PROJECT FINAL REPORT

Grant Agreement number: 211473

Project acronym: PLASMANICE

Project title: Plasmas for Nanoscale Industrial Surface Processing

Funding Scheme: Theme 4 NMP – Nanosciences, Nanotechnologies, Materials and New Production Technologies

Period covered: **from** 1.10.2008 **to** 30.9.2012

Name of the scientific representative of the project's co-ordinator[1], Title and Organisation:

Johanna Lahti, Senior Research Fellow, Tampere University of Technology

Tel: +358 40 849 0156

Fax: +358 3 3115 3751

E-mail: johanna.lahti@tut.fi

Project website address: http://hlab.ee.tut.fi/plasmanice/

[1] Usually the contact person of the coordinator as specified in Art. 8.1. of the Grant Agreement.

Contents

1. Final publishable summary report 3

1.1 Executive summary 3

1.2 Summary description of project context and objectives 4

1.3 A description of the main S&T results/foregrounds 5

1.4 The potential impact and the main dissemination activities and exploitation of results 25

1.5 Project website and contact details 28

1. Final publishable summary report

1.1 Executive summary

This is the final report of the FP7 project PlasmaNice (211473) 'Atmospheric Plasmas for Nanoscale Industrial Surface Processing'. PlasmaNice was a four-year project funded by the European Union 7th RTD Framework Programme in the context of the NMP - Nanosciences, Nanotechnologies, Materials and new Production Technologies. The project started on 1st of October 2008. The main objective was to develop equipment for in-line atmospheric plasma deposition of functional nanocoatings on various fibre- and polymer-based substrates. The project aimed at improvement of recyclability of conventional fossil fuel-based plastics and/or replacement by renewable bio-based (and biodegradable) materials. Most current materials used for packaging are oil-based, thus produced with resources which are non-renewable. Such resources are limited, cannot be regenerated, and their availability will decline. The volume of waste is predicted to continue rising and for this reason not only waste management but also waste prevention are crucial aspects in today's society. Renewable sources should be preferred and they should be used in a sustainable way, supporting efficiency and encouraging recycling.

Atmospheric plasma techniques as processing methods have a number of advantages which include their ability to tailor the surface chemistry at the nanometre level. As such, the plasma treatments are energy efficient, reproducible and environmentally clean. In-line, continuous reel-to-reel processing equipment has been developed in the last years. The wide scale application of this nano-processing technology in the pre-treatment of packaging materials in reel-to-reel processing has, however, been severely limited.

One of the main reasons for this is the relatively slow processing velocity for coating depositions. In general, the velocities need to be increased by 2-5 fold in order to fully exploit the new nano-processing techniques. This project addressed these issues in order to assist in the transfer of atmospheric plasma processing technology from the laboratory scale to industrial level in the packaging industry. Special attention went out to the very promising combination with sol-gel technology. A method and equipment for in-line plasma deposition of high-barrier bio-based coatings to be applied in conjunction with extrusion coating was developed. The target was to develop the process in order to achieve industrial line speeds. Laboratory and pilot-scale equipment were installed and tested during the project. The approach exploited plasma-assisted sol-gel coatings and coatings applied on the substrates by plasma deposition. The substrates included various paper and paperboard grades and plastic films. Renewable, bio-based and biodegradable materials were used as extrusion coatings. Industrial contribution was in an important role in the project. The guidelines for material and process development derived from real industrial challenges and needs. Thus, industry was closely working with the scientific partners to develop new solutions for packaging materials.

The project aimed also at replacement of fluoropolymer-based grease barrier materials with sol-gel coated bioplastics and substitution of non-renewable barrier packaging films with renewables based materials in general. The developed materials, solutions and processes were thoroughly studied and a wide range of analytics were used to define e.g. the properties of the new materials.

The PlasmaNice project aimed at the development of a packaging material with an overall better environmental performance. Looking at the environmental impacts of a product throughout its entire life cycle, from cradle to grave, allows better integration of sustainability within the product. As prevention is better than cure, to make sure that a product has a lower environmental impact, action should be taken starting from its design. The instrument which permits the assessment of the environmental impact of a product during its life cycle, from the extraction of raw materials through transport, production, use, until disposal, is called LCA (Life Cycle Assessment). A new process should also not provide a higher risk to workers and the society compared to established processes and products. Risk and safety analysis is the instrument which is able to identify and evaluate hazard, focusing on prevention or mitigation of unrecognised drawbacks to ensure the safety of workers and society during production, use and product disposal. The PlasmaNice project used both LCA and risk analysis to evaluate and monitor the environmental performance and the safety aspects of the new process and products.

1.2 Summary description of project context and objectives

FP7 project PlasmaNice (211473) 'Atmospheric Plasmas for Nanoscale Industrial Surface Processing' was a four-year project funded by the European Union 7th RTD Framework Programme in the context of the NMP - Nanosciences, Nanotechnologies, Materials and new Production Technologies. The project started on 1st of October 2008. The main objective was to develop equipment for in-line atmospheric plasma deposition of functional nanocoatings on various fibre- and polymer-based substrates. The project aimed at improvement of recyclability of conventional fossil fuel-based plastics and/or replacement by renewable bio-based (and biodegradable) materials. Most current materials used for packaging are oil-based, thus produced with resources which are non-renewable.

This project addressed these issues in order to assist in the transfer of atmospheric plasma processing technology from the laboratory scale to industrial level in the packaging industry. Special attention went out to the very promising combination with sol-gel technology. A method and equipment for in-line plasma deposition of high-barrier bio-based coatings to be applied in conjunction with extrusion coating was developed. The target was to develop the process in order to achieve industrial line speeds. Laboratory and pilot-scale equipment were installed and tested during the project. The approach exploited plasma-assisted sol-gel coatings and coatings applied on the substrates by plasma deposition. The substrates included various paper and paperboard grades and plastic films. Renewable, bio-based and biodegradable materials were used as extrusion coatings. Surface functionalisation and nanoscale coatings were used in the project for improved properties of the packaging materials and to find substitutes for current solutions.

Industrial contribution was in an important role in the project. The guidelines for material and process development derived from real industrial challenges and needs. Thus, industry was closely working with the scientific partners to develop new solutions for packaging materials.

The project aimed also at replacement of fluoropolymer-based grease barrier materials with sol-gel coated bioplastics and substitution of non-renewable barrier packaging films with renewables based materials in general. The developed materials, solutions and processes were thoroughly studied and a wide range of analytics were used to define e.g. the properties of the new materials. The PlasmaNice project used both LCA and risk analysis to evaluate and monitor the environmental performance and the safety aspects of the new process and products. In addition, the economical aspects of the new developed processes and materials were evaluated.

In the PlasmaNice project, one of the targets was to study and model various plasma process parameters in order to improve the efficiency of the plasma processes. One of the objectives of the project was also to evaluate in possibly implement method, which will enable the on-line monitoring of the efficiency of the plasma assisted coating deposition for high speed applications and for very thin nano-sized coatings. Such method does not exist yet. Requirements of such method were to be simple, fast, non-contact, robust and to provide information on the relative change in coating deposition or in plasma treatment process for feedback control of this process. Its realization was supposed to be difficult due to high speed of treatment process, what requires fast response time, high sensitivity due to thin coatings or affected layer during plasma activation, rough surface of substrates (paper), oscillating substrate between reel to reel transport, similar type of materials (organics) for coatings and substrates. Such method will facilitate the increase of coating homogeneity as well as their quality and will allow reducing coating thickness in a controlled manner.

1.3 A description of the main S&T results/foregrounds

<u>WP1 Plasma deposition equipment</u>

Task 1.1: design and construction of a lab scale plasma system

In the first phase of the project, an improved lab scale DBD plasma coating system (width 200 mm) was constructed based on know-how and experience at VITO and TUE. The precursor injection system is segmented in 100 mm units to facilitate scale-up. Based on experimental measurements as well as CFD modeling, special modifications were integrated to improve precursor distribution and treatment homogeneity. AFS develop and construct a special power supply (5 kW, 20-100 kHz) for DBD plasma processing with smart matching facilities and pulsed power modes to optimize power efficiency. The system was assembled and tested at VITO and subsequently installed in the lab line at VTT for use in process developments in WP3. (Figure 1)

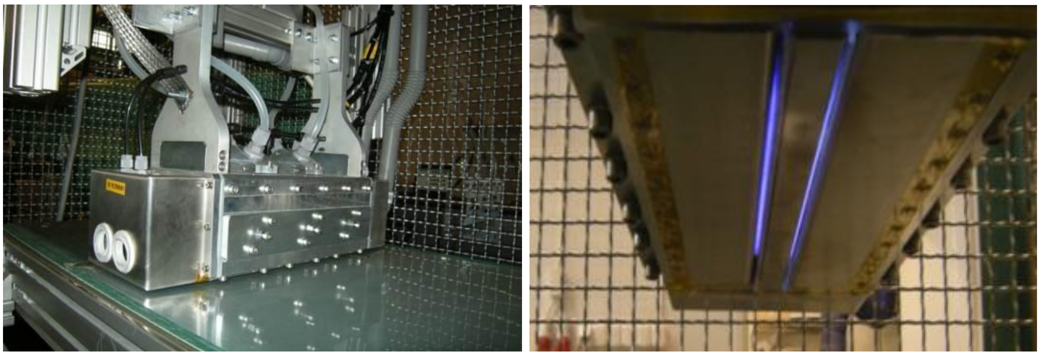

Figure 1 200 mm wide lab scale plasma system installed at VTT for process development.

