	sharp	none		△
S8	notched knives	blunt			○

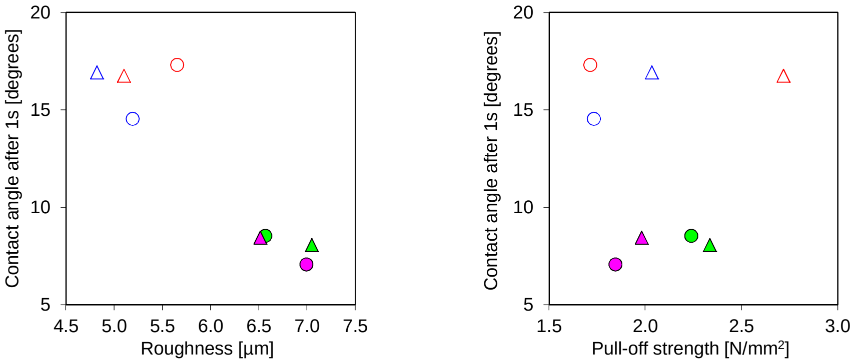

Figure 1: Relation between surface roughness, wettability and coating adhesion on differently machined wood surfaces (Data points show average values of several measurements on 3 replicate panels).

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(i/o) alkoxysilane / 3-butynoate-substituted Zirconium-oxocluster copolymers as coatings for wood preservation

Simona Maggini[1*], Elisabetta Feci[2], Sabrina Palanti[2#], Rosa Di Maggio[1]

[1]Dipartimento di Ingeneria dei Materiali e Tecnologie Industriali,
Università degli Studi di Trento, Via Mesiano 77, I-38123 Trento, Italy

*simona.maggini@ing.unitn.it

[2]CNR, IVALSA Istituto per la Valorizzazione del Legno e delle Specie Arboree,
Via Madonna del Piano 10, 50019 Sesto Fiorentino (FI), Italy

#palanti@ivalsa.cnr.it

Key words: i/o hybrid polymers, zirconium-oxocluster, wood preservation

ABSTRACT

An important area of research on wood coatings is controlling or slowing the destruction of wood due to long-term contact with oxygen, light, moisture and biotic decay. Traditional coatings for preventing and remedying environmental damage are one approach but new adaptable nanotech coatings have shown great promise. One class of nanotech coatings with outstanding mechanical and thermal properties is inorganic/organic (i/o) hybrid polymers. In particular, the preparation of i/o copolymers through the use of preformed organically modified metal-oxoclusters is a relatively untapped direction but has already resulted in coatings with appealing properties [1].

In this project, i/o hybrid copolymers composed of alkoxy alkyl silane $(MeO)_3SiR$ (R = vinyl, propyl mercaptan) and the 3-butynoate-substituted Zirconium-oxocluster $[Zr_6O_4(OH)_4(OOCCH_2C\equiv CH)_{12}]_2$ are proposed as coatings for penetrating treatments for wood protection [2]. The siloxane penetrates into the wood texture via hydrogen interaction and can Si–O–C bond with the wood biopolymers [3]. This improves water repellence and resistance to photochemical degradation, combustion, and shrinkage [4]. The modified Zirconium oxocluster, besides conferring particular properties to the coating (such as flame-retardance), is responsible for the organization of the polymer architecture and is grafted to the polymer matrix through covalent bonds, allowing a better control of its dispersion.

$[Zr_6O_4(OH)_4(OOCCH_2C\equiv CH)_{12}]_2$ was synthesised and characterised by infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopy, and elementary analysis. A spontaneous isomerisation of the 3-butynoate to buta-2,3-dienoate was observed for the 3-butynoate involved in $[Zr_6O_4(OH)_4(OOCCH_2C\equiv CH)_{12}]_2$. The isomerisation, which seems to be promoted by the Zirconium itself, triggered the polymerization process affecting the performance and properties of the samples.

The copolymers containing the vinyltrimethoxysilane (VTMS) or 3-mercaptopropyltrimethoxysilane (MPTMS) were prepared by sol-gel process with Zr to Si ratio of 1 to 10. The obtained i/o hybrid copolymers were chemically stable. Their thermal stability was tested in bulk via thermogravimetry (TGA), differential scanning calorimetry (DSC), and dynamical mechanical spectroscopy (DMS). All the copolymers showed excellent thermo-mechanical properties including high stiffness and high glass transition temperature in the absence of remark

able mass loss and shrinkage. This was partially attributed to the high reticulation of the copolymers set by the 3-butynoate ligand.

IR and solid-state NMR spectroscopy (^{29}Si, ^{13}C, and ^{1}H) were used for a complete characterization of the structure of the hybrid bulk materials and the coated wood samples. The surface morphology, determined by scanning electron microscopy (SEM), showed that the coatings did not alter the colour and structure of the wood. Energy dispersive x-ray analysis (EDX) showed a homogeneous distribution of the Zirconium-oxocluster in the coatings. The ^{29}Si MAS spectra indicate the T2 [$CH_3OSi(OSi)_2R'$] (51%) and T3 [$Si(OSi)_3R'$] (41%) as the main units; the nature of the alkyl pendant seems not to influence the degree of condensation of the alkoxysilane.

Wood samples coated with [$Zr_6O_4(OH)_4(OOCCH_2C{\equiv}CH)_{12}]_2$/MPTMS were further treated with a photoinitiator and the thymol ester, 5-methyl-2-(propan-2-yl)phenyl 2-methylprop-2-enoate. They were then exposed to UV radiation to react the free thiol groups in the copolymer with the double bond of the thymol ester, in order to graft the thymol group on the samples.

Efficacy tests against the brown rot fungus *Coniophora puteana* were run on a series of coated wood samples –[$Zr_6O_4(OH)_4(OOCCH_2C{\equiv}CH)_{12}]_2$/VTMS. The results obtained with accelerated mini block tests were promising, all the treated wood specimens were not decayed.

Similar tests on the two series of coated samples: [$Zr_6O_4(OH)_4(OOCCH_2C{\equiv}CH)_{12}]_2$/MPTMS/thymol ester, and [$Zr_6O_4(OH)_4(OOCCH_2C{\equiv}CH)_{12}]_2$/MPTMS, are currently under investigation.

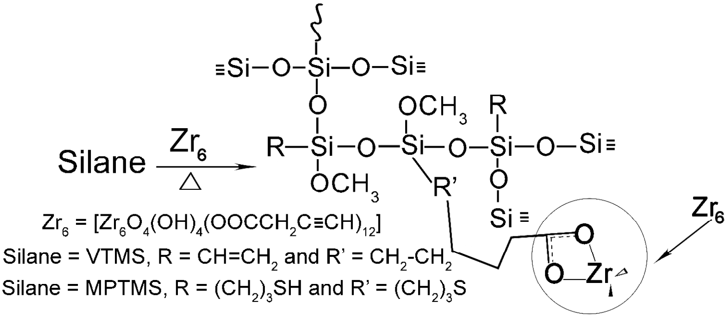

Figure 1: Schematic representation of the structure of the (i/o) hybrid copolymers.

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Modification of solid wood with glutaraldehyde to improve outside weathering performance

Carsten Mai[1*], Zefang Xiao[1#], Yanjun Xie[3]

[1]Wood Biology and Wood Products, Burckhardt–institute, Georg August
University of Göttingen, Büsgenweg 4, 37077 Göttingen, Germany

[*]cmai@gwdg.de

[#]zxiao@gwdg.de

[3]Key Laboratory of Bio-based Material Science and Technology (Ministry of Education),
Northeast Forestry University, 26 Hexing Road, Harbin, China

xieyanjuncn@hotmail.com

Key words: glutaraldehyde, water related properties, durability, weathering, photo-stability, tensile strength, moisture sorption, cracking

ABSTRACT

Wood is susceptible to abiotic erosion and biotic attack when it is exposed outdoors. As an effective protecting strategy, chemical modification can partly alter the polymeric structure of the wood cell wall and thereby improve the durability. Glutaraldehyde (GA, pentane-1,5-dial) is a dialdehyde which can in principle react with four hydroxyl groups of the cell wall polymers and may therefore be used as a cross-linking agent to modify wood. In this study solid wood was modified with GA in order to improve the water-related properties, fungal resistance and outdoor weathering performance.

Scots pine (*Pinus sylvestris* L.) sapwood and European beech (*Fagus sylvatica* L.) wood were treated with various concentrations of GA and magnesium chloride as a catalyst in aqueous solutions. Water related properties and outdoor performance were only tested with pine wood. The treatments reduced the equilibrium moisture content (EMC) at 90% RH up to 30% as compared to the untreated controls. Capillary water uptake of wood was also restrained by GA treatment (8.6% WPG) resulting in water reduction effectiveness (WRE) of approximately 50% in both radial and tangential direction after 244 h. Wood blocks treated to the highest WPG (22%) attained 70% anti-swelling efficiency (ASE) due to bulking and cross-linking of the cell wall matrix. During ten water submersion and drying cycles untreated and GA treated specimens displayed equal weight losses indicating that mainly wood constituents were wash out. These cyclic water submersion tests also caused approximately 10% reduction in ASE in samples treated to higher WPG [1].

GA treatments to a weight percent gain (WPG) above 7% obviously restrained the growth of the blue stain fungus *Aureobasidium pullulans* on both pine and beech wood. Above 7% WPG, GA-treated beech wood did not exhibit any mass loss due to incubation with the white rot fungus *Trametes versicolor*. The threshold to prevent decay of beech and pine specimens towards the brown rot fungus *Coniophora puteana* was at a WPG of only 3%. GA treatment to a WPG over 6% protected the Scots pine stakes from soft rot decay during 32 weeks exposure according to

ENv 807 [2]. Scanning electron microscopy revealed that GA-treatment to a WPG as low as of 2% inhibited basidiomycete decay of the cell wall structure [3].

Scots pine micro-veneers were weathered in a QUV artificial weathering tester over 168 h: The exposure involved a UV-A light over 56 cycles, each including 2.5 h of UV irradiation at 60°C, and 30 min cold water spray.

GA-treatment caused photo-protection of lignin with increasing GA concentration. In comparison with the untreated controls, GA-treated pine micro-veneer strips exhibited a lower tensile strength loss measured in a zero-span mode in course of weathering.

During 18 months of outdoor exposure according EN 927-3 [5], GA-treated pine wood boards exhibited a lower moisture content and water uptake than the untreated ones. GA-treatment also clearly restricted the penetration of blue stain fungi into deeper layers of wood. On the macroscopic scale, the surface of the GA-treated boards was significantly smoother due to less erosion, cracking and minor peeling of tracheids. Scanning electron microscopy further revealed that individual tracheids were detached from the cell compound and then washed away from the untreated wood surface, whereas tracheids on surfaces of GA-treated wood remained in the tissue compound but displayed many axial and transversal cracks.

GA is, thus, considered as a suitable modifying agent to improve the performance of wood used outdoors [4].

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Overview of possible uses of liquefied lignocellulosic biomass for surface finishing of wood

Marko Petrič[1], Franc Budija[2], Arnaud Cheumani-Yona[1,2], Borut Kričej[1], Andreja Kutnar[2], Matjaž Pavlič[1], Pavli Pori[1,3], Črtomir Tavzes[2]

[1]University of Ljubljana, Biotechnical Faculty, Dept. of Wood Science & Technology,
Jamnikarjeva 101, 1000 Ljubljana, Slovenia

marko.petric@bf.uni-lj.si, acheumani@gmail.com, borut.kricej@bf.uni-lj.si,
matjaz.pavlic@bf.uni-lj.si pavli.pori@bf.uni-lj.si

[2]Iltra d.o.o, Dolenjska cesta 42, SI 1000 Ljubljana, Slovenia

franc.budija@iltra.si, andreja.kutnar@iltra.si, crtomir.tavzes@iltra.si

[3]Chemcolor Sevnica d.o.o., Dolnje Brezovo 35, SI 8290 Sevnica, Slovenia

Key words: wood liquefaction, curing, self-crosslinking, surface coatings

ABSTRACT

Utilization of woody biomass is important not only for producing energy, but also for conversions into a liquid phase to be used as an alternative source of polymers. Conversion routes into a liquid state and other forms for the production of energy and various chemicals are well known [1]. Thermochemical techniques of conversion are nowadays the most commonly used and can be divided into gasification, pyrolysis, and direct liquefaction [2]. Direct liquefaction processes attempt to prepare a product without going through the gas phase [3]. With a correctly selected solvent system and a catalyst, the biomass can be liquefied under atmospheric pressure at a moderately elevated temperature (above 100 °C). One of the most frequently applied liquefaction systems is based on polyhydric alcohols [4].

Herein, an overview of our extensive investigations of liquefaction of various types of woody biomass is presented and supplemented with information on liquefaction of other kinds of lignocellulosic biomass, like for instance cork or residues of the production of tannins from chestnut wood. Further on, possibilities for preparation of wood coating formulations on the basis of liquefied biomass are discussed. We have studied interactions of novel bio-polymer based coatings with wooden substrates, processes of drying or curing after application and surface characteristics of the liquefied biomass based films.

Residues of various types of wood (predominantely Black poplar wood, but also Norway spruce wood and some other species) and lignocellulosic biomass (for instance cork) were liquefied either with glycerol, ethylene- or di-ethylene glycol as a reactive solvent. As a catalyst, H_2SO_4 was used. In addition, cork dust was not liquefied only with H_2SO_4 but also under alkaline conditions. Optimisation of a liquefaction process had a goal to reach the highest possible liquefaction yield (LY) and was carried out by adjusting the temperature of liquefaction and ratios between lignocelullosic biomass, a reactive solvent and a catalyst. For instance, when the ratio between the Black poplar wood and diethylene glycol exceeded 1:2, the LY of near 100% was reached in 95 min at 150 °C [4]. On the other hand, liquefaction of cork dust with glycerol was performed at 150 °C, 180 °C or 200 °C for 1 h or 3 h and rather low LY (65% to 85%) were obtained under alkaline (NaOH) conditions and even lower when H_2SO_4 (43% - 50%) was used as a catalyst [5].

Liquefied lignocellulosics were afterwards used to prepare wood coatings that were applied to glass plates to study process of drying/curing and to wooden substrates. After a film was formed, surfaces of coated wood were characterised by various standard and non-standard methods. The most promising results were exhibited by two-component polyurethane coatings prepared from liquefied Black poplar wood (the reactive solvent was diethylene glycol (DEG), T=180 °C, t=95 min, the curing agent was a commercially obtained isocyanate hardener and the catalyst for polyurethane formation 1,4-diazabicyclo[2.2.2]octane). Resistance against selected test-probe liquids and against scratching, dry and wet heat as well as flexibilty of novel biobased polyurethane films were comparable to those of commercial two pack polyurethane wood finishes [6]. Similarly, the coatings were prepared by mixing of liquefied poplar wood with selected commercial melamine- or urea-formaldehide resins. Their properties relevant for coating applications were comparable to the properties of selected commercial wood finishes. The exception was quite low resistance against water and humidity, exhibited also by decrease of hardness of the films after application and curing [7].

The problem of low resistance against water was especially pronounced at films, formed from liquefied wood by the self-crosslinking mechanism. Namely, we succeeded to perform crosslinking of the liquefied wood, after removal of the excessive reactive solvent – diethyleneglycol, without any curing agents or additives. The obtained crosslinked polymer film could be an ether and/or ester network [4]. Extensive DSC investigations indicated that the low resistance against humidity could be the consequence of rather low rate of crosslinking, obtained at the chosen curing conditions [8].

There are still some important limitations in possible applications of liquefied wood for wood coatings. First of all, the coatings are dark brown or even black. However, our recent discolouration experiments [9] gave very promising results. At the self-crosslinked liquefied lignocellulosic the curing temperature to obtain a solid film is still too high for wood finishing applications. Due to too low crosslinking rate and consequently low resistance to ageing, at the current stage of knowledge, liquefied biomass based coatings are still not appropriate for exterior applications. More research is needed to solve the mentioned questions.

