„Plasma Coating for Wood“ – PlaCoW”

Project Summary

Project content and main project data

Title: „Plasma based surface modifications of wood and wood polymer composites (WPC) materials and the application of electromagnetic fields for wood and WPC treatment”

Short title: „Plasma Coating for Wood“ – PlaCoW”

Duration: 01.01.2015 – 31.12.2017 (31.12.2018 for the Russian partners)

Partners: Tigres GmbH (Germany), IHD Institut für Holztechnologie Dresden gemeinnützige GmbH (Germany), INNOVENT e.V. (Germany), LLC “Tarnaya Baza” (Russia), LLC “Vakta” (Russia), Tomsk State University of Architecture and Building (Russia)

Project summary: Wood has a significant share of world market of materials used for external and internal finishing. Discoloration, cracking and low fire-resistance properties of wood requires additional expensive and time-consuming treatment processes. Novel coating methods would increase resource efficiency, improve product attributes and open new markets. Consortium of six partners, including SMEs and research organizations, proposes this project which is dedicated to improve significantly existing coating methods such as atmospheric pressure based plasma techniques, low-temperature plasma and electromagnetic field techniques. Research activities were focused on the comparison of different coating methods and of corresponding resulting surface properties of different types of wood. The main marketable results imply new wood surface modification methods and wooden products with protective hydrophobic bactericidal and fungicidal coatings, improved properties, and weather protection.

Funding agencies: The project was supported by the German AiF and the Russian FASIE within the 14th call of the EraSME network.

Technologies

Atmospheric pressure plasma jets (APPJ) as a chemical vapour deposition technique can be used for the preparation of thin functional coatings. Within this joint project the dry APPJ technology was developed further to create composite thin films based on silicon oxide as well as thin films based on titanium oxide. In case of the composite films certain functional agents were embedded into the growing SiOx film matrix. All the functional films could be applied successfully on certain kind of wood, on veneer as well as on WPC (wood polymer composites) materials. The deposition process itself will be realised by feeding (meandering) the plasma jet over the substrate area. The used gaseous chemical precursor reacts in the plasma plume and creates on the substrate surface a thin film. As plasma devices different systems can be used for coating purposes: the MEF and CAT technologies by Tigres, the OpenAir technique by Plasmatreat or the Inocon plasma technique .

It was shown that besides the APPJ method the combustion CVD (CCVD) technique can be used for creating thin films on the mentioned wooden based materials, too.

Sol-gel technology is a wet-chemical based method to create thin films. Functional silicon oxide based thin films were deposited onto different wooden based materials (certain kind of wood, WPC). The deposition process itself can be realised by dipping or spraying the sol onto the material´s surface.

Most of wooden materials show certain functional properties like improved weathering resistance or flame retardance by applying defined impregnation techniques. The main advantage of both APPJ and sol-gel techniques is to place the functional agents only on the substrate´s surfaces and following to reduce significantly the amount of agents necessary for the wanted application. The film thickness in the case of APPJ-produced films is in the range of up to about 200 nm only, in case of sol-gel based films the thickness can reach even 1 µm. Especially with view on the WPC material for the first time a coating method was developed to create a functional surface.

- APPJ: Useful for smaller surface areas as well as for more complex 3D geometries
- CCVD: Useful for smaller and bigger surface areas. The temperature impact has to be considered.
- Sol-gel: Useful especially for bigger areal surfaces

Main surface properties of modified wood and WPC

Antimicrobial properties were obtained for APPJ as well as for sol-gel based films on wood and on WPC surfaces. As active agents salt solutions can be used based on silver, copper and zinc. Furthermore, antimicrobial properties were achieved by using quaternary ammonium salts. Most of investigations were realised by using *Escherichia coli* as a test germ and applying the BTG test assay, additionally CFU tests were performed.

Fungicide properties were obtained for APPJ as well as for sol-gel based films on wood and WPC surfaces. It is important to mention that good fungicide properties were achieved only in the case of using a combination of active agents (silver, copper and zinc). The mould test is based on standard EN 60068-2-10. As the mould strains Aspergillus niger DSM 1957, Paecilomyces variotii DSM 1961, Penicillium funiculosum DSM 1944 and Trichoderma viride DSM 1963 were used.

