Plasma paints a brighter picture

Wood surface modification process enhances exterior durability

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Progress is reported on the development of an industrial fast plasma process which can modify the properties of wood, either improving the adhesion of waterborne coatings or making it more water-repellent without the use of coatings. Possible biocidal effects of the plasma process are also being examined.

Wooden surfaces need to be durable in order to be attractive to customers and compete with other materials. Biological, physical and chemical pretreatments are generally applied to wood to improve its resistance to the fungi that cause decay and staining, its dimensional stability and its slightly raised equilibrium moisture content in exterior exposure.
But these classical wood treatment techniques present many drawbacks, such as energy inefficiency and damage to the environment. In recent years, public concern about the environment has led to the creation of regulatory programmes to reduce air pollution. This has increased the pressure on wood manufacturers to reduce harmful emissions derived from both chemical treatments (Volatile Organic Compounds – VOC) and thermal treatments (CO_2).
European legislation (such as EC Directive 2004/42/EC) on coating products is driving a shift towards waterborne coatings. However, wooden surfaces treated with waterborne coatings are more susceptible to discolouration and damage by wood-destroying and blue stain fungi. This situation presents serious challenges to the European wood processing industry.

Table 1: FT-IR results identifying active changing bands on wood samples treated with DCSBD plasma in air and CO_2

Wavenumber [cm^{-1}]	Chemical bonds
1024	C–C and C–O stretching
1157	C–O–C asymmetric valence vibration
1263	Guayacil ring plus C=O stretch
1727	C=O valence vibration of acetyl- or COOH-groups

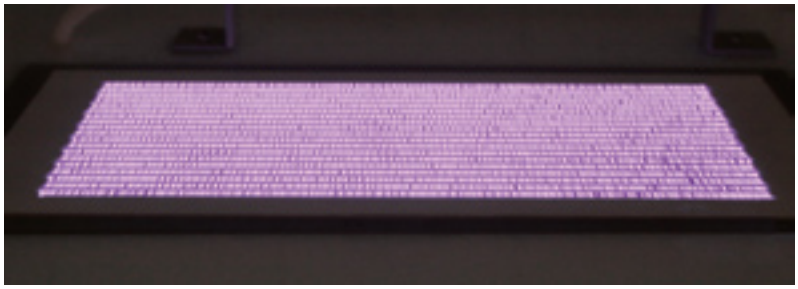

Figure 1: The ionised gases of a plasma (made visible in this picture) can modify readily wood surface porperties

Problems and benefits of plasma treatment on wood

Wettability is an important issue that determines a wood's adhesive and coating quality. Wood has a relatively polar surface that allows the general use of waterborne adhesives [1]; however, wood surfaces exposed to high temperature treatments are harder to wet [2].
Plasma treatment is a versatile and powerful technique commonly used to activate the surface of materials such as plastics, textiles, glass and metals. By producing high frequency electric discharges, plasma generates ionised gas (as shown, for example, in *Figure 1*) that can modify the surface properties of the material it is in contact with.
Plasma is used in many industries, typically to treat plastics. However, its use to treat wood thus far has been limited to academic research [3-6]. Although low-pressure plasma processes have been studied for this purpose [7, 8] atmospheric pressure processes are typically more attractive for wood industry applications because of their lower cost, higher throughput and ability to operate in-line without vacuum systems.
Atmospheric pressure plasma systems are typically based on a volume Dielectric Barrier Discharge (DBD) arrangement, where the treated material is placed between the discharge electrodes [3, 9, 12] or the material itself works as one electrode [4]. However, this arrangement is problematic for the treatment of thick and complex wood materials where the process is highly energy intensive (due to resistive power losses) and as a result a high voltage is needed, leading to safety concerns.
A more practical approach to solve the issue of power loss in the bulk of wood material, as pursued in the "Durawood" project, is to use a planar plasma electrode, such as the Diffuse Coplanar Surface Barrier Discharge (DCSBD) [10]. Due to the planar geometry of the discharge electrode, the electrical current and the discharge plasma are confined into a thin layer above the DCSBD electrode, presenting a high volume power density and thus generating a high concentration of reactive species.