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Surface modification of wood with functionalized alkoxisilanes

Elisa Cappelletto*, Rosa Di Maggio#

Department of Materials Engineering and Industrial Technology, University of Trento,
via Mesiano 77, 38123 Trento, Italy, Phone: +39-461282453, Fax: +39-461281945,

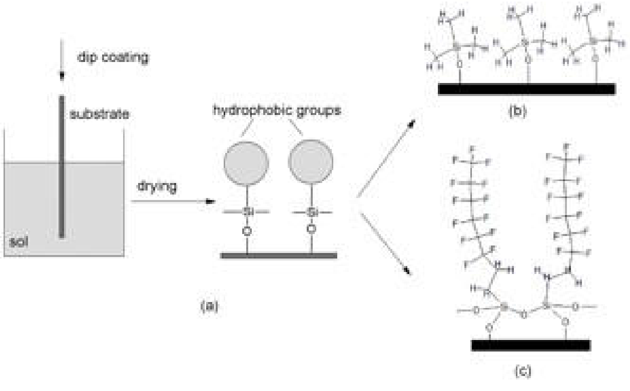
*elisa.cappelletto@ing.unitn.it, #rosa.dimaggio@unitn.it

Key words: surface treatment, hydrophobicity, functionalized alkoxisilanes

ABSTRACT

Wood is an excellent natural composite material, however its biodeterioration and combustibility represent a disadvantage for many applications. In order to reduce both of them, chemical surface wood modification with sol-gel coating results in enhancing of the behaviour of material. This paper describes the coating of wood substrates through the dipping into solutions of different functionalized alkoxisilanes, as precursors of modified silica. The chemical treatments of wood substrates are used to improve the UV-stability, change the surface energy of wood reducing the wettability by water and improve the thermal stability. The silanes used as precursors contain one or two organic functionalities (R’Si(OR’’)). These materials tend to deposit as inorganic-organic polymeric films, where the organic groups (aliphatic hydrocarbon, fluorinated hydrocarbon or aromatic substituents) show hydrophobic properties, which enable the wettability of the surface be reduced. The effects of these treatments on the surface of wood were extensively studied by various analytical techniques. The surface chemistry of coated specimens was characterized by Fourier transform infrared (FTIR-ATR) spectroscopy and Energy Dispersive X-ray Analysis (EDXA). Surface morphology was characterized by Scanning Electron Microscopy (SEM). The structure of the coating and degree of condesantion were investigated through Nuclear Magnetic Resonance (NMR). Contact angle (CA) measurements were used to assess the water repellency of the coated sample as well as the thermodynamic parameters. The effect of these sol-gel thin films on UV stability, fungal colonization and fire retardancy was investigated through certificated regulation.

The collected data are interesting and support the use of sol-gel wood modification against atmospheric agents, in particular UV light and moisture. The siloxane glass matrix also acts as a barrier against the heat, reducing the material the reaction to fire of the wood. The reaction to fire evaluation criteria involved in this study were time of post-combustion, time of post-incandescence, width and height of damaged area.



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Surface Modification for Bonding of Wood Surfaces – An Overview

Callum Hill

Forest Products Research Institute, Edinburgh Napier University

c.hill@napier.ac.uk

Key words: Surface modification

ABSTRACT

This presentation will give an overview of the state of the art in surface wood modification. There are a wide range of chemical approached that can be adopted and it is possible to exploit the chemistry of wood to allow for direct bonding of wood surfaces. There have been a number of studies concerned with the use of chemical modification for the purpose of providing a means of bonding between wood surfaces. Several approaches can be adopted [1]:

- Reaction of the wood surface with functionalised silanes.
- Bonding of a reagent to the wood surface in order to thermoplasticise the surface for self-bonding.
- Bonding of a reagent to the wood surface that provides the appropriate functionality for bonding sites.
- Activation of the wood surface by the use of chemical reagents such a Fenton's systems to generate surface free radicals.
- Activation of the wood surface using enzymatic means to generate surface free-radicals.

Functionalised silanes are of interest because the reagents are relatively inexpensive and there is a wide variety of functionality to exploit. However, the Si-O-C linkages that may be formed with wood using a conventional reaction are subject to hydrolysis reactions. This can be overcome if the wood is first reacted with maleic anhydride and then allyl glycidyl ether to give oligoesterifed wood. The modified wood can then be reacted with either bis(trimethylsiloxy)methylsilane, a hydride-terminated polydimethylsiloxane, or a platinum-divinyltetramethyldisiloxane.

There have been many studies where wood has been thermoplasticised using benzylation, or cyanoethylation. The modified wood samples are then hot-pressed to provide bonding between the surfaces. Chemical modification of wood surfaces can be employed in order to provide active sites to allow for self-bonding directly, or to allow for covalent bonding between wood surfaces *via* an intermediary reagent.

One approach is to chemically bond a group that has a double bond present onto the wood surface. It is then possible to graft monomers onto the activated wood surface using free-radical polymerisation reactions, or directly bond the activated surfaces together. For example methacrylic acid has been bonded to wood surfaces using the tri-fluoro acetic acid impelling method. The activated wood can then be hot-pressed into small discs in the presence of styrene and benzoyl peroxide (BPO). The methacrylated veneers can also be bonded using styrene monomer in the presence of BPO. Wood can be treated with aqueous NaOH and subsequently reacted with allyl bromide. The allylated wood specimens can be bonded together using hot-pressing and determined the bond strength. Apparently good bonding was achieved using this method, evidenced by the frequent failure of the wood in the tests, although infrared spectroscopy showed that the double bond of the allyl group had not reacted during hot-pressing. It was concluded that bonding occurred as a result of thermoplasticisation of the wood. The production of MDF from allylated wood fibres has also been reported. The IBS of the boards was superior to control boards (unmod

ified fibres bonded with PF resin), provided the temperature of the allylation reaction and board density was sufficiently high. The possibility of using graft polymerisation of styrene onto allylated wood to provide covalent bonding between surfaces has also been investigated. The reaction of TMP fibres with glycidyl methacrylate (GMA), maleic anhydride, or succinic anhydride followed by hot-pressing the modified fibres with methyl methacrylate in the presence of BPO has been reported. Infrared evidence was presented indicating that copolymerisation had occurred between the bonded GMA and methyl methacrylate. However, a later study could find no evidence to suggest that a chemical bond had formed between the GMA and wood. The reaction of wood flour with maleic anhydride (MA) and subsequent mixing of the modified wood with diallyl phthalate in the presence of BPO has been studied. Non-adhesive bonded wood was produced by modifying the surfaces of wood veneers with methacrylic anhydride and then forming lap joints using either styrene or methyl methacrylate in the presence of the free radical initiator azoisobutyronitrile. No reaction was found for the crotonic anhydride modified wood surface, which was thought to be due to steric hindrance of the double bond in this case. Rather than using free-radical chemistry, other reactions are possible, such as condensation reactions, which are used in certain classes of polymerisation. For example, wood fibres and veneers can be modified with succinic anhydride (SA) and then hexamethylene diamine (HMDA) was used to provide a flexible covalently-bonded bridge between the activated wood surfaces. Since it was anticipated that the HMDA would not react with the SA modified wood surfaces under the relatively mild conditions employed for the reaction, diisopropyl carbodiimide (DIPCI) was employed to promote the coupling reaction. SA modified veneers were placed against HMDA grafted SA veneers and hot-pressed in the presence of DIPCI to form covalent bonds between the surfaces. Direct grafting onto the surface of acetylated wood fibres has been studied. The method involves the production of an anionic polymer that is then reacted with a suitably modified lignocellulosic material. Scrupulously clean reaction conditions are required for this approach. There have been a number of studies investigating the grafting of polymer onto wood fibres that have been treated to produce free-radicals on the surface. The methods investigated include treatment with Fenton’s reagent, ceric ion, xanthate-mediated grafting, initiation with potassium permanganate, or using a halide/peroxide system.

In many cases, the presence of lignin in the wood has an inhibitory effect upon grafting efficiency. This is mainly due to the high mobility of the formed free radicals that are able to rapidly migrate from the surface initiation sites to lower energy traps within the cell wall. Thus, although grafting of isolated lignin may be possible in situations where it is present in a swollen gel-like state so that the radical trap sites are still accessible, this does not imply that such reactions are possible on the surface of solid lignified wood, since the radicals can readily migrate into the cell wall interior where they are no longer accessible. Many polymerisation techniques require the use of clean conditions to prevent the inhibition of polymerisation reactions and this is particularly so for free radical, or anionic polymerisation.

The introduction of wood fibres into a polymerisation reaction presents a number of problems, in that various extractible compounds (e.g. phenolics) can have an inhibitory effect upon polymerisation. The formation of homopolymer can also produce erroneous results, particularly if the homopolymer becomes entangled with the cell wall matrix or with the fibrillated surface of fibres. In which case it is very difficult to determine whether grafting has actually occurred. A halide/peroxide initiating system has been developed for the grafting of polymers onto lignocellulosic surfaces. Although the mechanism for the reaction does not appear to be fully understood, successful grafting requires the presence of chloride ions, hydrogen peroxide and a lignocellulosic substrate. Reaction of chloride ions with hydrogen peroxide is thought to produce chlorine radicals that then abstract protons from the cell wall polymers, generating radical sites where polymerisation occurs. There is very little homopolymerisation if the lignocellulosic material is not present. Reactions are usually performed in dimethylsulphoxide in which the wood pulp forms a gel. Successful grafting onto isolated lignin has been demonstrated using this system. Fenton’s reagent chemistry has been used for the direct self-bonding of wood particles.

Indirect methods, involving the use of surface activated fibres in combination with other bonding agents such as furfural and lignosulphonates, have also been studied. Since the use of Fenton's reagent requires the presence of hydrogen peroxide, this leads to a great reluctance on the part of composite manufacturers to use such systems because of safety concerns.

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Wood-adhesive interactions at cellular level by means of a new position-resolved micromechanical assay

Wolfgang Gindl-Altmutter, Michael Obersriebnig

BOKU – Universität für Bodenkultur, Konrad Lorenz Strasse 24, A-3430 Tulln, Austria

michael.obersriebnig@boku.ac.at, wolfgang.gindl-altmutter@boku.ac.at

Key words: Interfacial adhesion, Nanoindentation, Wood cell wall

ABSTRACT

The quantification of adhesion between solid phases in a composite material is essential for the development of a comprehensive understanding of its properties. At the macroscopic scale, different standardised types of shear- or delamination tests may be employed, whereas a direct characterisation of adhesion at the microscopic scale is more challenging. In a complex material like wood, macroscopic test results are affected by a number of variables such as surface roughness and wood microsctructure, and it is sometimes difficult to evaluate purely adhesion-related effects. Therefore, the present study aimed at developing a new approach of characterising adhesion directly at the interface between the wood cell wall and the adhesive. It is expected that such a method will further promote our understanding of wood-adhesive and wood-coating interactions.

Spruce wood specimens were surface-silylated according to three different protocols in order to progressively reduce hydrophilicity and, consequently, adhesion to urea-formaldehyde glue chosen for our experiments. Compared to the untreated reference, the macroscopic adhesive strength was drastically reduced in silylated specimens. Specimens treated with the most effective silylation method in terms of reduction of hydrophilicity showed near zero adhesion to urea-formaldehyde glue. Micromechanical characterisation by means of nanoindentation (Figure 1) revealed that the wood cell wall stiffness and hardness was not significantly affected by silylation.

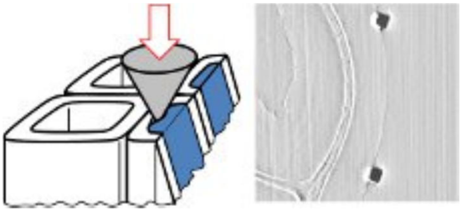

Figure 1: Scheme of nanoindentation set-up for the determination of adhesive energy at the wood cell wall-adhesive interface (left) and AFM image of the interface after indentation testing (right, image size approx. 10*10 µm)

Contrarily, indentation experiments performed directly at the interface between the wood cell wall and the adhesive using a conical indenter with 60° opening angle showed significantly reduced hardness and reduced specific work of indentation in silylated specimens. It is concluded that the measured correlation between reduced hydrophilicity in silylated specimens and the mechanical strength of the interface is due to reduced adhesion. This allows calculating the specific adhesive energy for the system wood cell wall – urea formaldehyde glue from the difference between the specific work of adhesion obtained from the unmodified reference and the most efficiently silylated specimen.

Having established the basic principle of this new method, a first application-oriented experiment was performed comparing the micro-scale adhesion of urea-formaldehyde resin (UF) and one-component polyurethane resin (PUR) to different regions of a wood surface. When a wood surface is freshly cut, it consists of freshly cut-open cell walls on the one hand, and of inner cell lumen surfaces on the other hand (Figure 2). It is reasonable to assume that the freshly cut cell walls are more hydrophilic than the inner lumen surfaces. Based on this assumption, micro-scale adhesion tests were performed at both types of interfaces using UF and PUR, respectively.

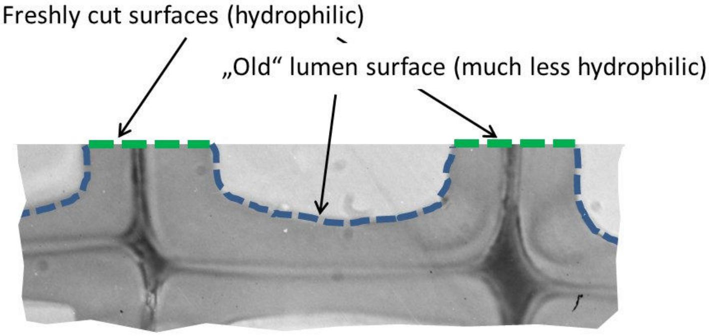

Figure 2: Scheme of different micro-surfaces on a freshly cut wood surface.

Results from such experiments showed that more energy is required to separate the surfaces at the UF-cell wall interface compared to the UF-lumen interface. Interestingly, the opposite was observed for PUR, which showed better adhesion to the lumen than to the fresh cell wall. This observation is not only of interest for the basic understanding of the adhesion mechanism of UF and PUR, but also for the procedure of adhesive bonding with PUR in general. Our observations may be interpreted as evidence that surface requirements which are valid for UF and comparable hydrophilic systems may not be ideal for PUR.

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Quality of Wood Based Panel Surface and Its Impact on Surfacing with Melamine Impregnated Paper

Sergej Medved[1], Vladimir Jambreković[2], Milanka Djiporović-Momčilović[3]

[1] University of Ljubljana, Biotechnical Faculty, Department of Wood Science and Technology,
Rozna dolina, Cesta VIII/34, 1000 Ljubjana, Slovenia

sergej.medved@bf.uni–lj.si

[2] University of Zagreb, Faculty of Forestry, Svetošimunska 25, 10000 Zagreb, Croatia

vladimir.jambrekovic@zg.htnet.hr

[3] University of Belgrade, Faculty of Forestry, Kneza Višeslava 1, 11000 Beograd, Serbia

milanka.djiporovic@sfb.bg.ac.rs

Key words: particleboard, fiberboard, melamine impregnated paper, surface modification, FTIR, surface density

ABSTRACT

Wood based panels; especially particleboards and fibreboard's are mostly used for furniture, where quality of surface is of great importance. Those boards are mostly surfaced with thin melamine impregnated paper, where surface must be smooth, good reactivity towards adhesive and relatively dense to give the surface enough strength and toughness. The first is relatively easy to achieve because all of the boards are sanded prior to surfacing process, hence giving the surface enough smoothness. Most of the problems related to poor quality of surfaced boards are related to inappropriate density of boards and unreactive surface.

Usually, when melamine impregnated paper is used for surfacing the pressure needed for its application is between 2 and 4 N/mm^2. To withstand this pressure boards have to have density high enough that allows pressing at high pressure, especially core layer, which usually have lower density. One of distinct property of wood based panels made from fibres and particles is their density profile that is M or U shape. Surface layer of particle and fibreboard have higher density compared to the core layer. The density profile of fibreboard is more uniform (lower difference between surface and core layer density) compared to particleboard. Despite the fact that core layer density doesn’t directly impact the surface quality, its state is important for the overall board quality. Due to lower density in core layer, high pressure used for surfacing and in combination with high temperature could cause:

- Inappropriate thickness of board (usually thinner board)
- Failure in core layer leading to lower internal bond and lower bending strength

Due to mentioned reasons core layer density has to be high enough to enable resistance against pressing at high pressure.

Looking only at the surface quality the quality of surface layer is important. Firstly we are going to address surface layer density. Higher density is from mechanical point of view better since boards will have higher bending strength, but with regard to the surfacing with melamine impregnated paper, higher density doesn’t necessary mean better quality. The adhesive that paper is impregnated with has to wet the surface and penetrate into the board surface. If the board is to dens than the adhesive won’t penetrate enough into the board surface, hence delamination of paper could occur.