Abrasion stability especially of the antimicrobial coatings on WPC was determined in accordance with the standard ASTM D4213 (1992) and ASTM D428-94 (2012). The APPJ as well as sol-gel coated WPC surfaces were stressed by 10, 100, 1000 and 10,000 of such washing cycles, and to evaluate the abrasive damage, the samples were characterized with SEM and the antibacterial effect with BTG assay.

Surface wettability: In dependence on the used precursor materials especially the APPJ technique is useful to prepare thin films with either hydrophilic or hydrophobic surface character on wooden materials. Hydrophilic films are useful in combination with subsequently following lacquering or gluing techniques. Hydrophobic coatings are useful in cases when a water wettability is undesirable. The water absorption properties of different APPJ and sol-gel films on spruce and pine were measured according to the corresponding national standards. Here, the sol-gel system protects the surface best comparing to APPJ coatings.

Natural weathering of test samples

Dynamic contact angle measurements showed the influence of a plasma treatment on the wettability, too. It has been shown that especially the treatment with the Tigres MEF plasma source can decrease the surface contact angle on beech and on larch (resinous wood!) significantly even over a storage duration of up to 24 days.

Adhesion promotion for a subsequently following lacquering can be obtained by using a combination of plasma coating and primering. These results were verified for douglas, pine and larch substrates. The samples were characterised by cross cut tests according to DIN EN ISO 2409:2013. Especially for moisture stressed samples a significant adhesion promotion of the lacquer was achieved.

The resistance to artificial weathering (EN 927-6:2006) of plasma-pre-coated and subsequently lacquered wood samples in comparison to conventionally lacquered samples was investigated for douglas, pine and larch substrates in context with corresponding cross cut tests. It has been found that plasma-pretreated samples showed a significantly better lacquer adhesion after twelve weeks weathering whereby the degrees of gloss as well as colour change of altered samples differed only marginally compared to “classically” painted (and plasma-untreated) samples.

The resistance to natural weathering (EN 927-3:2012) in comparison to conventional coatings was investigated, too. As in the case of artificially weathered samples the degrees of gloss as well as colour change of altered samples differed only marginally compared to “classically” painted (and plasma-untreated) samples. Furthermore, for SiOx films doped with a combination of copper, silver and zinc oxide agents and prepared by APPJ technique with a following lacquering it could be shown that they are just so effective as samples with conventionally anti-bluestain agents and following lacquering.

Overview

Based on the obtained results the following coating matrix was established:

wood (beech, larch, douglas, pine, pine sapwood)

"Dry" coating methods	APPJ (500 W Tigres)							APPJ (CAT600)		CCVD		
	SiO2	SiO2/Ag	SiO2/Cu	SiO2/Zn	SiO2/O	SiO2/Q	SiO2/Ag/Cu/Zn	SiO2/Ag	TiO2	SiO2/Ag	SiO2/Cu	SiO2/Zn
antimicrobial properties	↓↓↓	↑↑↑	↑↑↑	↑↑	↑↑	↑↑	↑↑↑	↑↑↑	N/A	N/A	N/A	N/A
fungicide properties	↓↓↓	↓↓	↓	↓↓↓	N/A	N/A	↑	N/A	N/A	N/A	N/A	N/A
algicide properties	N/A	N/A	↓↓↓	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
anti-blueing effects (agar diffusion)	N/A	N/A	N/A	N/A	N/A	N/A	↑↑	N/A	N/A	N/A	N/A	N/A
anti-blueing effects outdoor-weathering (+ barrier	↑	N/A	N/A	N/A	N/A	N/A	↑↑↑	N/A	N/A	N/A	N/A	N/A
photocatalytic effect	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Coating efficiency	↓	↓	↓	↓	↓	↓	↓	↑	N/A	N/A	N/A	N/A
wear resistance, abrasion stability	↑↑	↑↑	↑↑	↑↑	N/A	N/A	↑↑	N/A	N/A	N/A	N/A	N/A
lacquer adhesion	↑↑ (+ Primer)	N/A	N/A	N/A	N/A	N/A	↑↑ (+ Primer)	N/A	N/A	N/A	N/A	N/A