Task 1.2: Update and modifications to the lab scale equipment

A more user-friendly software interface was developed by VITO with integrated controls, sensors and safety interlocks. (Figure 2) All process parameters are logged and saved automatically.

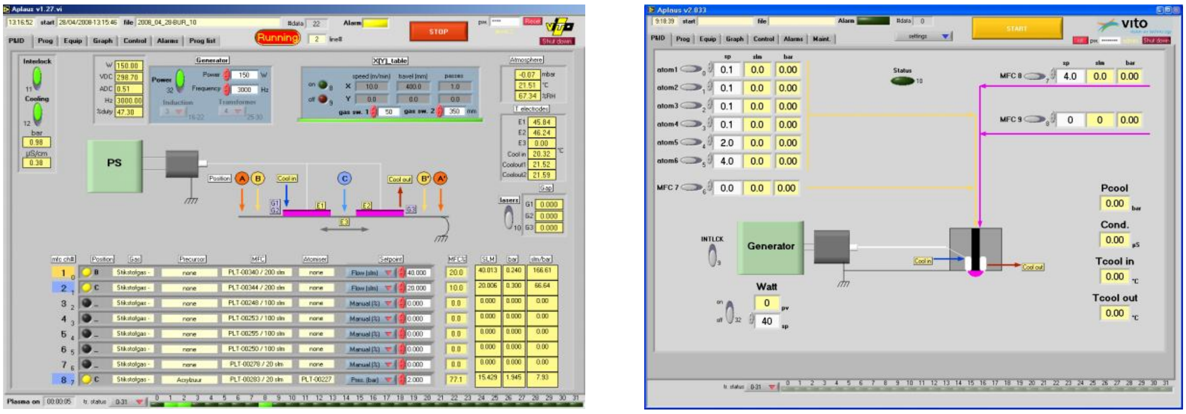

Figure 2 First interface (left) and new more user friendly interface (right) for plasma operation and process control.

Significant engineering efforts have been done to improve plasma deposition rates (up to 4 times better) and precursor efficiency as well as to reduce the gas consumption (target 33% reduction). The latter is the most important factor in the system running costs (>75%). Optimizations have been carried out to increase the reactive gas flow by lowering the discharge gap in the reactor to 0.5 mm. This was realised by crenulated ceramic spacers and allowed to reduce gas flow from 600 to 400 slm. Improved cooling of the plasma reactor was needed to ensure stable operation conditions at high power levels and reduced gas flows. This was solved by developing water cooled high voltage electrodes using high-ohmic water.

However, process development work in WP3 showed that the targeted reduction of the gas consumption by 33% also resulted in lower deposition rates. In general, plasma deposition rates were evaluated to be too low (5-50 nm.m/min), to enable significant coating deposition at high line speeds (> 500 m/min). Hence, at the first review meeting, it was decided to leave the primary processing option based on plasma deposition alone and to opt for the secondary processing option in which plasma pre-treatment and sol-gel spray coating are integrated on-line with extrusion coating technology. On the other hand, it was decided to continue investigations with plasma deposition using sol-gel chemistry for side applications at lower speeds.

Task 1.3: Design & building of the pilot scale equipment

A pilot scale plasma system (600 mm wide) was developed by VITO for process development and industrial demonstration trials on the TUT pilot line. A technical drawing and two pictures of the scaled-up plasma reactor (PlasmaLine) is presented in Figure 3.

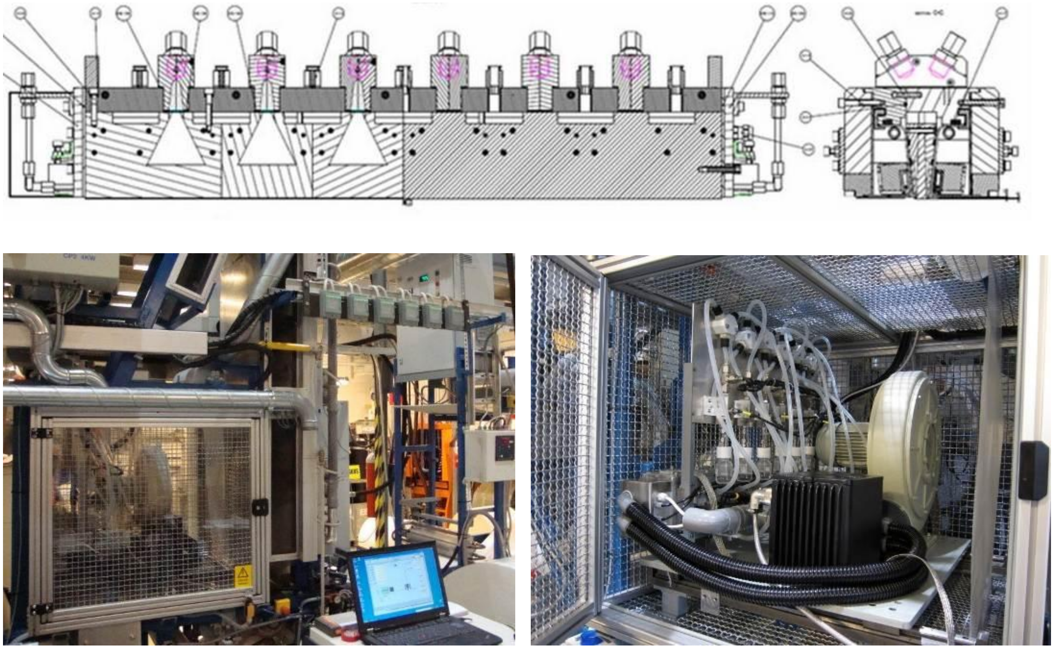

Figure 3 Technical drawing (top) and two pictures of the PlasmaLine 600 system on the TUT pilot line.

During testing it was observed that operation at high power and low duty cycle results in fast heating of the switching unit. This problem was solved by software modifications in the AFS power supply. Operation at a duty cycle of 60% or higher resulted in a much lower temperature of the switching unit and hence increase power efficiency.

Task 1.4: Update and modification of the pilot scale equipment

In order to optimize the system capabilities to work at industrial lines speeds of 500 m/min and more, the PlasmaLine 600 system at TUT pilot line was further improved for plasma pre-treatment. The main adjustment was the incorporation of extra mass flow controllers to allow admixing of additional reactive gasses to the main plasma discharge gas (nitrogen). The electrical cabinet and software also needed to be upgraded for this purpose.

In addition to the PlasmaLine 600, a new multi-jet air plasma system developed by AFS during the course of the project was installed on the TUT pilot line. In this way, the potential for plasma surface pre-treatment at high line speeds was increased drastically. The air based PlasMatrix system is used for oxidative pre-cleaning and the PlasmaLine can subsequently be used to graft specific functional groups. The first PlasMatrix prototype consisted of 66 jets which were mounted in three rows, each row of jets slightly displaced to improve treatment uniformity. The second generation prototype was designed for a treatment width of 600 mm. (Figure 4) It consists of 120 individual jets which are distributed over four rows instead of three. The power supply was upgraded to 60 kW and used at maximum power levels of about 26 kW. In order to control internal overheating and electrical breakdown, the air supplied to the plasma jets is pre-cooled with a turbo intercooler.

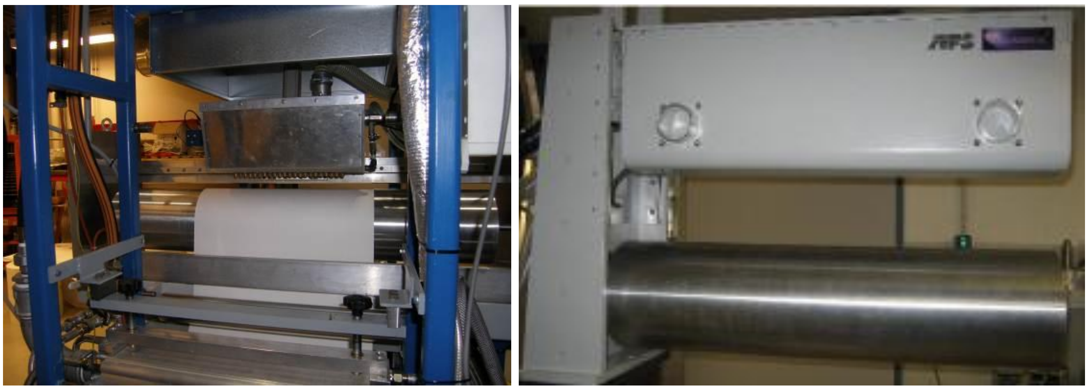

Figure 4 First (left) and second (right) PlasMatrix prototype systems from AFS.

Conclusions and design criteria for up-scaling

Scale-up of the PlasmaLine and PlasMatrix systems to industrial line widths of 1,6 m to 2 m is possible but will still require significant redesign and engineering efforts for both systems. For line widths over 2 m, a segmented approach is technically the most likely solution.

For high line speeds (> 100 m/min) it is best to use the PlasmaLine in combination with another surface pre-treatment system such as the PlasMatrix or a corona station. In this way, a pre-cleaning of the surface is done before plasma assisted grafting of specific chemical groups with the PlasmaLine. While multi-jet air plasma systems have already been implemented successfully in industrial lines at high line speeds, the effect of PlasmaLine at high line speeds is rather limited. Speeds up to 1000 m/min seem to be far out of range for the current concept and probably also for future system generations. Best performance is obtained at line speeds below 100 m/min and as a standalone technology even below 50 m/min. This means that applications are more likely in plastic foil converting lines than in paper converting lines which typically run at higher speeds.