Delamination of paper could also occur if the surface of the board is contaminated – unreactive. Such low reactivity of board could be due to the high density (as we mentioned before) usage of water repelling substance like wax emulsion or even due to the thermal modification, which partially already occurs during pressing. Quality surface of board is important because the melamine-impregnated papers used nowadays are impregnated with high reactivity resins. At the end of impregnation resin the resin is cured to a predetermined degree and when impregnated paper is paced together with the board into the press the resin has to be reactivated so that it can wet and penetrate into board surface and fully cure in a relatively short time (less than 30 seconds).

The aim of this paper is to present the impact of board quality, especially surface quality on the surfacing with impregnated paper. For this purposes commercially available unsanded and sanded particleboard and MDF boards furniture grade were used. For surfacing white melamine impregnated paper marked 80/200 was used. Sanded boards were thermally modified at temperatures 190, 210 and 230°C in oven. Unsanded and sanded boards were sprayed with wax emulsion. Prior to surfacing boards were conditioned at 20°C and 65% relative air humidity. After 5 days of climatization boards were surfaced at 190°C, 2.5 N/mm^2. At unsurface board density distribution, surface pH value, wetting contact angle was determined. Surface of board was also analyzed by FT–IR spectrometer. At surface boards only bond strength by surface soundness test was determined.

During experiment differences between the boards with regard to the treatment were determined. FT–IR analysis showed the differences between sanded, unsanded, thermally modified and wax emulsion modified boards. We have determined that wetting contact angle was lowest at sanded and unmodified board. The differences in pH value were also determined. During experiment we determined that surface soundness was affected by sanding and surface modification process. We have also determined the differences in the quality of surfaced boards determined by the water vapour test and by acid value test.

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Double cantilever I-beam test (DCIB) – characterization of adhesive content and wood raw material properties of particleboards

Jörn Rathke[*], Martin Weigl[+], Ulrich Müller[#]

Kompetenzzentrum Holz GmbH, Altenberger Straße 69, 4040 Linz

[*]j.rathke@kplus-wood.at

[+]m.weigl@kplus-wood.at

[#]ulrich.mueller@kplus-wood.at

Key words: fracture energy test, particleboard, resin

ABSTRACT

Particle boards were produced from different types of wood particles i.e.: spruce, willow and locust. Effects of the raw material as well as varying resin content on mechanical and fracture mechanical properties were investigated. For the analysis specific fracture energy, stress intensity factors and the industrial European standard methods internal bond strength (IB) [1] and bending strength [2] were used. The total fracture energy was measured and the stress intensity factor was calculated by means of FE simulated data. While IB and modulus of elasticity (MOE) showed a high variability, data scattering for fracture energy tests and bending strength (MOR) were smaller, yielding significant differences between varying resin content and wood raw material.

Introduction

Continuous raw material supply at low raw material costs is an increasing challenge for the forest products industry [3, 4]. A growing number of forest products industry plants are facing raw material shortages and some even operate below 50 % of their capacity [5]. The decreasing availability of forest based wood material for the PB production opens the question and the exploration for alternative resources. Studies dealing with wood material from plantation (e.g. eucalyptus, pinus radiata, poplar, willow and locust) showed that these resources have favorable characteristics such as rapid growth rates, short harvesting cycles, continuous availability and low cost. Weight reduced particleboards (willow and black locust) were produced and tested by Kowaluk [6] showing promising results especially for willow.

The adhesive content is one of the main effects on the board performance. In particle board production process the increase of resin content is used as a primary measure to control internal bond strength to guarantee sufficient strength limits of the boards produced [7]. In general the internal bond strength increases significantly with a raised resin content [8]. Similar tendencies can be seen with bending strength [8, 9]. However, the IB test provides only a strength value which refers to the bond strength limit and is therefore dedicated for a quality control. In contrast fracture energy concepts allow to derive much more information concerning material characteristics during the separation process [10]. Therefore fracture energy testing procedures were used beside standard IB tests for analyzing particle boards with varying resin content and alternative wood raw material.

Material and Method

Particleboards with a density of 600kg/m³ and varying resin content 5.6%, 7.0% and 8.4% were produced in a laboratory scale. From the boards specimen for internal bond strength (EN 319) and bending strength (EN 310) as well as for the newly developed double cantilever I-beam test, were prepared. The testing of fracture energy introduces a tensile load perpendicular to the middle layer area, which leads to fracture in Mode I. After testing the data recorded (i.e. force-displacement values) was analyzed by means of a one-way analysis of variance (ANOVA, $p < 0.05$), followed by a post hoc multiple t-test with Bonferroni procedure, using SPSS®.

Results and Discussion

Data presented in figure 1 shows clear trend of increased mechanical properties with increasing resin content for MOE, MOR, IB, fracture energy (G_f), and stress intensity factor (K_{IC}), respectively.

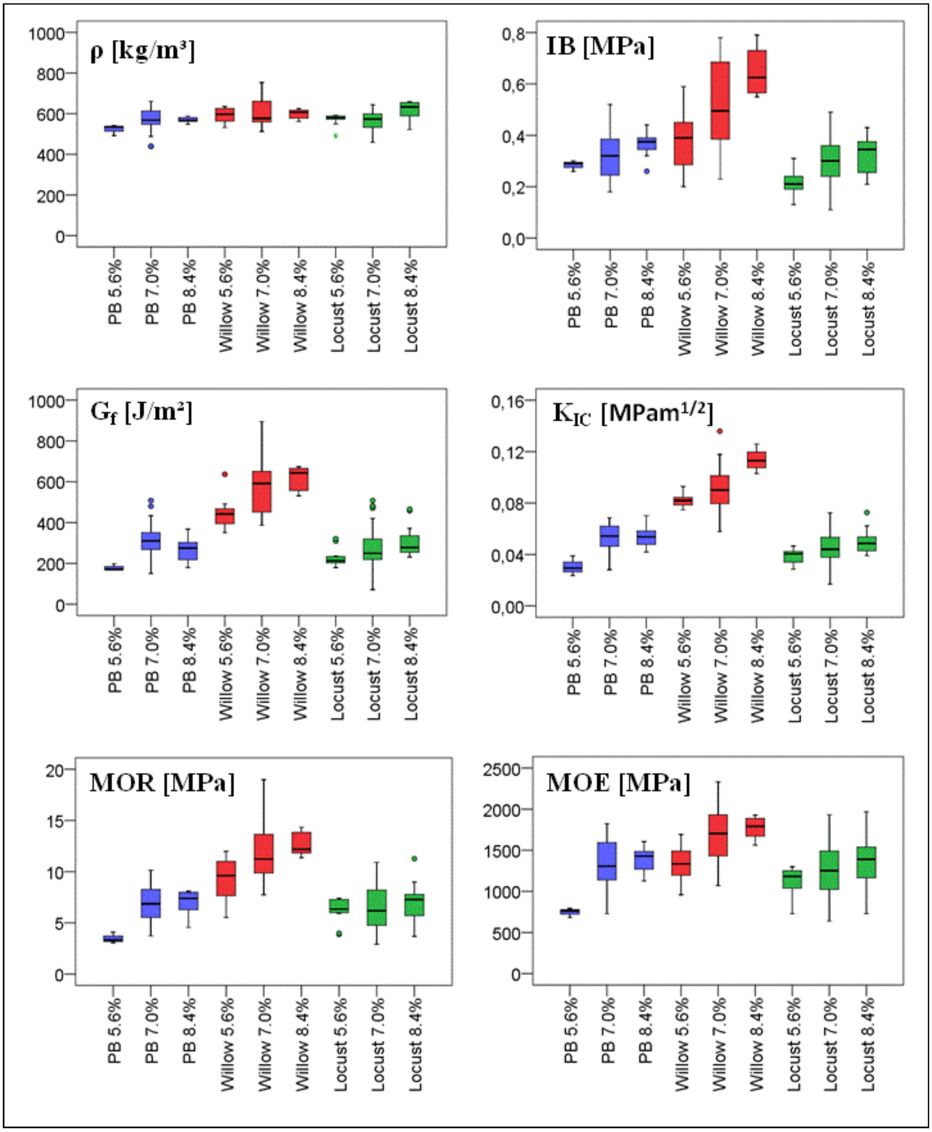

Figure 1: Results of density measurement and mechanical testing for particleboards with different raw materials and varying resin content

However, statistical significant differences between different resin content was only observed for the raw material type willow in the case of the stress intensity factor (K_{Ic}). Expecting for the bending properties of locust, specimen for all other wood raw material tested a significant difference was only observed for minimal (5.6%) and maximal resin content (8.4%).
Coefficient of variation of IB was in the range of 21.1% in the different groups of wood raw material at different resin content. However, CoV of G_f and K_{IC} is in the range of 14.8%. Therefore it is concluded that fracture energy tests are more dedicated to be used for analyzing effects of varying resin content and raw material effects. Bending strength shows trends for MOR but still, scattering is too high to perform a distinctive analysis, especially with MOE.

Conclusion

IB and bending properties of particle boards are widely used for the characterization of particle boards. Due to the high densification of the surface layers bending properties do not directly reflect bonding performance of the core layer. On the other hand IB is a standard testing procedure which is more dedicated to be used for quality control in the production process. It was shown that G_f and K_{IC} derived from the new double cantilever I-beam test yield valuable data which can be used to observe changed resin content as well as effects of the wood raw material on the mechanical properties of the entire board.

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Thermomechanical modification effect in contact drying of veneer

Olli Paajanen[*], **Matti Kairi**[#]

Department of Forest Products Technology, School of Chemical Technology, Aalto University
PO Box 16400 FI-00076 Aalto

[*]olli.paajanen@aalto.fi

[#]matti.kairi@aalto.fi

Key words: Veneer drying, contact drying, surface properties of veneer, veneer modification, veneer quality

ABSTRACT

A new contact drying method has been developed and patented in Aalto University through a co-operation between two departments; the Department of Forest Products Technology and the Department of Energy Technology. The method has been tested on several prototypes and the results are promising; drying times are reduced significantly [1], the veneer quality is good and the method is more energy efficient [2]. Figure 1 shows the structure and operating principle of the new drying device.

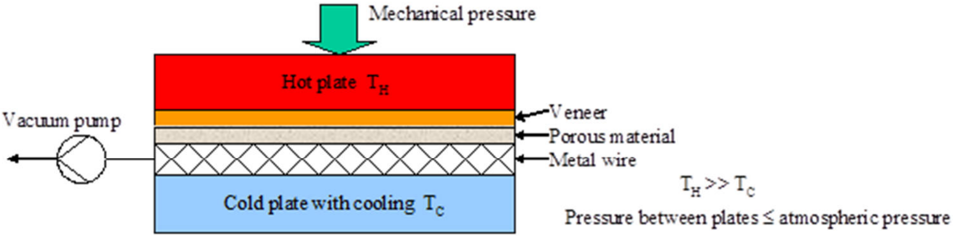

Figure 1: The operating principle of the new drying device

As can be seen from Fig. 1, the veneer is in contact with the heated plate at the top of the dryer. This contact is achieved by pressing the veneer on to the plate. A wide pressure range can be used. The temperature of the top plate can be up to 200 °C. As result of these process parameters, a thermomechanical modification effect may be achieved during the drying process. In the case of rotary peeled veneer, this is a very interesting proposition because the current convective drying process used in the plywood industry has an adverse effect on the quality of the veneer. The different temperature and pressure settings have an effect on veneer quality parameters, ranging from strength to adhesion properties. Also the orientation of the veneer is an important parameter, because the peeling checks have a big effect on the quality of the final product, plywood. As the new drying system presses the veneer during drying, the surface of the veneer is very smooth. The roughness of the veneer surface as well as the density profile of the veneer change during the process. Microscopic comparisons indicate changes in the surface of the veneer. Preliminary test confirm that the quality of the veneer dried with the new method is as good, or better, compared to reference veneers. The flatness and smoothness of the veneer is better and the first tests indicate that the dryer settings have a statistically significant effect on the hardness of the veneer.

The new, more efficient contact drying method could therefore provide better quality veneer than the current process, and with the correct set of parameters, could even improve the quality through modification.

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Wood surface modification for mussel imitation with protein adhesives

Ilaria Santoni, Benedetto Pizzo[*]

CNR-IVALSA, Trees and Timber Institute, via Madonna del Piano, 10. I-50019,
Sesto Fiorentino (FI), Italy

[*]pizzo@ivalsa.cnr.it

Key words: Wood, adhesion, bio-based adhesives, mussels protein, DOPA, metal ions, wood surface modification

ABSTRACT

Gluing wood by proteins is a topic of increasing importance due to the facts that synthetic adhesives come from non-renewable source, are subjected to price variability and their toxicity is ever more unappreciated by consumers. In fact, it is well known that formaldehyde based adhesives such as urea formaldehyde (UF) and phenol formaldehyde (PF) have tendency to release formaldehyde, although in smaller quantities thanks to the research efforts in past and current times. As a consequence, new adhesive systems more environmental friendly are ever more investigated.

Currently, the most studied proteins for this application are vegetable proteins, which have good bonding performance. The use of such proteins is not new, and the first patent dates back to 1923 and belongs to Otis Johnson who claimed that soy can be used as an adhesive [1]. Much of the research in the last 10 years has focused on soy protein, thanks to the sponsorship of the American United Soybean Board.

As formaldehyde-based adhesives are still superior in strength and water resistance compared to protein-based adhesives, it is necessary to continue the evaluation of how to improve the adhesion properties of protein-based adhesives.

An example in nature of protein-based adhesive good performing in problematic conditions is represented by the mussel-developed adhesive, that can even withstand under water. These molluscs glue themselves to surfaces by synthesizing proteins containing the uncommon aminoacid 3,4-dihydroxyphenylalanine (DOPA) [2, 3].

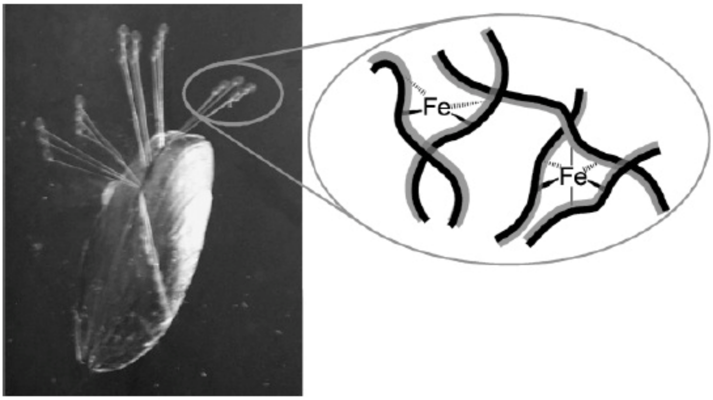

Figure 1: Proposed iron–protein cross-linking in marine mussel adhesive plaques. (From [1]).

But the cross-linking agents used by mussels to cure their adhesive as well as the chemical bonding within the final material is yet not well known. Potential cross-linking agents for mussel's foot protein include enzymes, chemical oxidants, and metal ions [2, 4, 5]. While the presence of ions as iron, zinc, copper and manganese was observed [6], no enzymes or simple oxidants have been found in the mussel adhesive proteins to date [2]. As for DOPA, the metal ions concentration is higher in proteins of the mussel foot than in other mussel's part.

In order to try to replicate what happens for mussels, we tried to improve the mechanical properties of glued wood joints by increasing the concentration of metal ions at the interface between wood and a protein-based adhesive. To such purpose, wood surface was treated with solutions of transition metals and with a salt solution of aluminium, which is a trivalent ion. The metal ion solutions are known to be a primer for a lot of surfaces: in principle, they could interact with several materials having polar groups. For example alum is used as a mordant for coloring protein-based fibers like wool and silk.

Moreover, wood surface was treated with DOPA solutions in order to study the effect of the concentration of this aminoacid on the adhesion with soy protein-based adhesives.

After treatment of surfaces with either metal ions or DOPA solution, wood was glued with soy protein. Glue was applied both after the solution was dried and with surface still wet. Standard bonding tests were then carried out according to EN 305 (tensile shear strength for structural adhesives); more specifically, samples were tested in dry condition after 7 days conditioning at 20°C and 65% RH.