"Wet" coating methods	sol-gel								
	SiO2/Ag	SiO2/Cu	SiO2/Zn	SiO2/O	SiO2/Q	SiO2/Ag/Cu/Zn	ZnO	TiO2	ZnO-Nanorods
antimicrobial properties	↑↑↑	↑↑↑	↑	↑↑↑	↑↑↑	↑↑↑	↑↑↑	↑	↑↑↑
fungicide properties	↑	↑↑↑	↓↓↓	↓	↓	↑↑↑	↑↑↑	N/A	N/A
algicide properties	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
anti-blueing effects (agar diffusion)	N/A	N/A	N/A	N/A	N/A	N/A	↑↑↑	N/A	N/A
anti-blueing effects outdoor-weathering (+ barrier	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
photocatalytic effect	N/A	N/A	N/A	N/A	N/A	N/A	(↑↑)	(↑↑)	(↑↑)
Coating efficiency	↑↑	↑↑	↑↑	↑↑	↑↑	↑↑	↑↑	↑↑	↑↑
wear resistance, abrasion stability	↑↑	↑↑	↑↑	N/A	N/A	↑↑	N/A	N/A	N/A
lacquer adhesion	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

used abbreviations:
SiOx silicon oxide
TiOx titanium oxide
Ag silver
Cu copper (oxide)
Zn zinc (oxide)
O Octenidin
Q 3(trimethylsilyl)propyldimethyl-octodecyl-ammonium chlorid
APPJ Atmospheric pressure plasma jet

WPC (wood polymer composites)

"Dry" coating methods	APPJ (500 W Tigres)							APPJ (CAT600)		CCVD		
	SiO2	SiO2/Ag	SiO2/Cu	SiO2/Zn	SiO2/O	SiO2/Q	SiO2/Ag/Cu/Zn	SiO2/Ag	TiO2	SiO2/Ag	SiO2/Cu	SiO2/Zn
antimicrobial properties	↓↓↓	↑↑↑	↑↑↑	↑↑	↑↑	↑↑	↑↑↑	↑↑↑	↑↑ (+ Ag)	↑↑	↑	↓↓
fungicide properties	↓↓↓	↓↓	↓	↓↓↓	N/A	N/A	↑↑	N/A	N/A	↓↓↓	↓↓↓	↓↓↓
algicide properties	N/A	N/A	↓↓↓	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
anti-blueing effects (agar diffusion)	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
anti-blueing effects outdoor-weathering (+ barrier	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
photocatalytic effect	↓↓↓	N/A	N/A	N/A	N/A	N/A	N/A	N/A	↑↑	N/A	N/A	N/A
Coating efficiency	↓	↓	↓	↓	↓	↓	↓	↑	↓↓	↑↑	↑↑	↑↑
wear resistance, abrasion stability	↑↑	↑↑	↑↑	↑↑	N/A	N/A	↑↑	↑↑	↓	N/A	N/A	N/A
lacquer adhesion	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

"Wet" coating methods	sol-gel								
	SiO2/Ag	SiO2/Cu	SiO2/Zn	SiO2/O	SiO2/Q	SiO2/Ag/Cu/Zn	ZnO	TiO2	ZnO-Nanorods
antimicrobial properties	↑↑↑	↑↑↑	↑	↑↑↑	↑↑↑	↑↑↑	↑↑↑	↑	↑↑↑
fungicide properties	↑	↑	↓↓↓	↓	↓	↑↑↑	↑↑↑	N/A	N/A
algicide properties	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
anti-blueing effects (agar diffusion)	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
anti-blueing effects outdoor-weathering (+ barrier	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
photocatalytic effect	N/A	N/A	N/A	N/A	N/A	N/A	↑↑	↑↑	↑↑
Coating efficiency	↑↑	↑↑	↑↑	↑↑	↑↑	↑↑	↑↑	↑↑	↑↑
wear resistance, abrasion stability	↑↑	↑↑	↑↑	N/A	N/A	↑↑	↑↑	N/A	N/A
lacquer adhesion	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A

used abbreviations:
SiOx silicon oxide
TiOx titanium oxide
Ag silver
Cu copper (oxide)
Zn zinc (oxide)
O Octenidin
Q 3(trimethylsilyl)propyldimethyl-octodecyl-ammonium chlorid
APPJ Atmospheric pressure plasma jet