Plasma treatment can reduce or increase wettability

The "Durawood" project is developing a tailored plasma-based system for treating wood surfaces under continuous conditions suitable for industrial wood manufacturing. Depending on its operating conditions, plasma treatment applied to a wood surface can either waterproof the surface or make it more compatible with waterborne coatings.

Tests were conducted with various atmospheres, powers, treatment times, gaps, etc. to optimise the conditions for different wood species depending on the desired effect (water repellency vs. wettability). The effect of plasma treatment on wood surfaces was studied by surface energy measurement, Atomic Force Microscopy (AFM) and Fourier Transform Infra Red (FT-IR) spectroscopy.

Figure 2 shows the influence of the plasma pretreatment on wood surface free energy as illustrated by the change of contact angle of a water droplet applied to an oak surface. The contact angle of the reference sample (a) was 59 °. A sample of the same wood hydrophilised using DCSBD plasma had a significantly lower contact angle (14 °) showing a much greater polarity and ability of water to wet the wood surface.

The hydrophobised sample reached a contact angle of 89 ° and thus had a much more apolar behaviour. Both hydrophilisation and hydrophobisation were carried out using a CO_2 atmosphere and the same DCSBD plasma system. Measurements were performed on a Surface Energy Evaluation system ("SEE" system), using apparatus from Advex Instruments. This instrument captures a droplet of liquid with known polarity, which is applied on the solid surface to be evaluated.

AFM, a very high-resolution scanning probe microscopy, was used to investigate the structural changes on

Results at a glance

»› Plasma treatment of wood can modify its properties in a controlled fashion, allowing on the one hand a thin hydrophobic surface layer to be deposited, or on the other hand, improving the adhesion of waterborne coatings by increasing the wettability of the surface.

»› Progress is reported on the development of an industrial low cost, low energy, fast plasma process based on the use of a planar electrode placed close to the wood.

»› The Durawood project has the potential to assist the wood industry by improving the quality of wooden products, both extending the lifetime of exterior waterborne coatings and increasing the durability of unpainted wood.

»› A biocidal effect created by the plasma could reduce the amount of fungicides required, but is still under investigation.

Figure 4: Stages in the "Durawood" plasma pretreatment of wood surfaces (preferably in-line with coating)

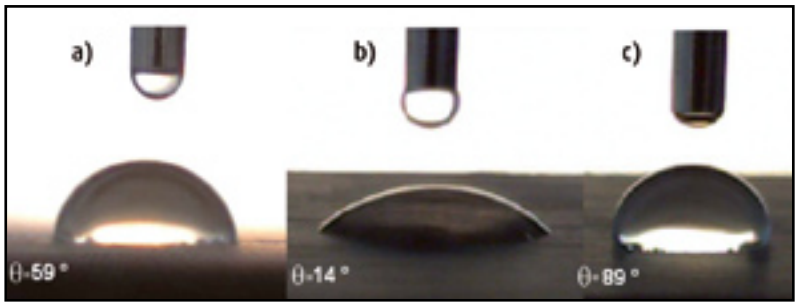

Figure 2: Water droplet contact angles on (a) reference oak wood surface (b) plasma-treated hydrophilised oak wood surface (c) plasma-treated hydrophobised oak wood surface (using DCSBD plasma system)

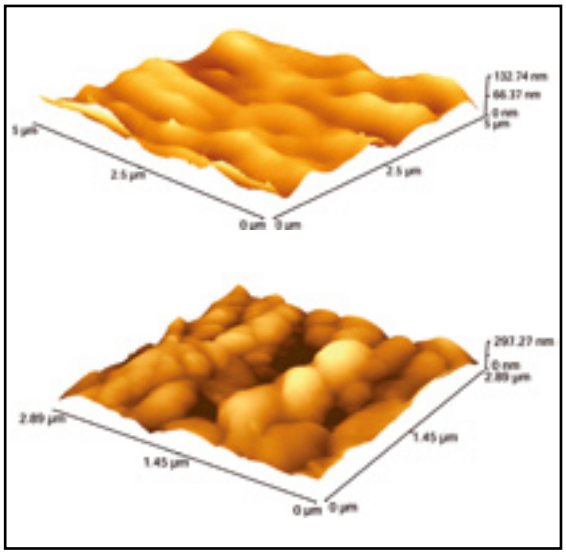

Figure 3: AFM image showing the plasma effect on the wood surface; upper, reference sample; lower, plasma-treated sample