Results showed that, in general, wood surface modification with metal ions increased the mechanical properties of bonded joints, but only when glue was applied on dried surface. In contrast, specimens glued when the metal salt solution was still wet decreased mechanical properties. Variations were evaluated in comparison to values obtained with joints glued by using soy protein without any pretreatment.

Wood surface treated with DOPA did not lead to an improvement of mechanical properties of the bonded joints. It is known that despite its virtues for mussel foot protein, DOPA has a troubling tendency that presents significant challenges to its use: in the presence of O_2, it is readily oxidized to dopaquinone. Dopaquinone formation diminished adhesion to titania and mica by at least 80%, but it also underwent crosslinking reaction [7, 8]. According to the latest studies on the composition of mfp the presence of thiols is necessary to bring dopaquinone back to the catechol form of DOPA. Other tests are therefore needed in non-oxidizing conditions to verify the possibility of using DOPA as wood surface modifier to improve protein adhesion.

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Colour change of different wood surfaces due to reactions with glues and during service life with and without indoor sun radiation

Róbert Németh*, József Ábrahám+, Szabolcs Komán# and László TolvajΔ

University of West Hungary, Bajcsy-Zs. u. 4, H-9400 Sopron, Hungary

*nemethr@fmk.nyme.hu

+abrahamj@fmk.nyme.hu

#komansz@fmk.nyme.hu

Δtolla@fmk.nyme.hu

Key words: colour change, glue, indoor sun irradiation

ABSTRACT

Introduction

During gluing technology in the wood industry the surfaces often suffers some discolouartion. Depending on the extent and the measure of this phenomenon, customers often claim about this problem. The user of the glues often claim the glue producer as the detected discolouration would be caused by the low quality, and/or changing quality of the glue. According to our experience in many cases the detected discolouration is a concequence of the inappropriate gluing conditions (e.g. applicators, temperatures) and the different wood species.

In order to verify the reasons for the discolourations the possible reactions between different materials and surfaces were tested:

1. Reactions between the glue and the material to be glued
2. Reactions between the glue and the applied tool (not discussed in detail here)
3. Reactions between the material to be glued and the applicator (not discussed in detail here)

Materials and Methods

6 different PVAc glues were tested (water resistant - D3, and not water resistant types).
7 different wood species were investigated: Oak, Robinia, Ash, Beech, Birch, Scotch Pine and Norway Spruce).
Applicators in everyday use in joineries were chosen to the tests: steel with stain, normal clean steel, aluminium, wood (oak, beech, birch, robinia, ash, pine, spruce), plastic, paintbrush.

Results

The discolouration of the wood surfaces after curing the glues is shown on Fig. 1. The different wood species showed different colour changes. All investigated colour properties (L*, a*, b*) changed considerably by the hardwoods. Measurable, but not pronounced colour changes could be observed by the softwood. The highest colour changes could be observed by Robinia wood, which is rich in extractives. Very probably chemical reactions between the extractives (robinetins, tannin) and the glue's components led to the severe discoilouration. The changes of red hues are shown on Fig. 2.
On Figure 3 the colour change after 1 year storage at indoor conditions is shown. The total colour changes (ΔE) were calculated as well.

We found that excluding the sun irradiation (storage on dark place) resulted in lower ΔE compared to the open storage. Pronounced colour changes after one year storage on dark place could be observed by Robinia only, and only for 2 of the 6 applied glues. Under open indoor storage conditions Robinia, Spruce, Pine and Beech showed considerable colour changes, while the glued oak, birch and ash samples could keep a stable colour, thus no further remarkable colour changes occurred after 1 year storage with indoor sunlight irradiation.
Further interesting results were found on the effect of the applicator's material on the colour change.

Fig. 1: Discolouration of the wood surfaces after curing the glues and 7 different wood species

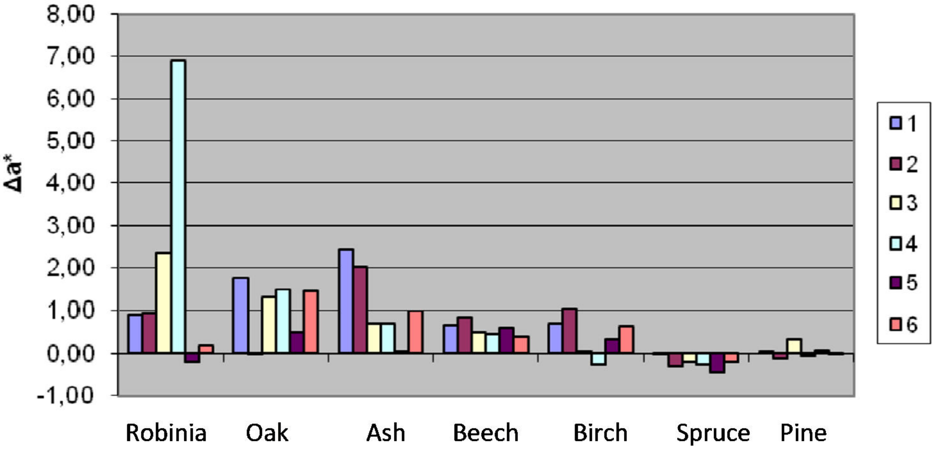

Fig. 2: Change of red hue of wooden surfaceas after curing the glue for 6 investigated glues

Fig. 3: Change of colour after 1 year storage at indoor conditions for different wood species – with indoor sunlight irradiation

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Study of the bonding performance of UF/PVAc formulations with low formaldehyde emission

João Ferra[1], Jorge Martins[2,3], Nuno Costa[3], Cristina Coelho[2,3], João Pereira[4], Paulo Cruz[1], and Luisa Carvalho[2,3]

[1]EuroResinas – Industrias Químicas, S.A., 7520-195, Sines, PORTUGAL

joao.ferra@sonaeindustria.com

[2]DEMad-Dept. of Wood Engineering, Polytechnic Institute of Viseu, Campus Politécnico de Repeses, 3504-510 Viseu, PORTUGAL

[3]LEPAE-Dept. of Chemical Engineering, University of Porto- Faculty of Engineering, Rua Drº Roberto Frias, 4200-465, Porto, PORTUGAL

lhcarvalho@estv.ipv.pt

[4]ARCP – Association of Competence in Polymer Network, Rua Drº Roberto Frias, 4200-465, Porto, PORTUGAL

Key words: urea-formaldehyde, polyvinyl acetate, formaldehyde emission, wood veener

ABSTRACT

Urea-formaldehyde resins are still the most widely used adhesives in the manufacture of wood-based panels. However, environmental requirements, as stringent formaldehyde emissions regulations, and new products specifications, have forced producers to find new tailor-made gluing solutions, without loosing productivity and quality. Three approaches currently been followed: optimization of UF resin synthesis, development of new catalysis systems and the combination of high performance UF resins with added chemical formaldehyde scavengers [1].

Another alternative is the formulation of two components systems, mixing a UF resin with a formaldehyde free adhesive, as PVAc (Polyvinyl Acetate Adhesive), an aqueous dispersion of polyvinyl acetate compatible with UF. PVAc based glues are very common in the furniture and joinery applications, because they are very easy to handle and apply and they have a long storage life. However, due to their characteristics, as the low moisture resistance and creep (thermoplasticity), the common PVAc adhesives are restricted to non-structural and interior applications [2]. Modified PVAc glues with the addition of crosslinkers allowed this type of glues to be used in water resistance classes D2 to D4 according to EN 204 standard [3].

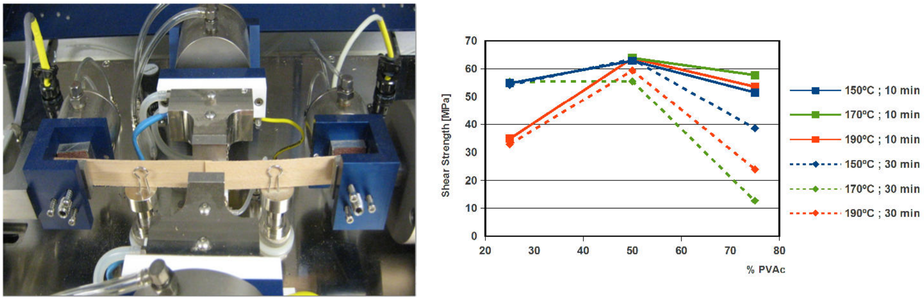

Figure 1: ABES (Automated Bonding Evaluation System) set-up and results: shear strength in function of the percentage of PVAc for thermally treated beech veneers bonded with UF/PVAc mixtures

There are already solutions in the market based on the combination of PVAc adhesives and formal-dehyde-based adhesives for furniture and flooring applications with negligible formaldehyde emission [4]. Although there are a few studies in the literature, further investigation [5] is necessary to tailor the glue mixture characteristics, not only to comply with application technologies (viscosity, solid content, pH, wettability), but mostly to improve process efficiency (fast setting times and less panel rejects).

The aim of this work is therefore to study the bonding performance of several adhesive formulations, based on the combination of an E1 UF resin and a PVAc adhesive. In order to assess the behaviour of different mixtures ratios of UF/PVAc, several tests were carried out on ABES (Automated Bonding Evaluation System) using beech veneers and several operating conditions (open assembly time, pressing temperature, pressing time) were tested. Since the acidity of PVA dispersion may reduce the pot-life of UF adhesive, the influence of the hardener quantity was also tested. The effect of a surface thermal treatment on UF/PVAc mixture bonding performance was also studied. Using the ABES hot-press, the veneer strips were pressed at three temperatures (150, 170 and 190 ºC) and for two different time periods (10 and 30 min). After conditioning, the strips were bonded with different adhesive mixtures (25, 50 and 75 % of PVAc) and the bonding performance was tested using ABES (pressing conditions: 80 ºC and 150 s). Figure 1 shows that the mixture UF/PVAc (50/50) gives the best results, which seems to be independent of the surface treatment.

The wettability of unmodified and thermally treated wood veneer by the different mixtures was also compaired using a contact angle meter. The most promising formulations were used for surfacing MDF with wood veneer in a pilot hot-press [6]. Results relating adhesive mixture composition with the mechanical properties of MDF overlaid with beech veneer (surface soundness evaluated according to EN 311 [7]) and formaldehyde emission are shown and discussed.

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Plasma Technologies for Interface Engineering in Wood and Cellulose (nano)Fibers-based Composites: Experiences and Prospects

Marie-Pierre Laborie

Institute of Forest Utilization and Works Science and Freiburg Materials Research Center (FMF),
Albert-Ludwig University of Freiburg, 79085 Freiburg im Breisgau, Germany,

marie-pierre.laborie@fobawi.uni-freiburg.de

Key words: Wood surface activation, interfacial Adhesion, Cold plasma polymerization, Pulsed Plasma polymerization, Wood-Plastic composites, Cellulose nanowhiskers, microstructured surface

ABSTRACT

Plasma technologies are widely used as adhesion promotion techniques in many fields of applications. Plasma technology is of particular interest for surface modification due to its environmental friendliness relative to wet chemistry approaches. It is a solvent-free method, which may not involve toxic chemicals. Furthermore plasma treatment can be relatively easily implemented on a production line. As such it is also interesting for surface modification and for the design of interphases for wood- and cellulose fiber-based materials. Within this context, this presentation will focus on the author' experiences in utilizing various plasma approaches for tackling adhesion problems related to wood and cellulose-based composites. Research avenues currently pursued at the Albert-Ludwig University of Freiburg will also be presented.

One first experience relates to the utilization of oxygen plasma as a surface activation method for wood plastic composites (WPC) [1]. In this work, a series of WPC formulations comprising either high density polyethylene (HDPE) or polypropylene (PP) and maple or pine were subjected to four different surface treatments, with a view to improving the adhesion of coatings on WPC. Oxygen plasma performed particularly well, improving the adhesion strength of an acrylic coating by more than 100%. Oxygen plasma treated surfaces and control surfaces were thoroughly analyzed by wettability, profilometry and attenuated total reflectance (ATR) fourier transform infrared spectroscopy (FTIR) studies [1, 2]. This provided insight on the adhesion mechanisms underlying the efficacy of the oxygen plasma activation method on WPC.

More recent work relates to the exploration of plasma polymerization techniques for tailoring the surface chemistry and properties of wood and cellulose fibers and for compatibilising these fibers with any polymer matrix. To that end, two routes are currently explored. In a first collaboration with Prof. Vincent Roucoules from the University of Haute Alsace (France), pulsed plasma polymerization of maleic anhydride in presence of cellulose nanowhiskers is performed with a view to creating well dispersed cellulose reinforced nanocomposite materials *in situ* [3, 4]. Under certain conditions, cellulose nanocomposite thin films with unique topographies and microstructures are produced. It is believed that buckling occurs in these cellulose whiskers / maleic anhydride polymerized thin films, generating ondulating topographies and micropatterned surfaces (Fig. 1). This "co-polymerization" of cellulose nanowhiskers with a precursor under the mild conditions of pulsed plasma polymerization therefore opens up interesting avenues for the design of microstructured surfaces. Current work aims at better understanding the dewetting mechanism responsible for this surface organization and at controlling the microstructuring pattern.

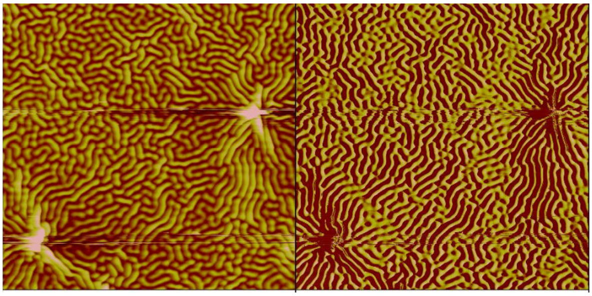

Figure 1: Topography of a plasma polymerized maleic anhydride film in presence of cellulose nanowhiskers observed by atomic force microscopy (tapping mode)

Finally, current efforts are ongoing in collaboration with Prof. Pat Pedrow from Washington State University (USA) to develop cold plasma polymerization technologies using acetylene and hexamethyldisiloxane as a precursor for the surface modification of wood and cellulose fibers [5, 6]. The objective here is to develop a low cost and rapid surface modification technology for tailoring the surface chemistry and properties of bio-based fillers for compatibilization with a specific polymer matrix. With a gas phase modification process working at atmospheric pressure, in line treatment of wood or cellulose fiber particles could be very easily implemented on a commercial production line for modified wood fiber.

Altogether, the various approaches taken to apply plasma technology to wood-based materials open up interesting perspectives for the design of wood- and fiber-based materials in the laboratory as well as on a an industrial setting.

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Surface modification of WPC products to improve bonding strength

J. Leßlhumer[1*], J. Sinic[1], M. Reif[1], A. Haider[1], D. Cascorbi[2#]

[1]Competence Center for Wood Composites and Wood Chemistry (Wood K plus);
Altenberger Straße 69, 4040 Linz, Austria

[*]j.lesslhumer@kplus-wood.at

[2]Pinuform GmbH & Co. KG; Blaubeurer Straße 70/1, 89077 Ulm, Germany

[#]diethard.cascorbi@pinuform.de

Key words: Flame treatment, plasma treatment, surface activation, wood polymer composites, gluing

ABSTRACT

Introduction

Wood polymer composites (WPC) are by definition materials or products made of one or several cellulosic materials with one or several thermoplastics [1]. The main applications are deckings and sidings. To develop new applications, which require gluability, it is important to activate and/or modify the non-polar thermoplastic matrix in order to improve the wettability, and increase surface energy and bonding strength [2]. Therefore, three different surface treatments (sanding, flame and plasma treatment) were tested for their effect on glue joint strength of highly filled WPCs. Sanding crosswise to the direction of stress is meant to roughen and enlarge the surface area. The activation by flame treatment is based on the oxidation mechanism [3]. The plasma modification cleans and activates the surface and causes a very high surface energy with a considerable polar component. The tensile shear strength of glued test specimens was determined according to EN 205 [4]. For the study acrylate-, epoxy- and polyurethane- based adhesives and one type of commercial wood glue were tested.

The aim of the study was to identify an effective surface modification technique and adhesive for WPCs as well as to evaluate influence of the storage time on the surface energy.

Experimental

For sample preparation, hollow chamber profiles were manufactured on a Cincinnati fiberex K38 conical counter-rotating twin-screw extruder. The test specimens were cut from the profiles with a CNC-milling machine. Four formulations, containing 60 and 70 mass-% spruce wood fibers, respectively, based on either polyethylene (PE) or polypropylene (PP), were employed.