<u>WP2 Sol-gel</u>

Task 2.1 Hybrid coatings for biolaminate adhesion

One objective of work package 2 comprises the improvement of the adhesion between an organic polymer and biodegradable substrates like paper which are laminated in a reel-to-reel process. The adhesion can be enhanced, for example, by the use of silylated biopolymers which were integrated into the coating increasing the surface energy. But as outlined in task 2.2 (see below), the grease barrier properties of hybrid coatings on pure Sappi Algro Finess paper were comparable to PLA (poly lactic acid) laminated Algro Finess paper, an additional PLA laminate seems to be unnecessary for a grease barrier application. Thus, the lamination process could be saved and adhesion promotion is not necessary.

Task 2.2 Hybrid grease barrier coatings

The main aim of work package 2 was to develop fluorine-free grease barrier coatings based on inorganic-organic hybrid materials synthesised via sol-gel technology for reel-to-reel substrates (paper, paperboard and plastic films) which could be applied by plasma-deposition. During the project it has been shown that plasma deposited coatings cannot be applied in a sufficient speed to obtain coatings with grease barrier properties. Therefore, spray application followed by UV curing were used as versatile methods. During the project, more than 50 different formulations were developed which are UV-curable at line speeds of ca. 120 m/min in laboratory scale and which exhibit good grease barrier properties.

The typical structure of the hybrid coating consists of an inorganic siloxane network formed by a sol-gel process in combination with an organic acrylate based network formed by a UV-induced polymerization reaction. The reactive acrylic groups are responsible for fast UV curing. With methylsiloxane moieties as well as by the use of silylated biopolymers, especially silylated polyvinyl alcohol, grease barrier properties were achieved comparable to that of fluorinated compounds. The silylated biopolymers were synthesized by the project partner VTT. Due to their modification with $Si(OR)_3$ groups the biopolymers can also react via the sol-gel process and are introduced into the hybrid network of the coating material.

Tests of grease barrier properties of the hybrid coatings on paper substrates were performed following the “ASTM F119 – 82 standard test method for rate of grease penetration of flexible barrier materials”: The behaviour of a droplet of oil on top of the coatings was observed over a period of up to four weeks. A sheet of blotting paper was placed under the coated paper to soak paraffin migrating through the paper. Figure 5 shows possible behaviours of the paraffin droplet on a coated substrate.

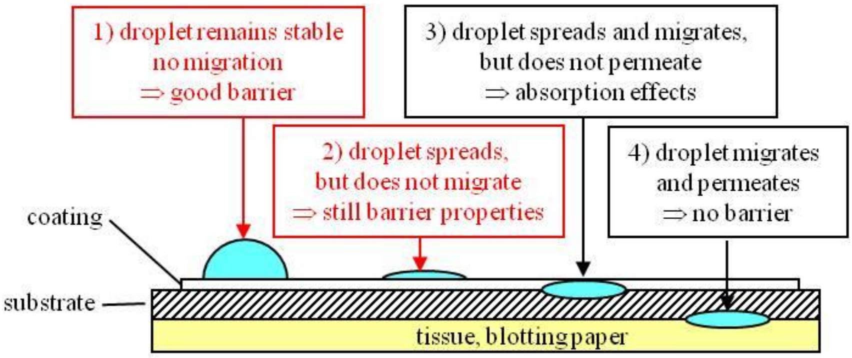

Figure 5 Possible behaviours of the paraffin droplet on a coated substrate.

From the 50 different formulations, two compositions were selected as "standard systems" taking into consideration technical, commercial and LCA aspects like commercial availability and cost, synthesis procedures, handling and storage and toxicity, respectively.

In preliminary biodegradation tests the hybrid coating material could be decomposed to 90 % which is also a promising feature for its use as coating on biodegradable biopolymers (e.g. paper) in packaging applications.

The selected standard formulations were based on a long-chained acrylic siloxane, hereinafter referred to as "Lgf", and combined with two different methyl siloxanes hereinafter referred to as "T" and "D". The mixtures were referred to as "Lgf_T" (molar composition of 50:50) and "Lgf_TD" (molar composition of 50:25:25). Figure 6 shows the grease barrier test of a paper substrate coated with Lgf_T compared to an uncoated piece of paper. The droplet of oil penetrates the uncoated paper completely, while on the coated paper, the droplet remains stable over four weeks.

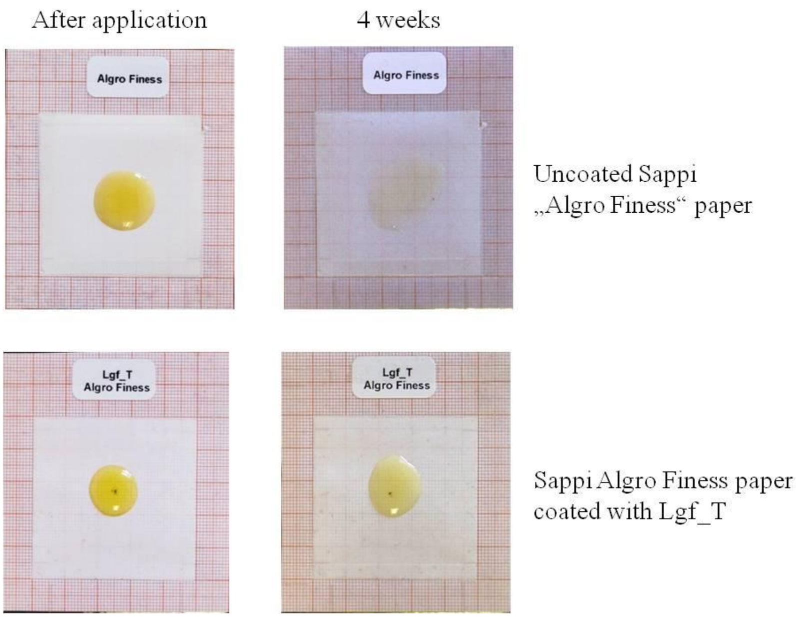

Figure 6 Comparison of the grease barrier tests on uncoated paper (Sappi Algro Finess, top) and on paper coated with Lgf_T. Left: after application, right: after four weeks.

Besides grease barrier properties, water vapour and oxygen transmission barriers of the coatings may also be necessary for different packaging applications. As the chemical composition of the hybrid coatings was optimized for grease barrier properties, other barrier properties have to be implemented in a different way. A suitable approach is the incorporation of fillers. In general, due to the presence of particles, molecules are not able to migrate directly into and through the coating due to a longer migration path.

While the water vapour barrier properties were not significantly improved by the incorporation of particles, the oxygen barrier properties of hybrid coatings containing silica nanoparticles (product name "Köstrosol") were higher than those of a paper/PLA (poly lactic acid) laminate. Since the hybrid coating is thinner than the PLA laminate, it is, moreover, possible to save material. The paper/PLA laminate exhibits an oxygen transmission rate (OTR) of 426 $cm^3/m^2/d$, while paper coated with Lgf_T containing 50 wt.-% of silica nanoparticles exhibits an oxygen transmission rate of 127 $cm^3/m^2/d$.

The OTR of hybrid coatings on pure paper was measured in different relative humidity in order to investigate the effect of dry and high moistur content on the oxygen barrier performance. The OTR results revealed that all the applied sol-gel coatings showed better oxygen barrier than the uncoated paper. Again it was shown, that especially the use of silica nanoparticles improved the oxygen barrier properties of the sol-gel coatings. It was noticed that the additional use of nanoclays, which are known to improve barrier properties, did not improve the oxygen barrier in this case. Furthermore, it was noticed that the change in relative humidity affected only on the coatings modified with nanoclays.