Application potential, commercialisation

The results of this project obtained so far can be of interest in the following industries:

- Consumer goods (e.g. glasses frames, watches…)
- Healthcare marketplace and indoor use in public buildings (e.g. handrails…)
- Furniture marketplace
- Restoration field (e.g. photocatalytic behaviour, air purification, wood treatment)
- WPC for outdoor use
- Window production (e.g. Velux-Badfenster)

Fairs and important congresses

A. Pfuch, O. Beier S. Spange, S. Gerullis, C. Wiegand, K. Horn, G. G. Volokitin, B. Grünler, A. Schimanski; „Composite thin films made by atmospheric pressure plasma CVD for bactericidal applications“, 12th International Conference "Gas Discharge Plasmas and Their Applications" (GDP 2015), Tomsk, Russia, September 6–11, 2015, published in Izvestia Vyshich Uchebnych Zavedeniy. Fizika v58 (9/3) (2015) p. 32-35

S. Gerullis, A. Pfuch, P. Kosmachev, F. Kettner, K. Plaschkies, B. Gruenler; „Antimicrobial coatings and coatings with high water repellency on beech veneer made by APCVD”, Plasma Surface Engineering PSE 2016, Garmisch-Partenkirchen, 12.–16.09. 2016

S. Gerullis, „Möglichkeiten zur Funktionalisierung von Holzoberflächen mittels Atmospheric Pressure Plasma Chemical Vapour Deposition (APCVD)“, DFO - Tag der Holzbeschichtung, 11.04.2016, Bielefeld, Germany

Vakta: 05.-07.09. 2017, Participation in ExpoDrev Russia, XIX International Industry Specific Exhibition (Krasnoyarsk)

INNOVENT: 18.-21.09.2017, LESPROM URAL 2017, Yekaterinburg, Russia

S. Gerullis, A. Pfuch, P. Kosmachev, F. Kettner, K. Plaschkies, B. Grünler; „Möglichkeiten zur Modifikation/Beschichtung von Holzoberflächen mittels Atmospheric Pressure Plasma Jet (APPJ)“, 18. Fachtagung für Plasmatechnologie PT18, 20.-22-02-2017, Göttingen, Germany

S. Gerullis, O. Beier, A. Pfuch, B. Grünler; „Highly Active Photocatalytic Coatings for Temperature Sensitive Substrates based on Titanium Oxide and Zinc Oxide prepared by Atmospheric Pressure PECVD and Sol-Gel Deposition” NANOCON 2017 Conference Proceedings, 1st Edition 2018, TANGER Ltd., Ostrava, Czech Republic, ISBN 978-80-87294-81-9, p. 302 – 307

Publications

A. Pfuch; "Ganz plasmatisch", EYE-COM, issue 02/2016

S. Gerullis, A. Pfuch, S. Spange, F. Kettner, K. Plaschkies, P. Kosmachev, G. Volokitin, B. Grünler; „Antimikrobielle Beschichtungen auf Holz mittels Atmospheric Pressure Plasma Chemical Vapour Deposition“ Holztechnologie 5/2016, S. 16 – 25

S. Gerullis, A. Pfuch, S. Spange, F. Kettner, K. Plaschkies, B. Küzün, P. V. Kosmachev, G. G. Volokitin, B. Grünler; “Thin antimicrobial silver, copper or zinc containing SiOx films on wood polymer composites (WPC) applied by atmospheric pressure plasma chemical vapour deposition (APCVD) and sol-gel technology”, online abrufbar, European Journal of Wood and Wood Products, DOI 10.1007/s00107-017-1220-9

A. Pfuch, S. Gerullis, B. S. M. Kretzschmar, F. Kettner, B. Küzün, G. G. Volokitin, P. V. Kosmachev; „Atmosphärische Plasmavorbehandlungen im Bereich der Holzverarbeitung“ WOMAG 12/2017, S. 12