To chemically and physically modify the surface properties of the WPCs, the test specimens were either untreated, sanded, flame- or plasma treated (see Fig. 1).

For the bonding tests according to EN 205 different adhesives (acrylate, epoxy, polyurethane) and one type of commercial wood glue were used.

Figure 1: Air plasma treatment (Wood K plus)

Results

Generally, the test specimens with PP matrix achieved higher tensile shear strength than samples based on PE. The flame- and air plasma treatments increased the tensile shear strength compared to the reference. The surface area enlargement through sanding also resulted in a significant improvement of the bonding strength. Furthermore, the storage conditions (temperature, time) have an influence on the surface energy, and, in further consequence, on the tensile shear strength.
In the tests according to EN 205, the acrylate adhesives showed the highest values, followed by the epoxy based adhesives. PUR adhesives are less suitable for wood polymer composites.

Conclusions

Overall, the study showed that plasma treatment is an efficient modification technique for gluing wood polymer composites. Furthermore, it is easy to install online in existing production lines.
WPC surface energy is influenced by the pre-treatment, sample handling and storage time.
Acrylate based adhesives, being applicable to polyolefins, also bring about the highest lap joint strengths in PP and PE based wood polymer composites.

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Atmospheric Plasma Treatment of Natural Fibres

Judith Sinic[1], Martin Weigl[2]

[1]WOOD Carinthian Competence Centre, Klagenfurter Strasse 87-89, 9300 St. Veit/Glan, Austria

j.sinic@kplus-wood.at

[2]Kompetenzzentrum Holz GmbH, c/o UFT Tulln, Konrad Lorenz Straße 24, 3430 Tulln

m.weigl@kplus-wood.at

Key words: natural fibres, atmospheric plasma treatment, contact angle measurements, wettability, absorption, adhesive strength

ABSTRACT

Due to an increasing environmental awareness in the automotive industry the deployment of natural fibres in reinforced thermoset pressing parts gain in importance. Hence, the performance requirements for natural fibres reinforced components did rise. In the first instance improved mechanical properties are required. To meet these demands, such as a superior tensile and bending strength, an optimized adhesive property between fibre and matrix resin is postulated [1].

An approach to improve the adhesive strength is the plasma pre-treatment under atmospheric conditions. By means of a plasma treatment with air as a process gas the natural fibre is activated. As a consequence the plasma treated fibre exhibits an increased wettability and a faster absorption capability. Both properties provide a better ability to impregnate the natural fibre for an intensified wetting with the thermosetting resin – basic prerequisite for an improved adhesive property of the fibre composite [2, 3].

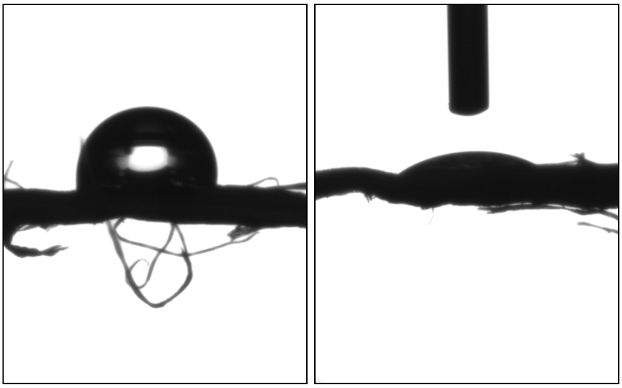

Figure 1: Water drop on the untreated wood fibre (left) and the plasma treated fibre (right)

To analyse the improved wettability affected by the plasma pre-treatment contact angle measurements were performed (contact angle measurement device OCA 35, DataPhysics). In the laboratory experiments individual wood fibres with a length of approximately 20mm and an average diameter of 2-3mm were fixed in a sample holder and accordingly pre-treated with plasma. Therefore, an atmospheric pressure - plasma machine was used (Plasma generator FG3001 with nozzle type RD1004, Plasmatreat). The device generates the plasma by means of pressure air flowing past two electrodes, a rotating nozzle induces a homogeneous plasma beam. The distance between plasma beam and fibre surface was about 10mm and the track speed amounted to 50mm/s. A damaging thermal impact of the plasma beam that evokes discoloration or charring of the fibre was not detected.

By means of the high speed camera the absorption time and the contact angle using water as test liquid were recorded. In comparison to the untreated fibre the contact angle decreases (68 → 38°) and the absorption time was reduced distinctly (28 → 18 sec.) (Fig.1). The influence of metered volume of water, special contours of the drop, specific properties of single fibres and pooled fibres will be discussed in the paper.
The experiments show that the used method gives a quantitative assessment of the success of plasma treatment on single fibres. Nevertheless, the variance of the values is high.

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Some experiences and tools for the assessment of surface and adhesion characteristics of wood

Magnus Wålinder[*] **and Dennis Jones**[#]

SP Trä/SP Wood technology, SP Technical Research Institute of Sweden
Box 5609, SE-114 86 Stockholm, Sweden

[*]magnus.walinder@sp.se, [#]dennis.jones@sp.se

Key words: Surface coatings, adhesion, analytical tools

ABSTRACT

There have been considerable advances in recent years in methods used to ascertain the surface properties of treated wood, allowing us to increase our understanding of how new chemicals and treatments interact with the wood surface as well as providing means of quality assurance for commercial products. The purpose of this paper is to summarize some of our experiences regarding the surface and adhesion characterization of wood.

A theoretical adhesion approach related to so-called wetting phenomena on wood, i.e. interactions between wood and liquids at the interface between them, has been extensively studied by means of the Wilhelmy plate and the so-called column wicking techniques. The main conclusion and recapitulation of these studies is that there exist a number of typical “pitfalls” that easily interfere such measurements on wood, mainly due to its complex heterogeneous, porous, rough, hygroscopic and anisotropic nature. Wetting parameters on wood must therefore be rigorously determined with a control of the strongly influencing factors such as wood extractives, wicking and bulk sorption effects.

The surface energetics of wood, wood fibers and polymers has also been studied by gas adsorption analysis based on inverse gas chromatography (IGC). Both the wetting and the gas adsorption analyses have involved the Lewis acid-base concept. A recent topic also relates to surface characterization of chemically modified wood, either regarding its wetting properties or its surface chemical composition determined by spectroscopy.

Another promising tool for studies and alternation of the wood surface and wood-polymer interface morphology involves so-called micro machining using a UV-laser irradiation (or ablation) technique. In future studies, further efforts should be made to combine theoretical with practical surface and adhesion characterization approaches.

The combined tools have a better potential to add valuable information for enhanced bonding between wood and adhesives or coatings, and also between the constituents in wood-based composites, especially for outdoor conditions.

Focusing on Wood Surfaces: Is it Worth the Effort?

Philip D. Evans

Wood Surface Science Laboratory, Department of Wood Science, Faculty of Forestry, University of British Columbia, Vancouver, BC, V6T 1Z4, Canada

phil.evans@ubc.ca

Key words: Wood surfaces, FTIR spectroscopy, photodegradation, lignin, confocal profilometry, plasma, X-ray micro-computed tomography, interface, adhesive, composites

ABSTRACT

Surface science is a branch of materials science that seeks to characterise, understand and engineer the material that occurs at the interfaces of two phases, solid-gas, solid-liquid etc. Characterisation of surfaces is one of the central elements of surface science and can be accomplished using a variety of powerful analytical techniques, for example, low-energy electron diffraction, time-of-flight secondary ion mass spectrometry, X-ray photoelectron spectroscopy, auger electron spectroscopy and atomic force microscopy (AFM). All these methods probe the outer layer of surfaces (1 to 10 nm) and hence they require very clean uncontaminated surfaces. These requirements are not often met at wood surfaces because wood readily adsorbs atmospheric contaminants, or its surfaces are modified by centrifugal migration of soluble materials from sub-surface cells. Furthermore, the cellular structure of wood makes it difficult to prepare very smooth surfaces required for AFM. For these reasons approaches that are less sensitive to surface contamination and roughness are more frequently used in our laboratory to characterise wood surfaces. Here I give examples of the analytical techniques that have yielded useful insights into the surface behaviour of wood and helped with our efforts to engineer wood surfaces with improved photostability and interfaces in wood composites with superior properties.

Infra-red spectroscopy of thin wood sections (in transmission) was used to examine the delignification of wood over 50 years ago (Liang et al. 1960). We still use the same technique today to obtain high quality spectra of wood, but more often FTIR internal reflectance (IR) spectroscopy is used because it probes the surface to a depth of the order of a few microns. Using FTIR-IR spectroscopy we showed that wood surfaces exposed to natural weathering for one week were completely delignified (Evans et al. 1996). This finding led (eventually) to the realisation that the photo-protective additives that are very successful at photostabilising polymers are unlikely to provide the solution to the goal of developing effective photo-protective treatments for wood. FTIR-IR spectroscopy also provided important insights into the remarkable photostability of wood surfaces modified with chromic acid (Evans et al. 1992). This finding stimulated years of research to find transition metal compounds that were equally effective as chromic acid at photostabilising wood surfaces (but less toxic). This research was unsuccessful, but significant progress has been made with other systems, and here too FTIR-IR spectroscopy has been used extensively to evaluate whether the systems modify and photostabilise lignin. We have also used weight and tensile strength measurements on thin treated wood veneers to screen chemicals for their ability to photostabilise wood. More recently we have started to evaluate the photostability of wood using erosion measurements. This research uses white light confocal profilometry to measure the differences in height of masked and unmasked wood surfaces exposed to natural or artificial weathering. Confocal profilometry can also map the topography of wood surfaces at high resolution. We have used this capability of confocal profilometry and its metrological output to quantify the etching of wood by glow-discharge plasma (Jamali and Evans 2011). We find that etching of wood surfaces by plasma is influenced by the duration of plasma treatment and

also by wood’s microstructure and chemical composition. Prolonged etching of wood surfaces results in the preferential removal of cellulose from wood cell walls revealing the location of lignin. We have used the capacity of plasma to differentially etch cellulose and lignin to probe the fine structure of cell walls in different wood species. We observe significant heterogeneity in the distribution of lignin in wood cell walls, which may explain the pattern of microbial deterioration of cell walls and differences in the resistance of some woods to soft-rot.

We have successfully used the ability of plasma to etch wood to improve adhesive bonding in laminates mades from high density eucalyptus species. We have recently extended our interest in engineering the interfaces between the elements of wood composites to include composites composed of particles and flakes. This research seeks to optimise the geometry of glue-lines in particulate wood composites (particleboard and OSB) to improve adhesive bonding. To-date we have used x-ray micro-computed tomography (μ-CT) and associated numerical techniques to visualise and quantify the spatial distribution of adhesive in particleboard and visualise zinc borate in OSB (Evans et al. 2010).

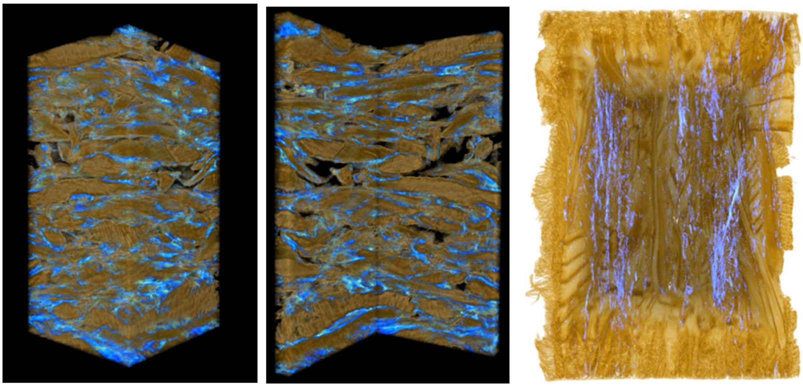

Figure 1: X-ray μ-CT images of wood composites: Particleboard (left and centre) showing adhesive (blue), wood (brown) and void (black); OSB (right) showing zinc borate (blue) in glue-lines within the composite

We find that adhesive migrates during hot pressing possibly aided by the wax that is applied to flakes to increase the dimensional stability of particleboard. The latter suggestion raises the intriguing possibility that it may be possible to alter adhesive bonding of wood composites by changing the surface energy of flakes and particles. Future research will seek to answer this important question and find additional ways of engineering wood surfaces to improve adhesive bonding in wood composites.

Our research focuses solely on the surface properties of wood. We have developed new methods of photostabilising wood surfaces that significantly improve the longevity of clear coatings on wood. Our research on plasma etching of wood is providing insights into the ultra-structure of wood cell walls, and our most recent research on wood-adhesive interfaces is hinting at novel ways of improving the properties of wood composites. These outcomes were not achieved quickly or easily, but they encourage us to continue with our focus on the surface properties of wood.

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Developments of wood based composites and the processing industries

Marius Catalin Barbu

Salzubrg University of Applied Sciences, Campus Kuchl, Markt 136a, 5431 Kuchl, Austria,

marius.barbu@fh-salzburg.ac.at

Key words: wood based composites, developments, markets, panels, coatings

ABSTRACT

The forecasts for the next decades point out new centers of economic development (South-East Asia) far away from those of the last century (Europe and North America), which will confirmed the changed balance of today's situation. The unprecedented demographic growth in Asia (close to 2/3 of the world population) and the aging of the European and North American population (life expectation over 70 years) will also result in the occurrence of controversial scenarios for the whole region in terms of economical evolution. China (20%) and India (17%) will continue to increase their population in the next 40 years and will concentrate over 3 bill, which was the population of the world in the 60's. In accordance with the present moderate forecasts, the world population will reach 9 bill. inhabitants before the year 2050. It is to be pointed out that USA and the European Union, with less than 11% of the world population, contribute with more than 52% to the world gross product (WGP). Also contrasting is the fact that Africa and the Indian Peninsula contribute with only 4% to the WGP, although possessing considerable natural riches (i.e. forests) and having about 40% of the world population. The hierarchy of the industrialized countries is now substantially modified by the fast growing countries i.e. China, Brazil, India, Mexico ranking among the top 10 as regards the national gross product [1, 2, 7].

From 4 bill. ha forests more than the half belongs to underdeveloped countries, 29% to Russia, 17,5 % to North America (half by Canada), 13% to Brazil and less than 4% to EU27. Inside EU27 the main area covered by forest represents 177,8 mill. ha (41%). Only 75% are suitable for the roundwood production. The main area of forest for the wood supply is owned by Sweden and Finland (each 15%), followed by France and Spain (each 11%) and Germany, respectively Poland and Italy (8% respectively 6% each). The growing stock of the world in 2010 by volume was above 500 bill. m³, from which Brazil accounts one quarter, followed by Russia and North America (each 16%) while the EU27 has less than 5%. The growing stock of EU27 is approximated at 21,75 bill. m³ at an yearly increment of 768 mill. m³. The annual average removal for roundwood in the world in 2009 was 3,28 bill. m³ (of which 57% as fuel) shared by EU27 (12%), USA and India (each 10%), China and Brazil (each 9%), Russia (5%) and Canada and Indonesia (above 3%). The difference between these world top 10 countries is the way to use the removed roundwood: processing over 90% in North America, over 80% for EU27, over 70% for Russia and less than 50% for Brazil vs. less than 10% in India and China. The production of roundwood in the EU reached an all-time high in 2007, peaking at 458 million m³ (2009 only 391 mill. m³) [1, 2, 5, 6].

In 2008 the EU27 wood-based manufacturing industry had a tourn-over more than 413 bill. €, employing 2,77 mill. manpower in 328.300 companies. The wood and wood-products industries employ 1,16 mill. manpower, the same figure like the furniture industry (1,2 mill.) vs. 0,7 mill. in the pulp and paper products industry. In term of turnover the pulp and paper products industry makes 180 bill. €, the wood and wood products 131,5 bill. € and the furniture industry 115 bill. € (more hand labour). China range on the world top with 1,25 mill. persons (more than EU 27),

followed by USA 536.000, Russia 340.000, Indonesia 300.000, Brazil 225.000, Italy 155.000, Poland and Germany (each over 135.000) [2, 3, 4, 8].