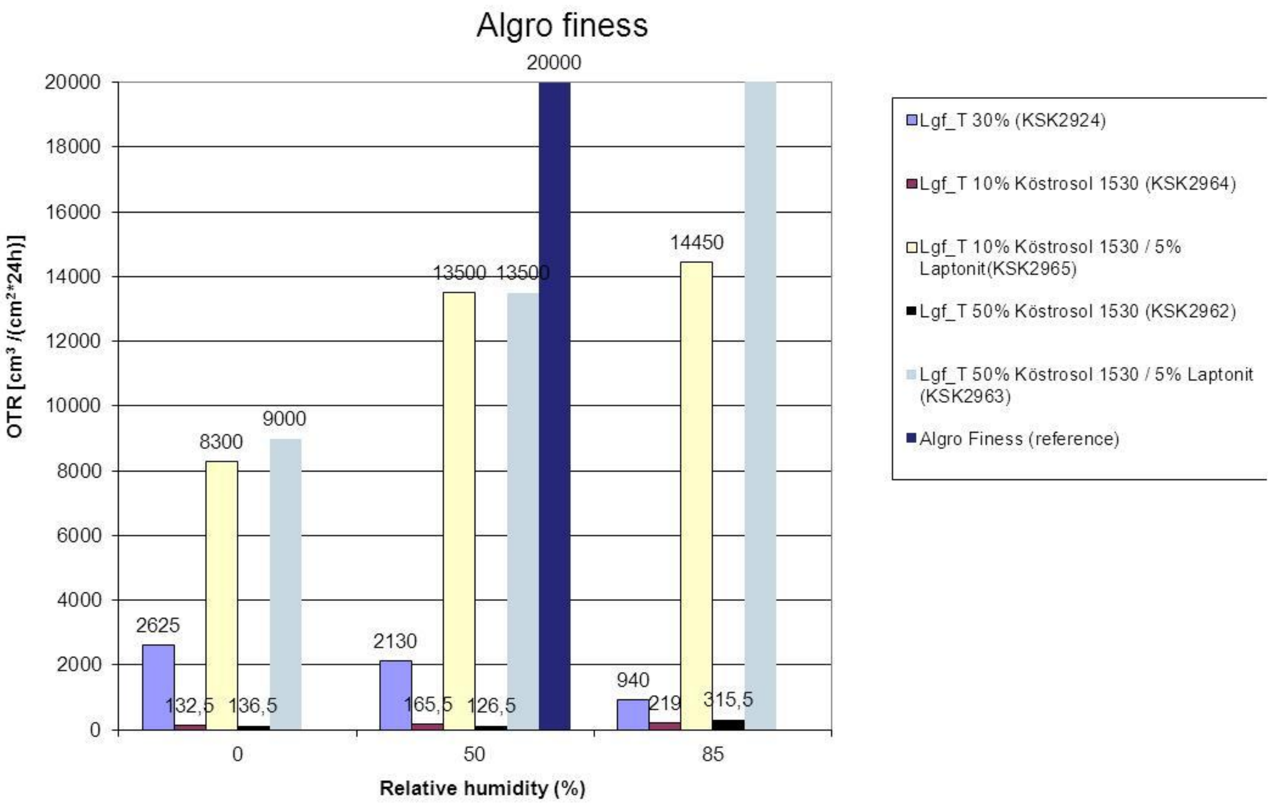

Figure 7 Results of oxygen barrier measurements of UV-cured coatings (Lgf_T) with different kinds and combination of nanoparticles on Algro Finess paper.

The good barrier properties of coatings which contain only silica nanoparticles are attributed to well distributed particles in the coating, which was confirmed by TEM investigations (Figure 8).

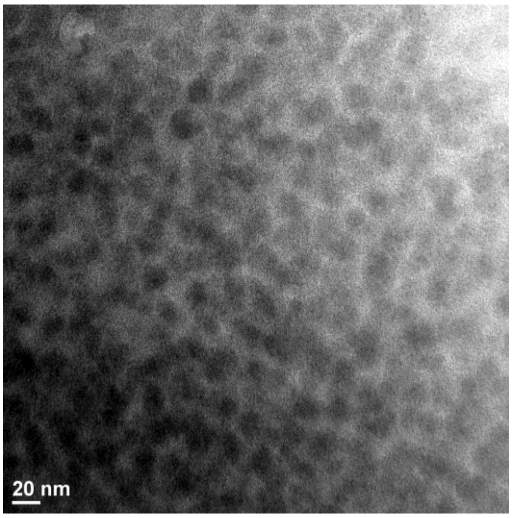

Figure 8 TEM picture of a UV-cured coating (Lgf_TD) with 50 wt.-% SiO_2 nanoparticles on Algro Finess paper.

Since nanoparticles are suspected to be hazardous when released from a product into the environment, the coatings containing nanoparticles were tested for possible particle release. Therefore, mechanical abrasion was conducted on coated glass plates with 100 revolutions with a taber abraser in 90 seconds. During the process, ambient atmosphere next to the treated surface was soaked and the caught particles were analysed. The range of the measured particle diameters was very broad: between 5 and 560 nm. The particle release measured during the abrasion process is considered to be in the range of the standard deviation, but no silica particles of the size previously incorporated were detected. Finally, it can be concluded that there is no release of nanoparticles from the hybrid coatings under mechanical stress.

The main drawback of UV curing in packaging applications is that fragments of reacted photoinitiators or non-reacted initiators are able to migrate out of the coating into the environment, i.e. into food. Therefore, especially for hybrid materials, silylated photoinitiators synthesized by SurA Chemicals were investigated in the project. They are able to undergo similar hydrolysis and condensation reactions as the coating components and, therefore, are incorporated into the siloxane network of the coating materials. In this way they are immobilized in the coating and migration is prohibited. It was shown in several experiments with the standard hybrid coatings that the immobilized initiators keep their reactivity and ability of radical formation during the sol-gel reaction and lead to well cured coatings even at high line speeds. Extraction tests with solvents followed by spectroscopic analysis of the extract as well as of the coating lead to the conclusion that leaching of the photoinitiator does not occur.

Plasma-deposited coatings could not be applied in a sufficient speed to produce coatings with grease barrier properties because the film thicknesses obtained with different parameters were too thin. Nevertheless, several attempts under different plasma conditions were conducted to obtain plasma-deposited coatings on paper and paper/PLA laminate with grease barrier properties at low speed and longer treatment times. It was possible to produce plasma-deposited coatings on PLA/paper laminate at deposition times of 54 s in nm scale, which exhibit very good grease barrier properties comparable to the grease barrier properties of UV-cured coatings in µm scale. On the other hand, it was not possible to achieve plasma-deposited coatings with good grease barrier on pure paper. Therefore, plasma deposition is no option to be used as coating process to obtain thick coatings with grease barrier properties on paper but seems to be an effective pre-treatment method for surface modification, e.g. to generate thin adhesion promoting interlayers.

Task 2.3 Optimisation to high speed conditions

At the pilot lines which were installed during the project at VTT and TUT several trials were conducted to apply UV cured hybrid grease barrier coatings at high line speeds. Additionally, industrial coating trials on PE, HDPE and PA plastic foils were conducted at a coating line of the project partner Segers & Balcaen. The resulting coatings show, in general, very good grease barrier properties. Although the application method and the UV curing in the industrial coating line have to be optimized and adapted, from the material point of view the trials were very successful because it was possible to transfer the lab scale trials to an industrial coating line resulting in coatings with good grease barrier properties.

WP3 Processing

The work of WP3 Processing is done with 9 partners, with major PM allocations by TUT, Vito and VTT. The work has been done in close cooperation particularly between WP1 Plasma Deposition Equipment and WP2 Sol-gel as well as WP4 Analytics.

Regarding to the activities directly related to equipment modification and installation (Task 3.1 and 3.2) the extrusion line modifications with PlasmaLine at VTT were done, with the additional objective of including the possibility of sol-gel spraying and curing unit also at the VTT line, thereby enabling the small scale trials. The plasma-assisted inline sol-gel coating line at VTT was set up and used in initial experiments. Figure 9 shows the position and components of the unit.

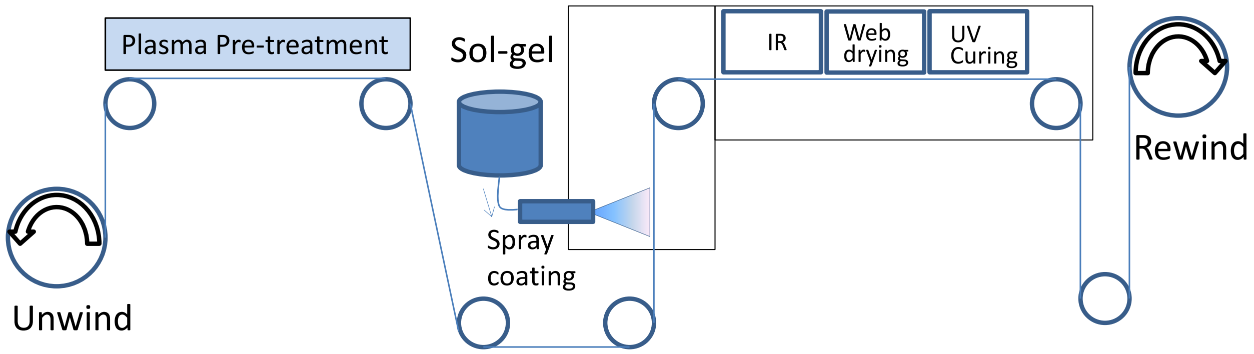

Figure 9 The laboratory scale sol-gel coating unit at VTT. The extrusion coating unit positioned before the unit is not shown in this schematic.

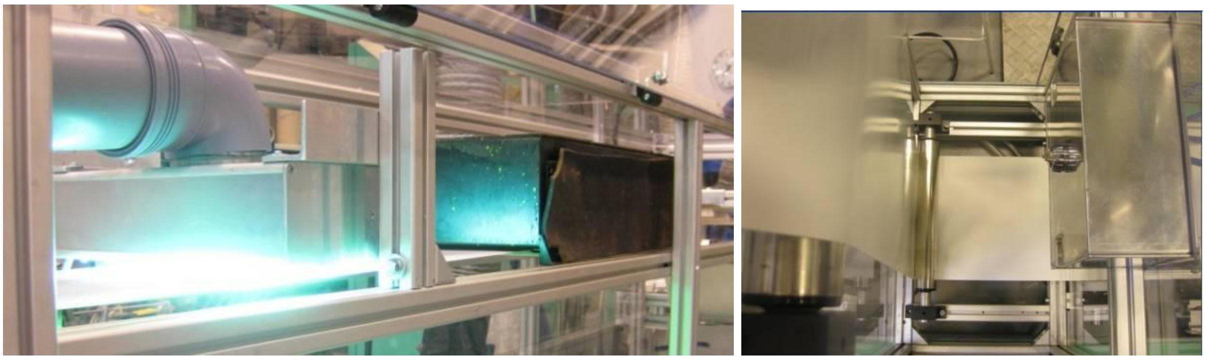

Figure 10 In the left: The UV curing, web and IR drying units from left to right. In the right: spraying chamber. Spray nozzle on the right.