the wood surface treated with DCSBD plasma. *Figure 3* shows newly created irregularities on the wood surface treated with plasma.
Irregularities appearing as bubbles are due to the creation of new active groups. The nature of these groups depends on the type of atmosphere used during the plasma treatment. AFM confirmed that the plasma treatment led to the creation of an invisible nano-layer on the wood surface.
FT-IR spectroscopy was used to characterise chemical changes on the wood surface caused by plasma treatment. The nature of the active groups generated depends mainly on the type of treated wood and on the atmosphere used during the plasma treatment. However, in most cases, the four characteristic bands listed in *Table 1* were observed, which correspond with the findings from surface free energy measurement in terms of polar vs. apolar groups.
These physicochemical changes are expected to provide a substantial and beneficial enhancement in the adhesion and durability of the coating, combined with a reduction of the susceptibility of the wood to biological decay.

More durable wood finishes enhance sustainability

The new plasma processing system will increase the performance and durability of wood surfaces treated with waterborne coatings, allowing them to reach a level comparable to those treated with solventborne coatings. This can decrease the frequency of maintenance of wooden articles used outdoors, thus greatly assisting the European wood industry in its shift towards safer environmentally-friendly wood treatments.
This technology will enhance the sustainability and competitiveness of the timber industry and offer differentiated solutions to its users, for example by waterproofing wood without the need to further coat it. The process will be versatile, depending on the application and type of wood.
Overall, it will be a low-cost, low energy consumption and high-speed wood pretreatment that the wood manufacturer will be able to perform on site by applying it immediately before wood coating operations (see *Figure 4*).
The effects of the plasma pretreatment on coating adhesion and weathering resistance are being investigated. Results will be published before the conclusion of the project.
In addition, plasma is expected to have a biocidal effect [11] on the one hand due to ozone molecules created during plasma operation, and on the other hand when using conditions leading to long-term surface hydrophobisation, as microorganism growth is then inhibited (*Figure 5*). The antifungal effect is being validated.
Finally, efforts are currently being made to scale-up this plasma treatment system to integrate it into the facilities of industrial wood manufacturers. Various demonstration sessions will be organised for the industry to become familiar with the new process. Dates and places will be announced on the "Durawood" website.

Figure 5: Enhancing the hydrophobicity of wood surfaces reduces moisture pick-up, discourages microbiological growth and thus improves exterior durability

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ACKNOWLEDGEMENTS

The authors wish to acknowledge funding from the European Community's Seventh Framework Programme [FP7/2007-2013] for the research leading to these results under grant agreement 232296, through the "Durawood" project "Development of a novel solvent-free coating process for wooden facades".

ABOUT THE PROJECT

"Durawood" is a collaborative two-year research project that started in December 2009 and is coordinated by Innovació i Recerca Industrial i Sostenible, Spain (IRIS). It involves nine partners from five countries. The research partners are IRIS, ttz Bremerhaven (TTZ) and the Slovak University of Technology in Bratislava (STUBA).
The consortium's industrial partners are composed on the one hand of the following wood-processing firms: Ing. Ján Šestina (SETA) from Slovakia, Kartas Kontrplak Sanayi Ticaret (KARTAS) from Turkey, and Aryecla S.L. (ARY) from Spain, and on the other hand of the following companies in the supply chain of the targeted technology: Plasma Technologic s.r.o. (PLASTECH) from the Czech Republic, which is a specialist in plasma technology; PAM-aks. r.o. (PAM-AK) from Slovakia and Setas Kimya San As (SETAS) from Turkey, which are both manufacturers of coatings.
For more information, please visit: www.durawood-fp7.eu.