The world production of sawnwood was 362 mill. m³ in 2009 (10% less than in 1999). More than one quarter is processed in EU27, same amount like North America (1/3 Canda and 2/3 USA, where actually only 2/3 of 1999 was processed), followed by China (9%), Brazil (7%) and Russia (3%). The continents with the lowest sawn production are Africa and Oceania (each above 2%). In 2007 the EU production of sawnwood peaked over 115 mill. m³. This figure dropped till 2009 by over 22%. The main share of sawnwood within EU27 (91 mill. m³) in 2009 was kept by Germany (23%), Sweden (18%), Austria, Finland and France (each 9%) [2, 5, 6].

The installed capacity worldwide for the wood based panels has risen from 2000 to 2010 by more than 25%, reaching 235 mill. m³/year. The capacity increase of the very last years was in South-East Asia and South America. Only in Eastern Europe are developing new production capacities, particularly in Russia and Turkey. Europe and China hold each more than 30% of the world capacity for wood based panels.

The European production of panels (comprising 60% particleboard, 22% fibreboard, 7% OSB, 5% plywood and solid panels) reached 70 mill. m³ in 2007 (-20% in 2009).The main panel producer in Europe is Germany (26%). Turkey increased its capacities at a high rate reaching 2nd place. Russia will become important players in this industry. The main market share in Europe belongs to Austrian group owners Kaindl (Krono Group) and Egger (28%, respectively 12%) and the top 4 of them (including Sonae and Pfleiderer) are controlling more than half of the European capacities.

Particleboard kept its significant market share (2010: 96 mill. m³) for decades with its popularity worldwide (above 40%), loses constantly ground in North America and Central Europe as well. A new generation of light particleboards with a density of less than 500 kg/m³ is established.

Plywood holds worldwide the second position (74 mill. m³) after PB. China is now the biggest plywood manufacturer of the world (over 35 mill. m³). Asia without China already surpassed North America (17 mill. m³). In South America (over 4 mill. m³), Brazil, is one of the worldwide main plywood exporter. In North America, Central Europe and Oceania, a constant decrease in the production capacities can be noted. Eastern Europe and Russia are other regions with a positive evolution in this respect. In Europe, the processed plywood represents 15% of the world production capacity and is covered by two thirds from imports (75% from China, Brazil, Russia).

MDF – after only 40 years of its apparition reached the same production capacity level like plywood (about 80 mill. m³) and is manufactured 46% in China, less than 25% in Europe (incl. Russia and Turkey), and the rest shared between Asian countries (11%, without China), Latin America (9%) and North America (7%). In the same period in North America (-20% in USA), Oceania, and parts of Asia the production activity was stopped and lines have been closed down, dismounted and relocated. One third of MDF is produced as thin HDF and coated for flooring. A new generation of thin HDF (<3 mm) started.

Oriented strand board had a growth of more than 40% in the same decade like MDF. In North America, where OSB launched as a building material to the detriment of plywood and PB, 85% of the global production capacity (30 mill. m³) was concentrated. In the last decade in Europe the annual production capacity has doubled, reaching 5 mill. m³ and more than 30% of the production is exported to Eastern regions. New lines are realised for the very first time the in Eastern Europe, Russia, Turkey and China (also from rice straw). Increasing requirements for indoor air quality are new optimization fields.

The production of wood pellets in the world grew at a phenomenal rate (2010: over 15 mill. t). More than two thirds of pellets are produced in Europe and close to one third in North America. Asia and South America started to install capacities. Russia owns the 1st pellets mill with one mill. t production capacity. According to Pöyry the global pellet market will triple the consumption within next decade [1-6, 8].

The traditional furniture manufacturers in the Central Europe and North America are hardly facing up to the competition of the new manufacturers from Eastern Europe and South-East Asia.

Also IKEA and similar other low budget furniture trading chains influenced a lot the developments of last decades. Furniture production reached 5 years ago the value of 200 bill. €. Since 2000 up to present, China has managed to double its furniture production and to increase exports threefold. Pöyry forecasts an increase of the world demand from 12 to 14,7 mill. m² for coating materials within 2015. Especially the melamine based paper coatings will reach 45% market share. This expected development has to follow the booming development in the emerging countries, the apparition of conurbations and new environmental aspects. Furniture made from low weight elements (sandwich type or foamcore) and very low emission panels especially for the "do it yourself" segment is a probable direction of developments in the near future. Other processing and finishing technologies adapted to the new quality of board should be extended in the market and accepted by processing companie [1, 3, 4, 6, 8].

For the first time after many decades and due to the high price of steel, modern wooden constructions can compete with the classical systems. The new wooden structures are favoured by their structure based on Glue Laminated Timber (GLT), I-beams, OSB faced frames and Cross Laminated Timber (CLT). Fireproofness, large spans, multi-floors, low weights at high dimensional stability in various environments and, last but not least, easy and fast assembling are the characteristics of the new generation of wooden constructions. New European regulations like the Energy Saving Certificate for houses and new regulation for building with more than 7 floors in urban areas could sustain positive developments.

The different regulations in the world states subventions of green energy generated from biomass and in environmental protection (waste air, waste water and noise) create precedents for unequal competition inside continents and between the industries. Some regions offered also important subventions or reduce taxes in order to settle down industrial production sites which also create different advantages [1].

The forecast for the coming years is further on a negative one for North America and Central Europe, stating a consolidation of the available new production capacities and closing of the lines with different accents depending on the financial crisis effect on the furniture and building industry from one continent and region to the other.

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Enhancing the bondability of wood veneers through surface activation treatment

P. Bekhta[*], **D. Tymyk**

National University of Forestry and Wood Technology of Ukraine,
Department of Wood-Based Composites, Lviv, Ukraine,

[*]bekhta@ukr.net

Key words: activating agents, birch, bondability, wood veneers, surface activation treatment

ABSTRACT

The manufacture of veneer-based products (plywood, LVL) involves many different processes; one of the most essential is the adhesive bonding of veneer sheets. Moreover, manufacturing processes including peeling and drying can essentially change physical and chemical surface properties of veneer. The interaction between liquid adhesive and the veneer surface depends, first of all, on the properties of the applied adhesive and conditions of the veneer surface. The strength of the adhesive bond is intimately associated with the surface and sub-surface properties of veneer. In order to achieve optimum adhesion between substrate and adhesive a clean solid surface is required. However, veneer surface is subjected to self-contamination that according to Back [2] is a result of a natural surface inactivation process where low-molecular wood extractives migrate to the surface.

In the production of veneer-based products a significant area of new wood surface is created in a short period of time. But, in many cases, the time between creating a new surface and adhesive spreading is too long. Within this period of time, freshly cut wood surfaces undergo a transformation termed surface inactivation. Wood surface inactivation is a surface phenomenon resulting in the loss of bonding ability [7]. Therefore, quality preparation of the surface is extremely important. The existing technique of manufacturing plywood does not provide the preparation of veneer surface before glue application, although such operation could have an essential influence on the reduction of the glue spread and on the improvement of the plywood performance [3, 4, 5].
Mechanical pre-treatments such as sanding and planning [1] or densification by rolling [3] or densification by pre-pressing [4, 5] can be applied to modify the surface characteristics that improve glue bonding of wood. In order to improve bonding ability, wettability and to reactivate wood surfaces for glue-wood bonds, some chemical pre-treatments are widely applied to wood surfaces [6, 8]. In accordance with this pre-treatment, the functional groups present on the wood surface are modified so that they can react and bond with the functional groups more effectively in the adhesive. Hereby, the surface of wood should be cleaned just before bonding in order to remove all foreign substances that interfere with bonding.

This paper presents a chemical method which utilizes activating agents such as hydrogen peroxide, aluminium persulfate, acetic acid, and sodium carbonate for minimizing surface inactivation and enhancing the bondability of wood veneers.
Rotary cut veneer sheets of birch (*Betula pubescens*) with dimensions of 500 mm by 500 mm and with thickness of 1.5 mm and moisture content of 6% were chosen for the experiments. Hydrogen peroxide (H_2O_2), aluminium persulfate ($Al_2(SO_4)_3$), acetic acid (CH_3COOH), and sodium carbonate (Na_2CO_3) were examined for veneer surface activation treatments. Three levels of the concentration solution of 1%, 2%, and 3% of activating agents were studied. Surface activation was accomplished by spraying the activating agent with consumption of 10, 20 and 30 g/m^2 on

the veneer surfaces before glue application. Surface activity of treated veneers was evaluated by measuring the hydrogen ion concentration (pH) and contact angle. In addition, five-layer experimental plywood panels were manufactured from veneers with treated and non-treated surfaces using commercial phenol-formaldehyde glue resin with a solid content of 42% and viscosity of 120s at following pressing factors: pressure of 1,8 MPa, temperature of 135^0C, and time of 6 min. The glue spread was 150 g/m^2 based on the wet mass. For each treatment, the shear strength of plywood panels was measured according to EN 314-1.
The results revealed that the surface activation treatment of veneer improved both surface properties of veneer and mechanical properties of plywood panels. Surface activated treated veneer decreases the contact angle and increases the shear strength of plywood panels with hydrogen peroxide treatment having the greatest effect followed by acetic acid, and sodium carbonate, and aluminium persulfate treatment. Contact angle of treated veneer surface had up to 36% improved values as compared for those of non-treated samples. That is, the surface activation of veneer increases the bondability of wood. Consumption of activating agents had greater influence on surface contact angle than concentration solution. Increasing concentration solution from 1% to 3% results to the reduction pH of veneer surface for all activating agents except sodium carbonate, for which the pH is increased.

Thus, surface activation can improve the bondability of veneer, as evidenced by higher values (1,7-2,4 MPa) of shear strength of plywood compared to the non-treated surface (1,6 MPa). Though, the increasing of the consumption of activating agents from $10g/m^2$ to $30g/m^2$ results even to a slight reduction by 3-7% in shear strength. This can be explained by increased moisture content of treated veneer and thus increased the probability of adhesive bonds failure under the effect of the excess pressure of gas-vapor mixture during pressing. The raising concentration solution of activating agents from 1% to 3%, on the contrary, leads to increase by 6-9% in shear strength. This may be cause by an increase in the reaction of activating agents with the veneer surface, producing a greater number of functional groups on the surface veneer that may react with the phenol-formaldehyde resin [8]. The highest shear strength of the panels were found for those panels made using veneer treated with 3% solution of hydrogen peroxide at $10g/m^2$ consumption. These samples had 1.5 times higher shear strength values than those of the control panels.

Based on the findings of this work such treatment process could have potential to be used as alternative method to enhance properties of the plywood panels.

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Reactivation of Inactivated Wood Surfaces

Milan Šernek [1]

[1] Department of Wood Science and Technology, Biotechnical Faculty, University of Ljubljana,
Rožna dolina, C. VIII/34, SI-1000 Ljubljana, SLOVENIA,

milan.sernek@bf.uni-lj.si

Key words: adhesion, bonding, wettability, wood surface chemistry, wood surface inactivation

ABSTRACT

The nature and condition of the adherend surfaces are critical to the success of any bonding. Wood surfaces are best prepared for maximum adhesive wetting, flow, and penetration by removing all materials that might interfere with bond formation to wood. A fresh surface contains all of the molecular attractive forces that previously held the material together. Thus, a fresh surface assures the highest adhesion. When the attractive forces on the surface are reduced, adhesion is diminished and weak.

A wood surface, which is exposed to a high temperature condition, can experience inactivation. Surface inactivation reflects physical and chemical modifications of the wood surface. Consequently, these changes result in reduced ability of an adhesive to properly wet, flow, penetrate, and cure. Thus, an inactivated wood surface does not bond well with adhesives.

The objectives of this study were to determine the effect of temperature exposure on wood surface inactivation. The relationships among the chemistry, wettability, and adhesion of the wood surfaces in relation to temperature were investigated. Furthermore, the reactivation of the inactivated wood surface was used to enhance the wettability and to improve adhesive bond performance.

The changes in surface chemistry, wettability, and adhesion of inactivated wood surfaces of southern pine (*Pinus taeda*) were studied. Wood samples were dried from the green moisture content condition in a convection oven at five different temperature levels ranging from 50 to 200 °C. The comparative characterization of the surface was done by X-ray photoelectron spectroscopy (XPS), sessile drop wettability, and fracture testing of adhesive bonds. Additionally, several chemical treatments were utilized to improve wettability and adhesion of inactivated wood surfaces.

XPS results showed that wood drying caused modification in wood surface chemistry. The oxygen to carbon ratio (O/C) decreased and the C1/C2 ratio increased with drying temperature. The C1 component is related to carbon-carbon or carbon-hydrogen bonds, and the C2 component represents single carbon-oxygen bond. A low O/C ratio and a high C1/C2 ratio reflected a high concentration of non-polar wood components (extractives/VOCs) on the wood surface, which modified the wood surface from hydrophilic to more hydrophobic. A hydrophobic wood surface repelled water and wettability of this surface was low (a high contact angle). Wettability was directly related to the O/C ratio and inversely related to the C1/C2 ratio.

Contact angle decreased with time and increased with the temperature of exposure. Inactivated southern pine had a lower wettability due to a greater concentration of non-polar hydrocarbon-type extractives and heat-generated volatiles on the surface. The maximum strain energy release rate (G_{max}) obtained by fracture testing showed that the southern pine was susceptible to inactive

tion particularly when bonded with phenol-formaldehyde (PF) adhesive. A typical wood surface inactivation occurred at drying temperatures higher than 156 °C.

Chemical treatments improved the wettability of inactivated wood surfaces, but an improvement in adhesion was not evident for specimens bonded with polyvinyl-acetate (PVAc) adhesive. Of the chemical treatments employed in this study, NaOH was most effective for improving adhesion of the PF adhesive bond. G_{max} of specimens treated with NaOH increased by a factor of three compared with inactivated specimens. Enzymatic treatment of inactivated surfaces with xylanases did not improve adhesion. The HMR coupling agent was not operative on inactivated surfaces bonded with PF adhesive. Bonding of inactivated southern pine with a polyisocyanate adhesive significantly improved the adhesive bond performance. However, this improvement reached less than 70 % of the adhesion established between freshly produced wood surfaces bonded with PVAc or PF adhesives.

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Wood protection using tannin-boron associations

Gianluca Tondi[1], Stefanie Wieland[1], Thomas Wimmer[1], Alexander Petutschnigg[1]
Nicolas Lemenager[2], Antonio Pizzi[3],
Marie-France Thévenon[2]

[1]Salzburg University of Applied Sciences, Forest Products Technology & Timber Construction,
Markt 136a, 5431 Kuchl, Austria

gianluca.tondi@fh-salzburg.ac.at

stefanie.wieland@fh-salzburg.ac.at

thomas.wimmer@fh-salzburg.ac.at

alexander.petutschnigg@fh-salzburg.ac.at

[2]CIRAD TA B 40/16, Wood Preservation Laboratory, 73 Rue J.F. Breton
34398 Montpellier Cedex 5, France

nicolas.lemenager@cirad.fr

marie-france.thevenon@cirad.fr

[3] ENSTIB, Lorraine University, 27 Rue P.Seguin, 88000 Epinal, France

antonio.pizzi@enstib.uhp-nancy.fr

Key words: Tannins, Boron, Wood protection, Surface properties, Methodology

ABSTRACT

Wood, a renewable resource used for many applications, needs to be preserved against biological degradation when its natural durability can not provide sufficient protection for an expected service-life in a use-class.
Amongst natural compounds, polyflavonoids (condensed tannins) are used by plants as defense against biological attack by insects, fungi and bacteria [1]. Tannins can be easily complexed to create networks fixing other molecules acting as active ingredients. These associations have already been experienced to protect wood [2, 3].

In this study, the concept is to complex boron (in the form of boric acid) with tannins and to waterproof this association by using a hardener (such as hexamine). Tannins and hexamine are already used as zero formaldehyde emission adhesives [4]. This system would allow to fix boron at much lower levels than those authorize by the EC directive 2008/58/EC in order to carry on using this biocide with many advantages [5].

Many combinations of tannins (different origins, quantities), boric acid, hexamine and other additives (phosphoric compounds, …) have been considered and used to treat Scot pine sapwood and beech. The treated wood samples, onced dried at 103°C, were conditioned prior to leaching (EN 1250-1 or 5 days leaching). The leaching waters were analysed for their boron content showing interesting boron retention.

The wood blocks were tested for resistance towards Basidiomycete fungi (brown and white rots, temperate and tropical strains, according to the guidelines of EN113), as well as termites (according to EN117) [6, 7]. Except for a few mixes, the treated and laeched wood blocks were protected against decay. The results of termite tests also showed a good protection compared to the controls. The results of the most interesting formulations will be presented with emphazise on the problems encountered when testing timber protected with a "non conventional" product/process.