The unit enables in-line spray coating followed by two drying units (IR and web dryer) which can also be used for thermal curing at low speeds (Figure 10). The drying units are followed by UV curing unit with an output power of up to 2 kW. By adjusting the process parameters, smooth, 0.2-3 µm coatings with variable precursors (sols) could be applied at speeds up to 80 m/min. Meanwhile, the modifications at TUT pilot line to host the 600 mm PlasmaLine system were completed, also including installation of new line configurations allowing plasma pre-treatment and sol-gel coatings

(Figure 11 and Figure 12). The above mentioned installation and modification were necessary for performing the actual coating and deposition trials were included in WP3.

The process parameters from VTT laboratory scale inline sol-gel coating line to the TUT pilot line were successfully transferred, enabling plasma-assisted inline coatings at 150 m/min. In addition, the experience and result obtained from the laboratory scale trials was transferred to the pilot scale trials conducted at SB site. Several trials with the new equipment were conducted, especially in relation to the case studies. Combinations of corona, PlasMatrix and PlasmaLine were evaluated concerning adhesion of PLA on paperboard. In addition, e.g. ageing behaviour, uniformity and backside treatment effect of the methods were analysed. On-line surface charge measurements were done both at VTT and TUT lines in relation to WP4. In Task 3.3, deposition trials have been performed on polyolefins to characterise the effect on barrier and surface properties. Smoothening of the surface as well as coating layer was observed with SEM and AFM and the formation of coating has been verified with FTIR and XPS.

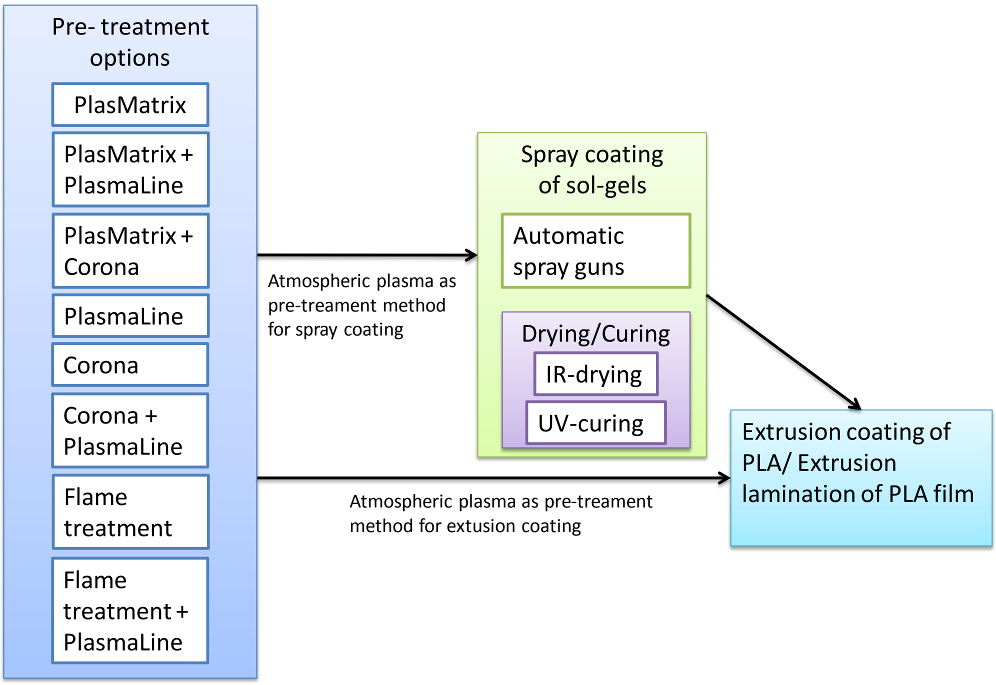

Figure 11 The possibilities for on-line processing and demonstration in the PlasmaNice project at the pilot line of TUT.

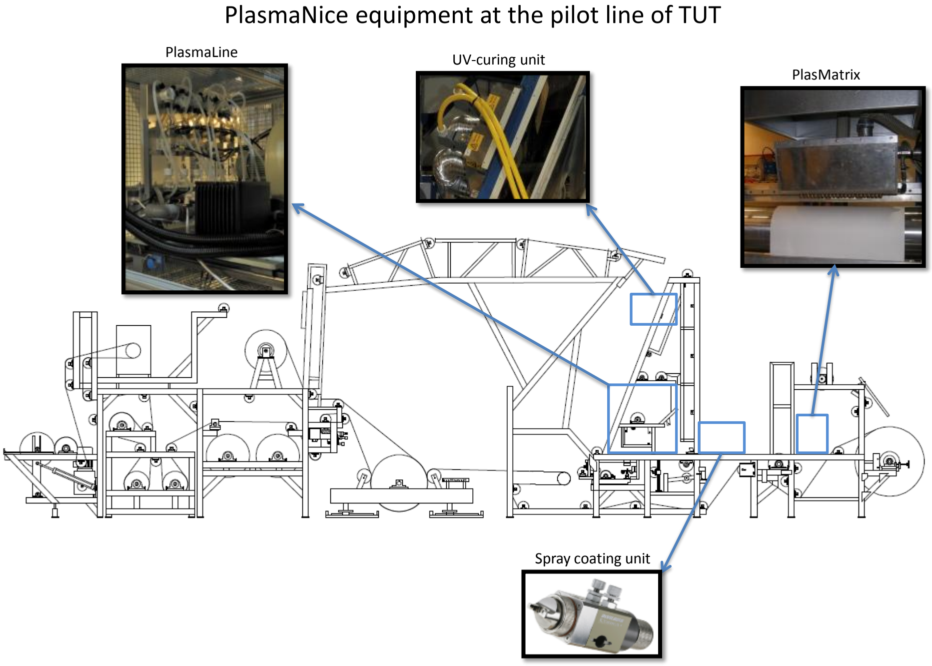

Figure 12 The locations of the devices installed to the pilot line of TUT in the PlasmaNice project.

Additionally the case studies related to grease, oxygen and water vapour barrier, the adhesion improvement as well as the binder reduction were investigated. The transfer of the promising barrier results from off-line coatings to inline environment was done. Requirement for some modification of the compositions is foreseen due to significantly lower coating thicknesses obtained on reel-to-reel substrates. Improvement of oxygen barrier by more than one decade and also improvement in the water vapour barrier performance were achieved. Especially, the development of grease barrier materials based on sol-gel and their deposition was obtained in Task 3.4. Several different sol-gel coating combinations with and without silylated polyvinylalchol (PVA) was performed. Based on the grease barrier test results the deposited sol-gel coatings provided improved grease barrier performance.

In order to evaluate the suitability of the hybrid sol-gel coatings for disposable products, a study of the biodegradability was conducted. Samples were tested in controlled composting test (EN 14046). This test is designed to resemble typical aerobic composting conditions for the organic municipal waste. The aerobic composting takes place in an environment where temperature, aeration and humidity are closely monitored. According to the results, all tested samples can be considered as biodegradable (criteria set by EN 13432) and there were differences in the rate of biodegradation between different samples. The rate of biodegradation and final biodegradation-% of Cupforma and Cupforma coated with LGf-1%PVA sol-gel were in the same level, i.e. the hybrid sol-gel coating did not interfere with the biodegradability of the paperboards. Furthermore, the percentage of degradation of the samples with the hybrid sol-gel coating was significantly higher than that of the PLA coated sample.

Case study work on pervaporation membranes was done by using plasma deposition. The challenge for this application is to deposit a dense pin-hole free coating on a suitable substrate for membranes like PVDF. The latter are in general very porous and it is not easy to deposit a thin coating on top without any pinholes, especially if the substrate is thermally also very sensitive. It was shown that the hybrid sol-gel coating did not interfere with the biodegradability of the paperboards.

WP4 Analytics

Tasks 4.1 and 4.3: Characterization of substrates, deposited coatings, plasma treated materials and liquid sols

The activities in tasks 4.1 and 4.3 of the work package 4 (Analytics) were oriented to comprehensive characterization of materials (coatings, substrates, sols). In this work package 6 partners (JSI, VITO, Fh-ISC, VTT, TUT and TUE) were involved. Results of comprehensive characterization of deposited coatings and substrates were passed to work packages 2 (Sol-gel) and 3 (Processing) to understand and optimize coatings deposition like plasma process parameters, sol-gel parameters, type of model precursors, solid content, type of solvents, aging effect on the coatings properties, degree of hydrolysis and viscosity of sols... Chemical characterization of deposited coatings, functionalized and pure substrates were performed at different partners with the different methods. At the JSI partner samples were characterized by the XPS method for surface composition, chemical bonding and in-depth distribution of elements, by the AFM and SEM methods for surface morphology and homogeneity and by TOF-SIMS for chemical structure. At VITO mainly the methods of laser interferometry and ATR-IR were used. At Fh-ISC the methods like FTIR, micro-Raman and surface energy measurements were applied. At TUT functional properties of deposited coatings like adhesion, permeability, wetting and surface energy were analyzed. Some of these results were presented at different international conferences and workshops and some of these will be published in scientific papers.

Task 4.2 Development of the on-line analytics

The goal of this task was to evaluate and implement methods for the on-line monitoring of the efficiency of plasma-assisted coating depositions and plasma treatment processes. Such methods don't yet exist. Different optical and electrical methods were selected and evaluated.

Spectroscopic method for coating analyses

A new on-line spectroscopic monitoring method was developed at VITO to follow the efficiency of coating deposition. It represents a new tool for improving quality control of plasma-assisted coatings and also may be used for other types of reel-to-reel deposited coatings. The method, for which a patent application has been submitted, will allow evaluation of the homogeneity of deposited coatings, monitor their quality and facilitate reduction of coating thickness in control manner.

Spectroscopic ellipsometry of deposited coatings

The possible application of this method was tested at TUE. The samples consisted of single-side glossy paper, which was coated further by plasma deposition on the glossy side. No distinct differences between the non-coated and coated samples were evident using ellipsometry. This was likely related to the roughness of the paper substrate and/or the low thickness of plasma-deposited coatings. This is also indicative for the main application limitations of this method for on-line monitoring.

Laser-induced breakdown spectroscopy - LIBS

With this method a small portion of the coating was ablated by the focused laser beam and subsequently the optical emission spectrum (OES) of the ablated material was recorded. It was expected that on the base of different specific spectral features from coating and substrate one can detect the presence of the coating. At JSI it was found that the OES spectra from coated and non coated samples were very similar. The reason was that the spectral features related with organic materials were very similar. Other limitations of this method were low depth resolution, traces of laser ablation left on the coating and the need for a high power laser beam.

Gloss measurements of deposited coatings

This method was tested at JSI and proved to be very sensitive for surface flatness, vibrations and morphology, which are crucial issues during the web transport. It was concluded that gloss measurements are suitable for off-line analysis of thick coatings but not suited for on-line monitoring.

Measurement of electric characteristics of coating

A method based on measurement of electric characteristics of deposited coatings was tested for on-line monitoring. This method showed promising results and it will be considered for possible applications.

WP5 Diagnostics and Modelling

Task 5.1: Diagnostics

To better understand the chemical processes taking place in the plasma, it is important to know its composition. For this purpose several diagnostic methods were adapted to the VITO PlasmaLine system, mainly focusing on techniques easily adapted to an industrial setting.

• The light emission from the jet and source has been investigated, which provided qualitative insight into the relevant plasma radicals (atoms and fragments of molecules) produced by the PlasmaLine.

• Measurement of the gas flow velocity of the plasma jet using a specially built flow sensor with a high spatial resolution (< 1 mm) and large flow velocity range (0.1 - 20 m/s).

• Measurement of the ion/electron density in the plasma jet using an electrical probe system. Existing electrical probes for plasma (Langmuir probes) were determined to be unsuitable for measurements at atmospheric pressure; hence a custom-built system was designed. Results are depicted in Figure 13. It is concluded from this data that ions and electrons have a minority role in the deposition process, as their density decays rapidly in the jet due to fast recombination of ion-electron pairs at atmospheric pressure.

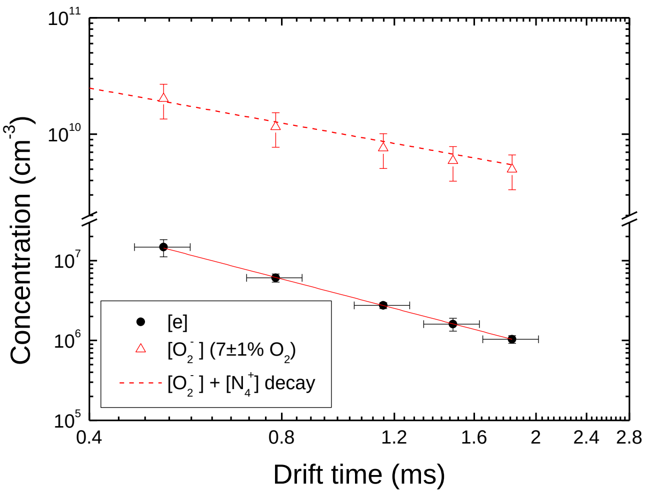

Figure 13: Electron density [e] and negative ion density [O_2^-] as a function of drift time in the plasma jet, determined using the custom-built electrical probe system. The electron density was determined directly from the probe measurements, while the negative ion density was derived indirectly using a chemical model. A molecular oxygen content of 7 ± 1 % in the jet is needed to account for the data.

• Using direct imaging of the light emission of from the plasma jet around 600 nm (red light), it was possible to determine the optical emission related to atomic nitrogen recombination ($N + N + x \rightarrow N_2$) with a high spatial resolution. Analysis of this data provides the absolute atomic nitrogen density in the plasma jet, see Figure 14 for results. It is concluded from this data that atomic nitrogen is the dominant plasma radical in the plasma. The chemical reactions leading to thin film deposition are therefore (initially) driven by reactions with atomic nitrogen. This knowledge can be used to optimize the plasma chemistry for future applications.

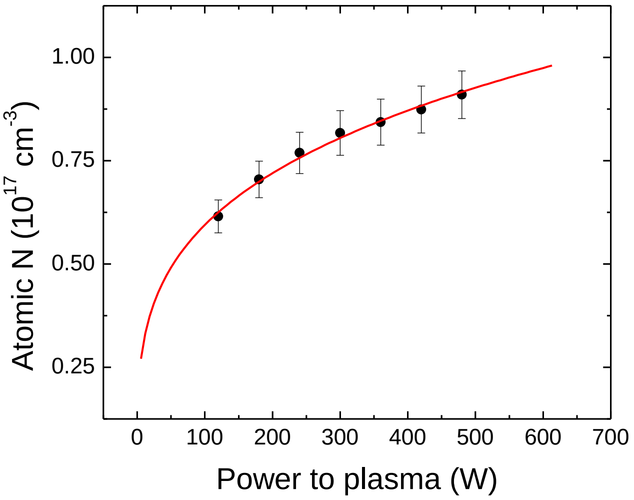

Figure 14: Atomic N density at source exit for increasing electrical power to the plasma source. The atomic nitrogen density is at least 104 times larger than the ion/electron density and also decays much more slowly in the jet (not depicted).

• The PlasmaLine system utilizes Dielectric Barrier Discharges (DBD) to produce plasma. The characteristics of a DBD will depend critically on the design of the system (for example the dielectric material covering the discharge gap). Since this knowledge can be highly valuable to create an efficient and uniform plasma, the characteristics of plasma discharges were measured in small DBD systems (25 mm^2) of various designs, using electrical circuits to analyze the current through the plasma at high time resolution (up to 1 nanosecond). This method provided new insights into DBD's, including the effect of different dielectric materials on the discharge properties.

Task 5.2: Modelling of lab and pilot scale equipment

• Experimental flow data was combined with chemical reaction data to accurately calculate species densities in the PlasmaLine jet. See Figure 15 for examples of two calculated density plots. The model includes over 240 known chemical reactions in oxygen/nitrogen mixtures.

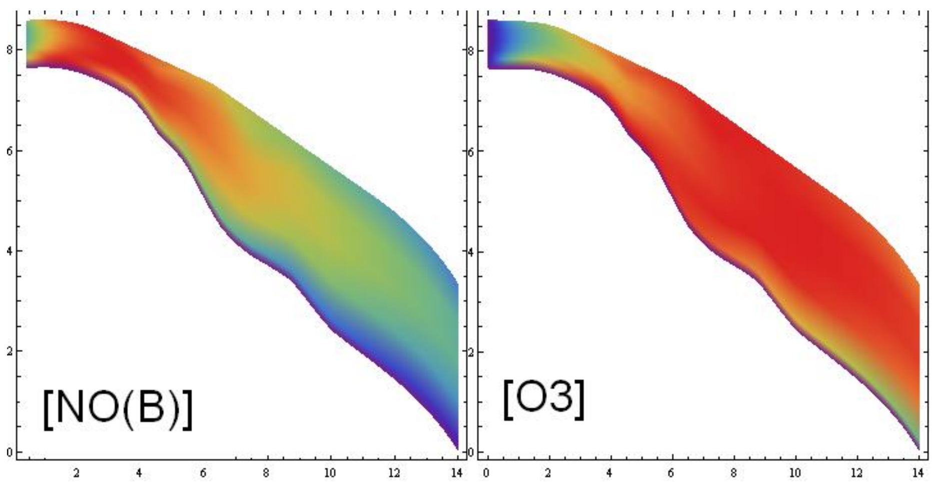

Figure 15: Calculated densities of species in a side-view of the plasma jet (source exit on left-hand-side, blue colour indicates low density, red high density). The model can be used to verify densities obtained from light emission data, but also provides qualitative insight into e.g. ozone formation.

Task 5.3: Modelling of plasma deposition system

Plasma deposition models for the PlasmaLine have been developed. Two components are considered, one part considering chemical reactions of precursor molecules with plasma particles in the torch/jet and one part treating the actual deposition of molecules on the substrate. The ultimate goal is to use the models to suggest changes in torch design. Geometry modification may improve the rate at which molecules are deposited on a given surface. See Figure 16 for an example calculation of deposited mass versus precursor diffusivity. The precursor diffusivity will depend on the precursor molecule size and the turbulence of the gas flow near the treated surface.