The treated wood also presented different surface properties, and interesting behaviour in terms of fire resistance [8]

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Factors influencing mould growth and modeling of aesthetic service life

Lone Ross Gobakken[1] and Olav A. Høibø[2]

[1]Norwegian Forest and Landscape Institute, 1431 Ås, Norway

lone.ross.gobakken@skogoglandskap.no

[2]Norwegian University of Life Sciences, Department of Ecology and
Natural Resource Management, P.O.Box 5003, 1432 Ås, Norway

olav.hoibo@umb.no

Key words: aesthetic service life, blue stain fungi, coating, mould, wood substrate, wooden cladding

ABSTRACT

The aesthetic service life of outdoor exposed wooden surfaces are often decided by growth of moulds and blue stain fungi, but also other visual changes caused by weathering such as colour changes, abrasion or wear, blistering, flaking, and even cracks in the wood or coating will contribute. When developing models that describe changes in the wood material and aim to predict the service life, it is essential to understand the impact of different climatic factors, the effect of variation in the wooden product itself and in the quality of craftsmanship and building design.

The objective of this presentation is to gather knowledge about which factors influence surface mould growth on wood substrates in an outdoor environment. The analysis and the model development are based on data from evaluation of mould growth coverage on outdoors exposed wood panels consisting of different combinations of wood substrates and surface finishes from a number of field studies performed over the last years [1, 2, 3, 4, 5, 6 and 7].

Modelling aesthetic service life and mould growth

Predicting performance may encompasses multiple goals, including both development of a better understanding of the mould growth processes and the measurements, as well as having a model development and evaluation process for on-going monitoring of surface mould growth and possible other characteristics. An ordinal measuring system for human evaluators has been the traditional method of visual rating of mould and blue stain on wooden substrates [8 and 9]. The rating is based on an increase in percentage or numbers of mould colonies and also takes into account the mould growth pattern. Several modelling approaches have been used to localise the contributing factors, for describing the variation in mould rating and to predict aesthetic service life in our field studies. In situations with an underlying continuous variable of interest, common models used for characterizing the observed ordinal data are cumulative logit models, also known as a proportional odds logistic regression models. Using a proportional odds model the probability of low mould growth ratings versus high mould growth ratings was modelled as a function of the fixed effects wood substrate, coating and exposure time, and a random effect due to repeated measurements. This model was also used to extrapolate average performance at 6, 8, 10, and 12 years of exposure. Also ordinal logistic regression was used for model fitting where, in a first step, mould rating was a function of exposure time and coating typology, in a second step the function was expanded with wood substrate as explanatory variable, and in a third and final step the function consisted of the effects wood substrate, coating typology, exposure time, relative humidity and temperature.

Surface finishing and exposure time

The factors surface finishing (i.e. coating typology or coated/uncoated) and exposure time were shown to have a highly significant effect on mould growth. Furthermore, wood substrate, temperature and relative humidity also affected the mould growth significantly, but comparatively less than surface finishing and exposure time. The physical surface structure of the paint film also affected the mould growth. A hard model paint was significantly more susceptible to mould growth than the other model paints. A soft model paint performed best, with the least mould growth coverage.

Assuming favourable growth conditions, surface moulds assessed using a fixed rating scale will, as a function of time, adapt a sigmoid curve. The shapes of the curve and slope coefficient that describe the degree of mould growth were found to be strongly dependent on exposure time. Figure 1 shows a predicted and extrapolated mould growth curve for Scots pine sapwood in combinations with two different paint systems. Similar growth curves were also found for combinations of wood substrates and coatings in other studies [3 and 4].

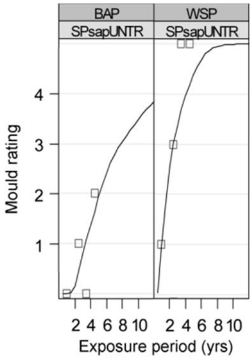

Figure 1. Predicted and extrapolated mould ratings (solid line) versus observed mould ratings (squares) for untreated Scots pine sapwood coated with two different paint systems [2].

Wood substrate and wood properties

Wood substrate had a significant influence on mould growth, but comparatively less than coating typology and exposure time. As an example Siberian larch heartwood, copper-organic preserved Scots pine and Scots pine heartwood was less susceptible to mould among a variety of wood substrates. Heartwood as wood type was less susceptible to mould growth than a mix of sapwood and heartwood wood and pure sapwood. Acetylated Scots pine wood and Aspen wood had lower resistance to mould growth than the other wood substrates. In a study performed on coated spruce claddings, outer boards had higher mould ratings than inner boards (boards close to the pit). On the other hand, neither origin, annual ring with, density nor knot properties were found to have any significant effect on mould growth.

Relative humidity, temperature and cardinal direction

Effects of relative humidity, precipitation and temperature, based on several combinations of threshold values, were tested in initial models to try to capture the effects of the local climate. A specific set of threshold values for relative humidity and temperature were found significant and kept in a final model. Simulations performed to predict mould rating over a wide range in relative humidity and temperatures, indicated, as expected, that a general increase in relative humidity, but also in temperature will give more mould growth on coated and uncoated spruce. This indicate that a climate change to a more humid, but also to a warmer climate may induce an increase in surface mould growth on painted and unpainted wooden claddings. Cardinal direction also affected the mould growth. Claddings exposed towards north had a tendency to have more mould growth than claddings exposed towards south.

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The effects of HALS compounds in the prevention of photo-degradation of acrylic clearcoats and wooden surfaces

Boris Forsthuber[*], Gerhard Grüll[#]

Holzforschung Austria, Franz Grill-Straße 7, 1030 Wien

[*]b.forsthuber@holzforschung.at, [#]g.gruell@holzforschung.at

Key words: HALS, Acrylates, Meth(acrylates), Photo-degradation, Wood coatings, Clearcoatings, Coating stabilization, ATR-FTIR Spectroscopy

ABSTRACT

A study of the photocatalytic degradation of an acrylic dispersion based coating and its prevention using two hindered amine light stabilizers (HALS) was carried out on solid films by exposing them to Xenon arc light. The degradation rates were compared using ATR-FTIR techniques by plotting the differential build up of the hydroxyl and hydroperoxide bands as function of exposure time. UV-Vis spectroscopic studies were carried out as well to obtain data about the light stabilization of organic UV Absorbers and inorganic UV screeners by HALS. The effectiveness of an aqueous primer comprising a specific lignin stabilizing HALS in combination with clear topcoats with UV Absorber or UV screeners in the prevention of photo-induced discolouration of wooden surfaces was investigated by measuring the colour change during exposure time

The comparison of the efficiency of different organic UV Absorbers (BTZ: UV Absorber of the Hydroxybenzontriazole-class, HPT: UV Absorber of the Hydroxyphenyltriazine-class) and inorganic UV screeners (micronized rutile TiO_2, micronized ZnO) in a transparent topcoat during exposure to Xenon arc light on the colour stabilization of wood showed that TiO_2 leads to the least discolouration of the wooden substrate. However, TiO_2 leads to a slight discolouration of the coating film itself. Therefore, the coated wood panels had a hazy appearance and this may be distracting on dark wood species, like oak. HPT in clear topcoats also showed a good colour stabilization of the wooden substrate during exposure to light but had a slightly yellow colour. BTZ showed also good colour stabilization behaviour. Additionally, BTZ is nearly colourless within the clear coats. BTZ seems to have lower photo stability than HPT as UV-Vis spectroscopic measurements during light exposure suggested. ZnO showed also a nearly transparent appearance, but the colour stabilization of the wooden surface was the lowest of all examined UV Absorber and UV screeners.

The combination of two UV Absorbers with HALS showed promising results. The usage of HALS lead to an inhibition of the photo-oxidation of the UV Absorber and the coatings retained their UV absorbance. BTZ was stabilized very well especially in combination with the HALS 1, whereas HPT showed in combination with the non-basic HALS 2 a better behaviour. The stabilization of the polymeric binder was more effective with HALS 1 in combination with BTZ, whereas HPT showed a much better stabilization in combination with HALS 2 according to ATR-FTIR measurements.

The combination of UV screeners with HALS showed different results. Firstly, inorganic UV screeners were not degraded by light. Therefore, no HALS was necessary to inhibit their photo-oxidation. However, due to the photo catalytic effect, the polymeric binder undergoes a much faster degradation process than with UV Absorber, as comparative ATR-FTIR measurement suggested. The results showed, that with ZnO, the non-basic HALS 2 gives the best inhibition of

the photo-degradation of the polymeric binder, while for TiO_2, further conclusions where difficult to make, because the linear fit did not cross the origin. The analysis of the degradation mechanisms depending on the UV Absorber/UV screeners and HALS showed that HALS does not change the degradation mechanism in principle but an inhibition of photoinduced side chain scission was observed. The formation rate of unsaturated compounds was not changed significantly, suggesting, that the rate of main chain scission was nearly even. By the incorporation of lignin stabilizing monomeric HALS into an aqueous primer and using topcoats with UV Absorber/UV screeners (BTZ, HPT or TiO_2), the discolouration of the wooden substrate was strongly reduced, as shown in figure 1. The combination with a ZnO comprising topcoat showed a strong antagonistic effect. All colorimetric values were increased compared to the ZnO containing topcoat without primer.

It was possible to show that a careful selection of light stabilizers, such as TiO_2 or UV Absorber in combination with HALS in the topcoat, as well as a lignin stabilizer in an aqueous primer can significantly improve the colour retention of wood.

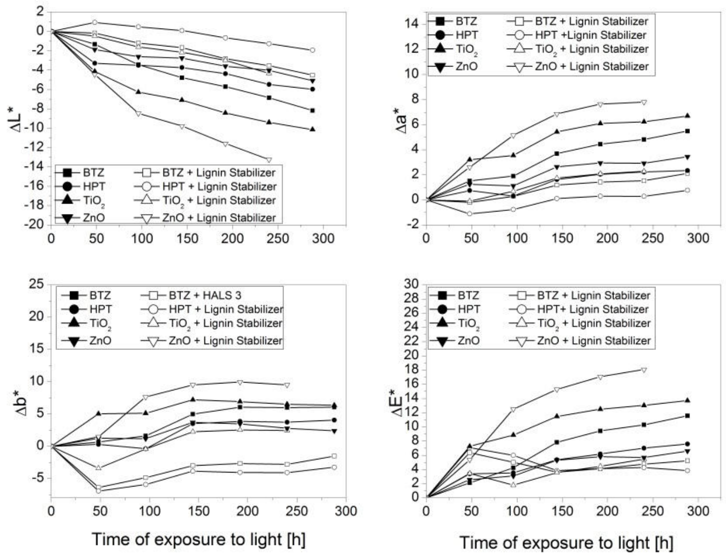

Figure 1: The effect of a lignin stabilizer in an aqueous primer, topcoated with UV Absorber and UV screeners containing clear coats on the colour change of wooden surfaces

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Multi sensor approach for monitoring of the changes to wood surface exposed to natural and artificial weathering

Jakub Sandak[1*], Anna Sandak[1], Dusan Pauliny[1], Sandro Bonfa[2#], Simone Meglioli[2]

[1]Trees and Timber Institute IVALSA/CNR, via Biasi 75, 38010 San Michele, ITALY

[*]sandak@ivalsa.cnr.it

[2]Cormo Società Cooperativa, Via Magnanini, 40, 42018 San Martino in Rio, ITALY

[#]s.bonfa@cormo.com

Key words: wood weathering, infrared spectroscopy, surface characterization

ABSTRACT

The goal of this work was to attempt understanding and modeling the combined effect of time, geographical location, exposition, and coating type on the physical-chemical mechanisms for wood surface weathering. The series of wooden samples non coated and coated with top industrial coating has been exposed to natural weathering conditions in seven locations varying in climatic conditions, including whole Italy and southern part of Germany. The set of samples has been exposed for four years, collecting representative sample each year. Four exposition directions (North, South, East and West) were investigated. All the samples have been collected from the field site and stored in a dark and conditioned room including non weathered reference samples.

A separate set of corresponding samples has been also used for artificial weathering on three different instruments, including standard EN927-6 (2006), UNI EN ISO 11507 (2002) and custom “time machine” developed in CORMO S.C.

All the measurements have been conducted after four years of project and included:

- Near infrared spectroscopy scanning of surface
- Mid infrared non-contact spectroscopy scanning of surface
- UV-VIS spectroscopy scanning of surface
- Color measurements
- 3D gloss measurements
- 3D surface roughness measurements
- X-Ray Fluorescence spectroscopy
- Photogrametry

Such a wide set of information collected has been used for investigation of the collective effect of the above mentioned variables on the surface properties and its appearance. Some of the example results are presented in Figure 1.

By near infrared spectra analysis it is possible to refer the artificial weathering methods to naturally weathered surfaces. Figure 2 presents a cluster analysis of the spectra. It is clear that the surface degradation by means of custom “time machine” has nearly not degraded the surface samples. Weathering according to EN927-6 corresponds to chemical changes of surfaces exposed to ~two years of exposition in to south direction in Italian Reggio Emiglia. The most degrading artificial weathering method was according to UNI EN ISO 11507 where the NIR spectra corresponded to that of 3 to 4 years of natural weathering.

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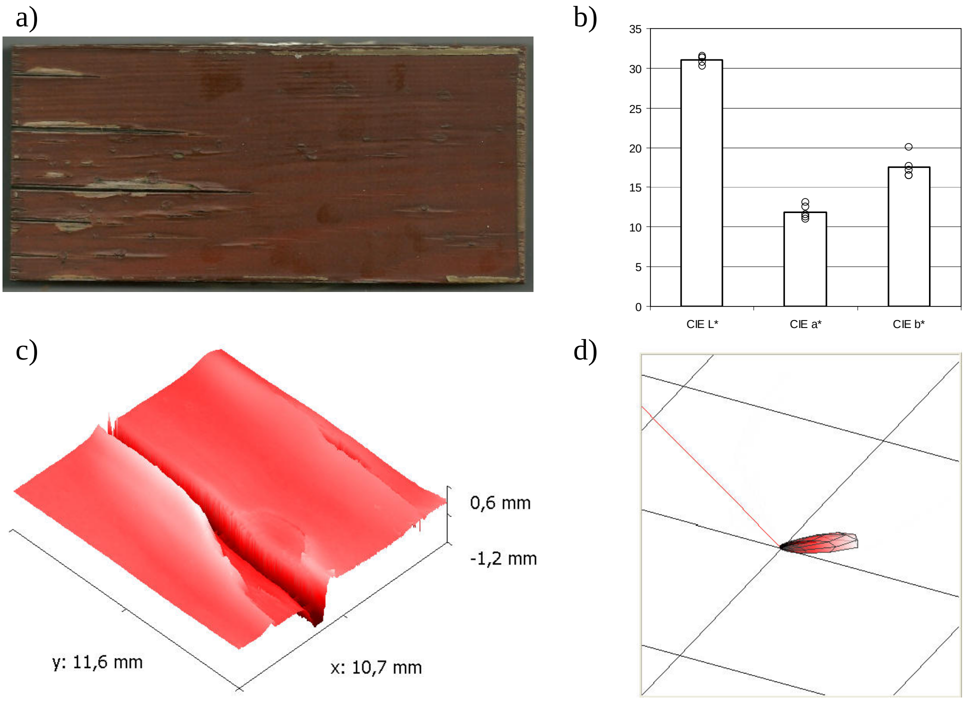

Figure 1: Example of the results obtained when measuring naturally and artificially weathered samples; color image (a), CIELAB color coordinates (b), 3D roughness map (c), 3D gloss map (d)

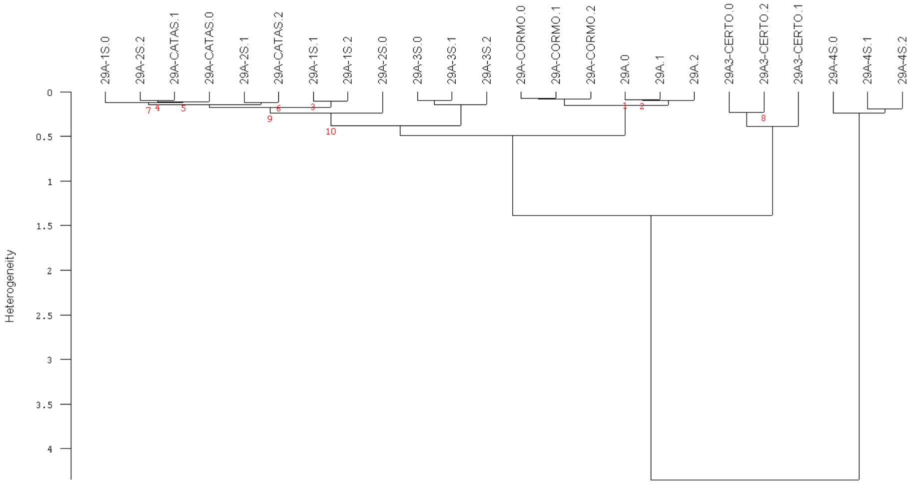

Figure 2: Cluster analyses of NIR spectra scanned from surfaces weathered naturally (Regio Emiglia, Italy, south exposition) and three artificial methods

WoodExter- Service life and performance of exterior wood above ground

Jöran Jermer[1], Dennis Jones[2]

[1]Editor of WoodExter project, SP Trä, Box 5609, 114 86 Stokholm, Sweden

joran.jermer@sp.se

[2]SP Trä, Drottning Kristinas Väg 67, 114 86 Stockholm Sweden

dennis.Jones@sp.se

Key words: Surface coatings, service life prediction, Use Class 3

ABSTRACT

WoodExter was a multi-national project funded under the Wood Wisdom programme. Its aim was to take the first steps towards introducing performance-based engineering design for wood-based building components in outdoor, above-ground end uses. The project included 10 research institutes – SP (SE), LTH (SE), VTT (FI), FCBA (FR), HFA (AT), TUW (AT), BRE (UK), Univ. Gent (BE), Norwegian Forest & Landscape Inst (NO) and Univ. Göttingen (DE) and 8 industrial partners from 8 European countries. The pan-European appraoch was necessary to gain as thorough an assessment method for wood in service as possible.