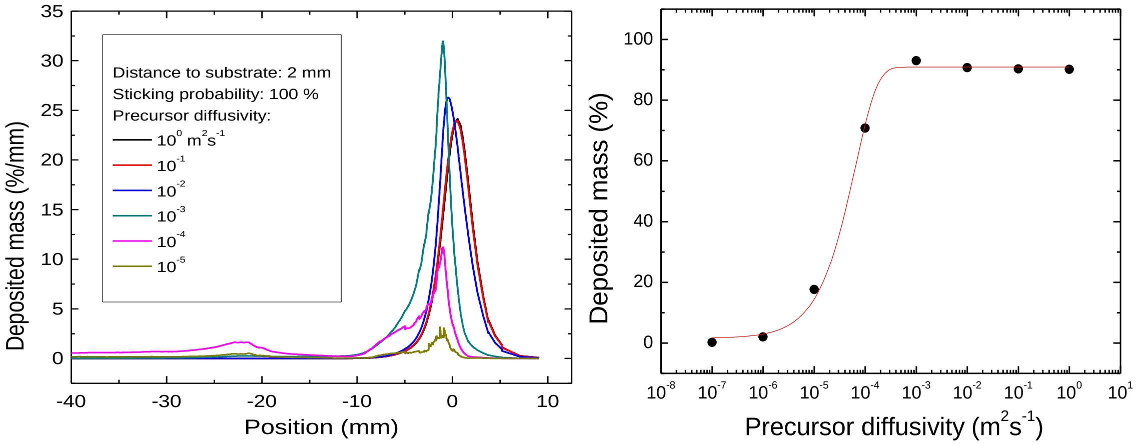

Figure 16: Deposited mass as a function of position on the substrate (left) and total deposited mass for different precursor diffusivities (right), in the absence of reactivity. The deposited mass is expressed as a percentage of the precursor mass flow into the system. The substrate is stationary, though no accumulation of deposited material is assumed.

WP8 Environment and Safety Assessment

Task 8.1: LCA parameter definition and modelling

The work in task 8.1 selected the base products and processes. The objective and scope of the assessment and the future application of the life cycle assessment and safety analysis are defined. In order to get a more comprehensive picture of the sustainability of the new packaging products and to better understand were the possible emissions of nanoparticles may occur the LCA is done together with a Risk Assessment (RA). The concept of Life Cycle Check was applied in the initial phases of the project for screening purposes to minimize the number of products and systems to be assessed and to support the definition of the functional units.

Task 8.2: Comparative LCA and LCC

The methodological approach establishing the LCA in PlasmaNice is using the international standards in the field ISO 14040:2006 & 14044:2006 [1-3]. These reports describe the objectives and scope of the LCA. This assessment is based on input from the project partners and recognized standard databases, e.g. the Ecoinvent vs.2.2 and the Simapro software. LCC is using the same model, but the methodology is not defined by a standard so far. An overview and good practice recommendation of the LCC methodology are found in the literature.

The outcome of task 1 is considered to perform life cycle assessment (LCA) and a life cycle costing (LCC) studies comparative to standard base cases. PlasmaNice had defined five case studies. In task 8.2 Case 1-Plasmacup and Case 3 binder reduction are detailed analysed using LCA or LCA combined with LCC, respectively. These two cases are assumed representative to the processing of all case studies. The following production system and materials have been modelled for the comparative LCA and LCC studies:

- Base material: Paperboard: case 1; Fine paper for case 3
- Coating materials: PLA /PE/ sol-gel[2]: for case 1; latex binder/lime stone for case 3
- Plasma treatment based on calculations for the TUT pilot equipment with and without additional nitrogen atmosphere.
- Extrusion process for paperboard and fine paper coating
- Waste scenario

The stages are defined assuming a cradle-to-factory-gate investigation including the stages of material extraction and agriculture, material processing, coating process of paperboard and waste treatment. The functional unit is chosen to be 1 m2 of coated paperboard for case 1 and 10000 m^2 for case 3. It has been shown within the PlasmaNice project that PLA can be reduced by 50% using plasma treatment. The LCA study includes also the additional application of a sol-gel coating directly on the PLA/paper surface followed by PLA finishing coating. It is relevant in connection with case study 4 on the bakery wrapping paper, as described below. In order to evaluate the life cycle four different waste treatment scenarios are described, analysed and compared with each other.

For case 1 the same service is provided using 35 g of PLA, but only 12 g of LDPE. The overall score for the PLA coating case is found to be about 20% higher. The main contribution is the reduced of material needed in the PE case where the amount of material is reduced by 66%. The PLA is contributing significantly more in the land use category and carcinogens. The process contributions are further compared and it is found that the agricultural processes are dominant with those related to the paperboard manufacturing at top three closely followed by the ”corn” process at 4th place. The processes related to the fossil fuels are of following on 5th and 7th place. Additional, for the 50% reduced PLA coating an extra layer made of sol-gel material is included. It is not part of the case 1 and naturally the results are slightly increased. Still the environmental performance of the 50% reduced PLA coating is significantly better than the original PLA coating. The study shows that the

[2] Sol-gel chemistry based spray coating (the paperboard is coated with 2.6 g/m2 sol-gel compounds)

application of plasma treatment and the additional use of sol-gel layers have only a very minor increase on the overall environmental impacts of the products considered here. Potential further improvements would therefore enable a larger decrease of environmental impacts making plasma treatments and sol-gel chemistry a potential valuable option for future product processing to gain more sustainable products. The development of new methods to produce PLA e.g. the use of the whole plants should e.g. reduce the Land use related impacts and contribute to a better environmental performance.

Four waste treatment scenarios are modelled and it is found that the impacts from the waste treatments are only a minor fraction of the overall impacts from the life cycle of the coated paperboard. Analysing the waste treatment scenarios separately, it is found that the Dutch scenario provides the least impacts and the landfill the largest. The long term effects are important to consider as the impacts of the carcinogens and the ecotoxicity largely increase compared to the short term impacts. This is important for the comparison between the incineration and landfill options.

A combined LCC/LCA has been performed for Case Study 3 on binder reduction in paper coating. It is shown that there is potential for a cost reduction using a coating mixture with reduced latex binder content in combination with plasma pre-treatment in air (PlasMatrix system) to activate the raw paper surface. The cost reduction found is about 6-7 Euro per ton dry paper. The standard coated paper costs about 440 Euro giving about 1.5% cost reduction per ton dry coated fine paper produced on a 500 m/min line 0.6m broad (about 30min production time). This may seem to be very little, but has to be seen in the context of a very huge paper production during a year. The potential annual cost saving depends on the actual production volume and should be compared against investment costs for a plasma system which depends on the line specifications (width and speed). Application of plasma pre-treatments using nitrogen or other chemicals would increase the costs and should not be considered for binder reduction only. This type of plasma treatment seems only relevant for special paper qualities giving higher prices on the market.

The price reduction for the simple case of using plasma pre-treatment to reduced latex binder compared with standard paper coating is also beneficial regarding the environmental impacts. It gives a slight decrease in the category “Resources” as the amount of fossil fuels needed is reduced. It may be concluded that the environmental impacts are overall about the same or slightly less for the reduced latex binder.

The plasma treatment allowed a reduction of the amount of latex binder giving a cost reduction and at the same time a similar (slightly decreased) environmental impact of the paper product. Cost reduction due to reduced binder use still needs to be compared with investment and maintenance costs for the plasma system. A rough estimate of investment costs for a plasma system based on the current status of the technology would be about 250 k€/m line width. For a production line of 3.5 metres wide this would be an estimated budget of 875 k€, hence clearly lower than the profit made. Maintenance costs are still hard to predict at the moment and also need to be taken into account in more detailed cost estimates.

Task 8.3: Risk Assessment

A specific risk assessment of the process equipment at the TUT facility was performed to find potential occupational health and safety problems concerning the processes used and as well as the materials used with special regard of the used nano-materials. It comprises a review of the hazards and concerns related to the manufacturing and handling of nanosized materials, this includes the results of an assessment using the precautionary matrix for the case of nano silica.

The synthesis of the nano-sized sol-gel oligomeres is done at about room temperature using commercial available precursors. The oligomers have few nanometer large amorphous shapes and are not assumed to have e.g. needle form. The suspension of the oligomeres in the isopropanol solutant is stable for some time, but capable to react to larger polymers over time. The potential spills of such suspensions therefore need to be regarded as potential nano material spills in the detailed risk assessment. An important point concerning the nano safety of the process is found during the plasma-treatment of the sol-gel oligomers. During the spray coated process nano-sized alcoholic droplets containing nanosized sol-gel oligomers are generated by the atomizer equipment.

The finalized coated paper and films will have a “polymeric” coating and have nano scale in only 1 – dimension (the thickness of the coating). Depending on the degradation of the coatings under use there could be a possibility to regenerate nano sized particles, but at this stage this is assumed to be of low likelihood, as abrasion measurements do not provide indications that the dust contains nano-particles.

The potential risk of nanomaterial hazards for workers was estimated using the precautionary matrix on the case of nano silica materials. These materials are considered to most likely to cause concern of the nanomaterials considered in the PlasmaNice project. This assessment distinguished two phases of the production process: exposure to nano-silica in manufacturing and handling of nano-silica in the sol-gel solutions, and the exposure to nano-silica in generation of nano-silica in atomizer and plasma processing. The evaluations for both production phases are the same and clearly above the “no concern” level. By that precautionary measures are considered necessary to control the potential nanomaterial hazards in the sol-gel technology This means that it is strongly recommended to collect additional knowledge on the hazards of nano silica and, in absence of that knowledge, to implement measures to control and reduce the exposure of employees to the nanomaterials.

The hazard identification (HI) has been performed with a focus on the PlasmaNice systems installed on TUT’s coating and laminating pilot line. It was intended to reveal hazards for life and health not only at TUT’s pilot line, but also for future full-scale and commercial applications. The HI did not reveal unexpected hazards. Hazards related to nanomaterials are dealt with using the principles of enclosing and engineering controls. Apart from nanoparticles, the PlasmaNice technologies require consideration of other safety issues such as: flammable and toxic solvents and other chemicals; strong electro-magnetic radiation; electrical hazards; UV radiation; pressurised equipment; and fire.

Finally, we observe that extract ventilation without proper exhaust gas cleaning may move the occupational safety problem to an environmental problem.

1.4 The potential impact and the main dissemination activities and exploitation of results

The goal of PlasmaNice project was to bring the promising results of laboratory scale tests of plasma surface treatments to an industrial level by first demonstrating their performance on pilot-scale processing, and thereby stimulating the industrial viability of promising results beyond the laboratory scale. Implementation of the recent breakthrough developments in the area (*e.g.* new possibilities to generate ultra short plasma pulses) is expected to significantly shorten the time to industrial implementation. This in turn should allow translating Europe's technological leading position in this area into a strong economically leading position as well, thus creating new business activities at the European level. Development of innovative, durable and reliable new production processes at a competitive cost was the first target of the project. This was carried out by focusing on the rational and economical use of precursor materials in nanoscale coatings, sustainable development achieved by bio-based and biodegradable raw materials, and by the minimisation of production losses while keeping in mind operator safety and environmental aspects.

The plasma equipment development in WP1 resulted in a scale-up of the PlasmaLine system from VITO from 200 mm to 600 mm width. In addition, significant improvements have been realized regarding system robustness and optimization of process conditions and treatment uniformity. Requirements for further scale-up have also been evaluated. In addition, a new type of multi-jet plasma system, PlasMatrix, was developed by AFS in WP1. The system is based on a controlled arc discharge in air and allows efficient surface pre-treatment, even at high line speeds.

Scale-up of the PlasmaLine and PlasMatrix systems to industrial line widths of 1,6 m to 2 m is possible but will still require significant redesign and engineering efforts for both systems. For line widths over 2 m, a segmented approach is technically the most likely solution.

For high line speeds (> 100 m/min) it is best to use the PlasmaLine in combination with another surface pre-treatment system such as the PlasMatrix or a corona station. In this way, a pre-cleaning of the surface is done before plasma assisted grafting of specific chemical groups with the PlasmaLine. While multi-jet air plasma systems have already been implemented successfully in industrial lines at high line speeds, the effect of PlasmaLine at high line speeds is rather limited. Speeds up to 1000 m/min seem to be far out of range for the current concept and probably also for future system generations. Best performance is obtained at line speeds below 100 m/min and as a standalone technology even below 50 m/min. This means that applications are more likely in plastic foil converting lines than in paper converting lines which typically run at higher speeds. Based on current state of the technology, both PlasmaLine and PlasMatrix can already be considered for application in label converting lines which have typically a width of 10 cm to 50 cm and run at relatively low line speeds (20 to 60 m/min).

Industrial prototypes of the PlasmaLine and PlasMatrix systems have been demonstrated to professionals involved in the conversion of flexible web materials, such as paper, film, foil and nonwovens on the International Converting Exhibition (ICE) in Munich, Germany in November 2011.

The packaging industry, particularly food packaging, is actively seeking an alternative to replace currently used fluoropolymer-based grease-barrier materials. In PlasmaNice project, specific attention was targeted to the production of bio-based biodegradable food packaging materials. Replacing the non-degradable materials such as polyethylene and fluoropolymer films with bio-based materials provides an alternative to incineration of the waste and reduces the pollution of the environment by natural decomposition, filling the European standard for biodegradability and composting (EN 13432:2000). Furthermore, substituting the polyolefin and fluoropolymer films and coatings with fully bio-based materials offers a CO_2 -neutral alternative for these packaging materials. This improvement is also based on reduced materials consumption by the replacement of the currently used relatively thick laminates with nanoscale coatings.

Sol-gel coating process with fast UV-curable system was successfully transferred from laboratory back coating process to inline-environment at speeds of 50 and 150 m/min at VTT and TUT as well as to the industrial trials carried out at SB. The sol-gel coatings were successfully applied on several different substrates including uncoated and PLA coated kraft paper, paperboard and polymeric films such as polyamide (PA) and high-density polyethylene (HDPE). The sol-gel coated specimens showed improved grease barrier and oxygen barrier performance. Furthermore, the hybrid sol-gel coating did not interfere with the biodegradability of the paperboards.

PlasmaNice results obtained regarding to up-scaling of the coating process as well as the improved performance by using the hybrid thin coatings, suggest that the particular combination could be used in several reel-to-reel applications to provide functional properties to different substrates. For example from the material and processing development point of view, the results show potential to replace existing harmful silicone or fluorine-based grease barrier coating. It could have remarkable impact in the future since there has been recent discussion about the alternatives for the existing grease barrier coating. Especially, bio-based grease barrier packaging approach could increase the number of green solutions in future. Nevertheless the PlasmaNice results indicate that the oxygen barrier performance of existing polymeric packaging films PLA or PE can be improved. Especially in food packaging applications the increased shelf-life of the food products would decrease the amount of food waste.

Further exploitation of PlasmaNice results is foreseen in follow-up R&D and technology dissemination projects on national and EU level as well as industrial process innovation projects. As indicated above, further scale-up of the PlasmaLine and PlasMatrix systems is still needed as well as further improvement of the process efficiency. Implementation on small width industrial lines is already possible in the near future but will also require limited extra engineering efforts. Main partners involved will be VITO and AFS.

A new on-line spectroscopic monitoring method was developed inside the project to follow the efficiency of coating deposition. It represents a new tool for improving quality control of plasma assisted coatings and also may be used for other types of reel-to-reel deposited coatings. The method, for which a patent application has been submitted, will allow evaluating the homogeneity of deposited coatings, monitor their quality and facilitate reduction of coating thickness in control manner. Altogether, the new method can increase the competitive position of industrial coating producers.

A new knowledge in chemical characterization and metrology obtained during comprehensive characterisation of materials (coatings, substrates, sols) will be further explored for studies of similar systems of organic coatings for different applications in laboratories of partners involved. Obtained knowledge and metrology will increase the level of analytical service and expertise at laboratories of partners involved providing state-of-the art service in future for industrial and academic partners.

The results of application of TOF-SIMS analytical method for characterisation of depth distribution of elements and of functional groups in siloxane coatings on polymer substrates will be published in scientific articles. This will help to improve applications of siloxane based materials as adhesion promoters, sensors and for corrosive protection, etc.

The equipment, process and material related know-how developments in this project will be used in continued industrial research, development and innovation projects. Scientific dissemination is foreseen on conferences (e.g. Tappi PLACE 2013, Dresden, Germany and EUROFINISH 2013, Ghent, Belgium) and workshops as well by means of publications in peer reviewed journals. Commercial exploitation of the developed plasma systems will be done by AFS (project partner) in close collaboration with VITO. Results will be shown to the broad public on industrial fair trades like the K2013 (Düsseldorf, Germany) and ICE 2013 (Münich, Germany).

Main dissemination activities

For the dissemination of the PlasmaNice project results to experts and non-experts, various activities have been performed:

- PlasmaNice logo and animation character Mr. PlasmaNice have been created and used in dissemination.
- Development of dissemination material for partners about PlasmaNice in order to better explain purpose and goals of the project but also the context of nanotechnology. The approach chosen is to be transparent and offer different levels of detail to satisfy readers with different backgrounds (also non-experts).

- Different documents have been developed to communicate the PlasmaNice project to non-experts & experts. Three brochures have been created, each one both with a digital and a printable version available. The brochures are about the following subjects:
    1. PlasmaNice in general
    2. Risk Assessment and Life Cycle
    3. Project results (draft only at the moment)
- Other material has been developed to enable communication in different occasions:
    - Cards to be sent by e-mail, to use as imagery on websites or as give away during meetings and events
    - Posters to hang in trade fair stands at the office
    - Video animations of the brochures to be used in websites or social networks (e.g. YouTube)
- Several publications have been made to disseminate project results including posters, conference presentations, lectures in workshops, articles and brochures.

1.5 Project website and contact details

Project website: http://hlab.ee.tut.fi/plasmanice/

PlasmaNice contact details

Project Coordinator
Dr. Johanna Lahti
Tampere University of Technology
Department of Energy and Process Engineering
Paper Converting and Packaging Technology
P.O.Box 589, FI-33101 Tampere, Finland

Tel: +358 40 849 0156
Fax: +358 3 3115 3751
E-mail: johanna.lahti@tut.fi

Figure 17 PlasmaNice logo

PlasmaNice partners and contact persons

- Tampere University of Technology (TUT), Finland (Coordinator)
  Johanna Lahti
- Flemish Institute for Technological Research (VITO), Belgium
  Dirk Vangeneugden
- Fraunhofer Institut Silicatforschung (Fh-ISC), Germany
  Klaus Rose
- Technical Research Centre of Finland (VTT), Finland
  Kalle Nättinen
- Eindhoven, University of Technology (TUE), The Netherlands
  Richard van de Sanden
- Jozef Stefan Institute (JSI), Slovenia
  Janez Kovac
- Stora Enso Oyj (SE), Finland
  Ville Ribu
- AFS Entwicklungs- und Vertriebs GmbH (AFS), Germany
  Gerhard Arlt
- Segers & Balcaen NV (SB), Belgium
  Paul Balcaen
- Print 2000 Nyomda Kft (PNK), Hungary
  Roland Meszaros
- SurA Chemicals GmbH (SurA), Germany
  Guido Leibeling
- Sappi Netherlands Services B.V. (Sappi), The Netherlands
  Ronald van de Laar
- Technical University of Denmark (DTU), Denmark
  Frank Markert
- 2B Consulenza Ambientale de Leo Breedveld (2B), Italy
  Leo Breedveld