The project successfully delivered against its original objectives, and this paper will describe the work undertaken in:

- Providing the first European technical guideline and practical tool for engineers and architects for design of wooden constructions with respect to durability and service life.
- Generating new, important, knowledge generated, in particular concerning :
    - exposure conditions and risk of decay
    - effect of decay on micromechanical properties of wood
    - performance of different coating systems on different wood substrates and in particular chemically modified wood
    - the use and development of a novel technology, quantitative real-time PCR (Polymerase Chain Reaction), qPCR, as a tool for identification and quantification of early decay in wood as well as for studies of colonization pattern of decay fungi in different wood materials
    - mode of action of modified wood against decay fungi
    - evaluation of field trials and the possibilities to predict the expected average service life based on early results from inspections.

Further development of the technique is needed, however.

- The development of standardised evaluation criteria for systematic performance assessment of cladding and decking and the extensive database established following the inspection of over 100 buildings carried out by partners. The database will serve as input for testing the model and engineering tool.
- Contributing to kick starting CEN/TC38 WG 28 Performance Classification.

The work undertaken by project staff and students will be beneficial for future research in the areas of wood durability, wood protection and service life prediction to support the European Research Area and the wood industry sector.

As to future activities the following can be foreseen:

- The Guidance document and related software will now be tested in practice on a national level. There are plans for capturing feedback in order to further improve the technique, e.g. by professionals or in future research projects.
- Work on early indicators for decay from various test procedures will continue to give useful input to standardization work within CEN/TC 38 WG 28 and accommodate requirements for performance data expressed in the CPD.
- The standardised evaluation criteria for systematic performance assessments of cladding and decking will be further used and tested in practice and improved.
- A number of field tests started within the WoodExter project will continue and generate important data for future assessment and evaluation and input to CEN/TC 38 and CEN/TC 139.
- Research work on micromechanical techniques will continue within the framework of other projects. Together with local chemical and physical properties, the micromechanical model can help to enhance the current understanding of effects of fungal decay on the microstructure of wood.
- Research on decay mechanisms linked to climate change and service life will continue in ongoing and new projects. A more global approach is needed to consider the full range of deterioration resistance causing factors of wood. In such a global approach, one needs to compare exposure-dependent decay patterns and durability mechanisms for different wood species and wood-based materials.

Acknowledgement: Funding for all the partners from the Wood Wisdom network is hereby acknowledged, as well as the support from the eight industrial partners.

Evaluation of the weathering behaviors of natural and synthetic protective coatings for wood

Carmen-Mihaela Popescu[1,2*], **Bogdan C. Simionescu**[1,2#]

[1]Gheorghe Asachi Technical University of Iasi, Romania

[2]Petru Poni Institute of Macromolecular Chemistry of Romanian Academy, Iasi, Romania

[*]mihapop@icmpp.ro, [#]bcsimion@icmpp.ro

Key words: lime wood, dammar resin, poly(hydroxy urethane acrylate), photodegradation, FT-IR spectroscopy, 2D IR correlation spectroscopy, thermogravimetry

ABSTRACT

A series of experiments were carried out to investigate photodegradation of *Tilia cordata* wood coated with natural (dammar) and synthetic [poly(hydroxy urethane acrylate)] protective resin during artificial UV/Vis light irradiation at a temperature of 40 ^{o}C and 65% relative humidity, for 600 hours. Photodegradation of the treated lime wood samples was evaluated by FT-IR, 2D IR correlation spectroscopy and thermogravimetry.

Due to the presence of chromophores wood is a good light absorber. The change of wood colour is mainly due to the UV light, which acts in combination with moisture, temperature, and oxidative agents and depolymerise the main components from the wood cell wall. To limit photodegradation of wood, attempts have been made with traditional protective materials employed in the past (natural resins and waxes), which have been replaced by synthetic ones.

The relative intensity of the characteristic aromatic lignin band at 1505 cm^{-1} decreased by 28% of its original value after weathering during 600h for the wood coated with poly(hydroxy urethane acrylate) resin and by 49% of its original value after weathering during 600h for the wood coated with dammar resin, both values lower than the value obtained for uncoated wood (52%).

The results obtained indicate a shifting of the DTG maxima to higher temperatures for treated wood with dammar resin which may be related to a crosslinking of the resin. In the same time, it was observed a slow shift to lower temperatures for treated wood with the synthetic resin, indicating a decrease in the stability of the polymer and wood during photodegradation.

The decrease of the weight loss with increasing time of exposure was observed, while the global kinetic parameters for the main peak decrease when increasing exposure time of the wood to the UV light.

All results indicate that poly(hydroxy urethane acrylate) coating film provides a higher protection of wood against photodegradation as compared to the natural resin coating film.

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Review upon the colour stability of black alder veneers under sunlight influence

Emilia-Adela Salca*, **Gavril Budau**#

Faculty of Wood Engineering, “Transilvania” University of Brasov, Bd. Eroilor Nr.29, Brasov – 500036, Romania

*emilia.salca@unitbv.ro

#g.budau@unitbv.ro

Key words: colour, black alder, cherry, veneers

ABSTRACT

The wood of black alder, considered just a secondary resource, was less studied and somehow ignored within the wood processing industry in Romania. During last few years, some authors approached alder topics, both from the perspective of its workability and from the colorimetric point of view, through the identification of colour changes occurred when solid wood is exposed indoor to artificial light (Temiz, 2005; Oltean, 2007) or when alder veneers are exposed to natural sunlight (Aydin, 2005; Salca, 2008).

The objective of the present research work resided in establishing the natural light influence upon the colour changes of black alder (Alnus glutinosa) veneers after sunlight and darkness exposure, for 1 and 3 months, under indoor conditions.

The experimental approach was carried out in two distinct situations:

1. when using two wood species, but having similar appearance, namely black alder (*Alnus glutinosa*) and cherry (*Prunus avium*). The veneers were cut from logs after performing their thermal treatment at the temperature of 60-70ºC for 10-12 hours. Alder veneers were cut by half-round slicing method and cherry veneers were cut by flat slicing method. The veneer sheets were dried at temperatures of 90-100 ºC.
2. when using freshly cut veneers made of black alder (*Alnus glutinosa*) log (70% moisture content). The log was peeled and cut in flitch and veneers were cut by slicing, without any thermal treatment, on the vertical slicing machine. Veneers were dried by respecting three drying stages (90ºC, 90ºC, 100ºC).

The dimensions of veneer samples were: 250mm x 150mm x 0.5mm. For each case, 10 veneer samples were used, out of which 5 samples were exposed to sunlight under indoor conditions and other 5 samples were exposed to absolute darkness. The sunlight exposure followed the south direction and it was achieved by means of an experimental stand, positioned behind a window glass of 4mm thickness and for keeping the absolute darkness conditions, veneers were kept within a totally free-light space.

The exposure conditions were daily recorded during the exposure period of 1 and 3 months respectively.

All colour measurements were performed at LOSAN Company from Braşov, according to ISO 7724-2 standard, with a Chroma Meter Konika Minolta CR-410 device. 5 colour measurements were made on distinct circular areas of 50mm diameter, for each veneer sample.

*L**, *a** and *b** colour coordinates were determined before and after the sunlight and darkness exposure, under indoor conditions, for 1 and 3 months, on the same circular areas.

The relation between the total colour differences and the four independent variables (*wood species, log treatment, exposure conditions and period of exposure*) involved within this study supported a factorial variance analysis. The results highlighted a global significant effect which came from the main effect of each one of the factors.

Figure 1: Chroma Meter Konika Minolta CR-410.

When compared the results achieved for veneers obtained from thermally treated logs (black alder and cherry) and for black alder veneers (freshly cut and from thermally treated log), after their exposure to sunlight and darkness influence, the following conclusions are to be noticed:

a. The sunlight mostly influenced the colour changes, in the case of cherry veneer especially, which recorded significant colour differences of about 10.87 just right after the first month of exposure, while for alder veneers, the maximum colour difference of about 8.67, hardly appeared after 3 months of sunlight exposure.
b. The maximum colour differences, both after the first month of sunlight exposure and after 3 months as well, were recorded for black alder veneers obtained from non-treated log, the value of ΔE^* being of about 15.29 units, higher than the maximum one established for black alder veneers obtained from thermally treated log, for the same exposure period.
c. After darkness exposure, for both experiments, the same relative constant colour tendency was noticed, a light decrease of lightness and a slow increase of a^* and b^* colour coordinates, which produced relative similar colour differences under exposure.

The study results complete the colorimetric database regarding veneers used in furniture industry, but contribute to the rehabilitation of black alder as wood species with a real potential of use in furniture industry in Romania.

Acknowledgement: We acknowledge the Losan Company from Brasov for the involvement and support offered during the experiments.

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The study of structural changes of *Tilia cordata* wood induced by exposure to accelerated UV/Vis - light

Maria-Cristina Popescu*, Carmen-Mihaela Popescu#

“Petru Poni” Institute of Macromolecular Chemistry of Romanian Academy, Department of Physical Chemistry of Polymers

*cpopescu@icmpp.ro, #mihapop@icmpp.ro

Key words: lime wood, photodegradation, FT-IR spectroscopy, 2D IR correlation spectroscopy, thermogravimetry

ABSTRACT

In this study the weathering behavior of lime wood (*Tillia cordata* Mill.) has been examined using FT-IR, 2D IR correlation spectroscopy and thermogravimetry, which evidenced chemical changes induced by exposure to weathering conditions. It was shown that lignin is most sensitive component to the photodegradation processes as indicated by considerable decreases in the intensities of the characteristic aromatic lignin band at 1505 cm^{-1} and other associated bands.

By 2D correlation spectroscopy has been observed the moment of C=O from carboxyl and acetyl groups in hemicelluloses (xyloglucan) is changing first, followed by the C=C of aromatic skeletal (lignin), C=O in non-conjugated ketones, carboxyl groups and lactones, absorbed O–H and conjugated C–O in quinones.

The carbonyl formation corresponded well with lignin degradation, indicating a close relationship between them. Comparing the rate of carbonyl formation and lignin decay clearly showed that the former is remarkably higher than the latter, indicating the formation of carbonyl bands at 1738 cm^{-1} probably resulted from not only lignin oxidation but also from reactions occurring in other components of the wood. Quinine formation is combined with the decay of aromatic structures (loss of the skeletal vibration at 1505 and 1600 cm^{-1}) and the formation of conjugated carbonyl groups (increase of the carbonyl absorption at the 1738 cm^{-1}).

The alteration of wood was also observed by means of the peak temperatures of DTG variation and by the mass losses observed during heating, evaluated on the basis of the measured thermal data. Shifting of the shoulder temperature at 308 ^{o}C to lower values is due to formation of carbon radical, alkoxy radical, formyl radical structures after photodegradation, which make the hemicelluloses less stable. DTG peaks deconvolution allows making some correlations with lime wood components decomposition.

The lignin decomposition shows decreases of the temperature of exposed wood, meaning the formation of the phenolic radicals, which in turn transforms into *o*- and p-quinonoid structures. The third peak may be due to the loss of –OH groups of monomer units of cellulose and the break-down of the pyranosic rings; the temperature of this peak is shifted to lower values and the integral area of this peak decreases in the 0-200h period of exposure and then increases.

The global kinetic parameters for the main peak decrease with increasing exposure time of the wood to the UV light evidencing once more the formation of different structures due to photodegradation process.

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The use of the CIEDE 2000 colour difference equation for quality assessment of high quality hardwood

Markus Hauptmann*, Hedwig Hanea, Marcus Müller, Ulrich Müller, Christian Hansmann

Kompetenzzentrum Holz GmbH, Altenbergerstraße 69, A-4040 Linz

*m.hauptmann@kplus-wood.at

Key words: colour difference, CIELAB, CIEDE2000

ABSTRACT

An important quality criterion for interior wood surfaces is defined by its color. This requires a correct measurement method to compare color differences (ΔE) on wood. An often used method to measure color is the CIELAB system. In this three dimensional geometric room every specific color is defined and can be described as a vector. The calculation of the difference between two vectors is therefore trivial to calculate. This system is described and recommended in the DIN 6174 [1] standard.

As our human color perception is not strictly geometrical and various color differences are perceived in certains areas more or less, the CIE has found it necessary to solve the problem by using mathematical correction of the color formula. In the year 2001 the CIE published a new method to calculate color difference which has not yet been documented in a standard. The new equation is called CIEDE2000 [2].

$$\Delta E = \sqrt{\left(\frac{\Delta L'}{k_L S_L}\right)^2 + \left(\frac{\Delta C'}{k_C S_C}\right)^2 + \left(\frac{\Delta H'}{k_H S_H}\right)^2 + R_T \left(\frac{\Delta C'}{k_C S_C}\right)\left(\frac{\Delta H'}{k_H S_H}\right)}$$

The equation was derived from several datasets. Each dataset was comprised of visual judgment of simple patches. It was proven that between simple patches the CIEDE2000 equation is able to accuratly predict the perceived color difference [3, 4]. So the formula currently known as best suited for visual perception is the CIEDE2000 [4].

This study examines the correlation between human perception and the colorimetric distance of selected hardwood surfaces. Bleached oak wood as well as walnut wood were sorted by color quality standards into three classes. Theoretically, the average color difference of class 3 (worst) to class 1 (best) should be higher than the color difference of Class 2 (medium) to Class 1. To analyse that, the color of all wood samples were measured and the quality classes were correlated with the color-difference formulas CIELAB and CIEDE2000. It should now be compared if a general difference in perception exists between color differences on bright and darker wood samples. On that basis it should be investigated which of those two color difference equations showed the perceived color difference more precisely.

It was found that the CIEDE2000 equation correlates more strongly on bright surfaces with the sorting into quality classes, compared to the CIELAB equation. Since the CIEDE2000 formula affects the ΔE in the gray and colorless areas of the color scale significantly stronger, the ΔE of bright wood samples correlates much stronger with the human color perception. It is identifiable that the CIELAB equation results in an overestimation of the color difference ΔE data. The CIEDE2000 equation optimized specific areas of the L-axis and the h-axis of the color space,

since the human perception underestimates color differences in bright colorless areas. In broad terms, differences in color on a bright wood sample are better represented by the CIEDE2000 equation. Conversely, it can be established, that dark colorfull wood surfaces can also be represented by the trivial color difference equation CIELAB.

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Bringing new functions to wood
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