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Effect of the Electron Transport Layer on the Interfacial Energy Barriers and Lifetime of R2R Printed Organic Solar Cell Modules

Marja Vilkman,†,* Kaisa-Leena Väisänen,‡ Päivi Apilo,§ Riccardo Po,¶ Marja Välimäki,⊥ Mari Ylikunnari,‖ Andrea Bernardi,§ Tapio Pernu,† Gianni Corso,§ Jani Seitsonen,¶ Santtu Heinilehto,⊥ Janne Ruokolainen,‖ and Jukka Hast‡

†VTT Technical Research Centre of Finland, Tietotie 3, P.O. Box 1000, FI-02150 Espoo, Finland
‡VTT Technical Research Centre of Finland, Kaitoväylä 1, P.O. Box 1100, FI-90571 Oulu, Finland
§Eni S.p.A, Renewable Energy & Environmental R&D, Via Fauser 4, 28100 Novara, Italy
‖Department of Applied Physics, Aalto School of Science, P.O. Box 15100, FI-00076 Aalto, Finland
⊥University of Oulu, Center of Microscopy and Nanotechnology, Erkki-Koisokanttilan katu 3, P.O. Box 7150, FI-90570 Oulu, Finland

ABSTRACT: Understanding the phenomena at interfaces is crucial for producing efficient and stable flexible organic solar cell modules. Minimized energy barriers enable efficient charge transfer, and good adhesion allows mechanical and environmental stability and thus increased lifetime. We utilize here the inverted organic solar module stack and standard photoactive materials (a blend of poly(3-hexylthiophene) and [6,6]-phenyl C61 butyric acid methyl ester) to study the interfaces in a pilot scale large-area roll-to-roll (R2R) process. The results show that the adhesion and work function of the zinc oxide nanoparticle based electron transport layer can be controlled in the R2R process, which allows optimization of performance and lifetime. Plasma treatment of zinc oxide (ZnO) nanoparticles and encapsulation-induced oxygen trapping will increase the absolute value of the ZnO work function, resulting in energy barriers and an S-shaped IV curve. However, light soaking will decrease the zinc oxide work function close to the original value and the S-shape can be recovered, leading to power conversion efficiencies above 3%. We present also an electrical simulation, which supports the results. Finally, we study the effect of plasma treatment in more detail and show that we can effectively remove the organic ligands around the ZnO nanoparticles from the printed layer in a R2R process, resulting in increased adhesion. This postprinting plasma treatment increases the lifetime of the R2R printed modules significantly with modules retaining 80% of their efficiency for ~3000 h in accelerated conditions. Without plasma treatment, this efficiency level is reached in less than 1000 h.

KEYWORDS: organic solar cell modules, R2R printing, lifetime, adhesion, energy barrier, zinc oxide

INTRODUCTION

Several groups have demonstrated roll-to-roll (R2R) processes for flexible solar cells with the maturity level of high volume production increasing yearly.1−5 Organic materials are one of the promising options for flexible solar cells, especially as novel high-performance organic photoactive materials are continuously emerging, showing power conversion efficiencies (PCE) above 14%.4 In addition to a cost-efficient processes and high performance, the lifetime of the solar cell modules needs to be at an acceptable level in order to meet market demands. Based on estimates5 and due to short energy payback time of OPVs, lifetimes of 10 years and a PCE of 10% could allow OPVs even to compete with traditional silicon photovoltaics in addition of utilizing them in niche applications where lightweight, transparency and flexibility are of high importance. However, based on some calculations, even efficiencies of 2% and lifetimes of 3−5 years would make organic solar cells equivalently priced with current conventional solar energy technologies.5

The stability is measured using standardized tests in accelerated conditions,6 which then allow estimates of real lifetimes for the modules.8 In addition, OPVs have been tested in harsh outdoor conditions.9 Lifetime of organic photovoltaics (OPV) has been improving,10 e.g., due to more stable materials,11−14 proper selection of solvents,15 better encapsulation processes,16,17 and transferring from the conventional unstable device structure to one with enhanced stability.18 The degradation of well-encapsulated flexible solar cells is known to start from edges of the modules, where water and oxygen can diffuse into the device easiest.9 Degradation mechanisms include photo-oxidization of...
the active layer and delamination at interfaces (often between the active layer and the hole transport layer in the case of the inverted design\textsuperscript{29}), which leads to decreased active area in the modules and thus to lower performance.\textsuperscript{20}

Interfacial layers, i.e., the electron transport layer (ETL) and hole transport layer (HTL), are key elements in gaining high performance and stable OPVs. As we have presented previously,\textsuperscript{30} postprinting plasma treatment of the printed ZnO nanoparticle ETL will increase its adhesion on indium tin oxide (ITO) and improve the module performance due to removal of the organic insulating ligands around the nanoparticles. In addition, many other methods, e.g., UV ozone treatment\textsuperscript{22} and chemical additives,\textsuperscript{23,24} have been used to modify the ZnO layer to match its energy levels with the photoactive blend for maximizing the performance. The encapsulation process itself is also known to affect the electrical properties of the solar cells, especially if pressure sensitive adhesives (PSA) are used.\textsuperscript{25} We present here an optimized R2R process for inverted organic solar cell modules and a model to explain the changes and the appearance, or recovery, of an S-shape in the current–voltage characteristics due to postprinting plasma treatment of ZnO, light soaking, and encapsulation. A well-known photoactive blend, i.e., a mixture of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C61 butyric acid methyl ester (PCBM), is used as the model material, allowing us to concentrate on the interface effects. We also compare the results with our previously presented data where indene-C60-bisadduct (ICBA) with lower LUMO level was used as the acceptor molecule.\textsuperscript{26} Modules with ICBA and PCBM require different amounts of light soaking, emphasizing the importance of energy level alignment. Finally, we show also that the lifetime of R2R printed inverted organic solar cells can be improved by increasing the adhesion at the ETL interface.

**MATERIALS AND METHODS**

Figure 1 shows a photograph of the R2R printed OPV module, a schematic of the inverted OPV device stack and the processing methods for each layer. An ITO-coated PET roll from Eastman was patterned by a screen printed etchant (Isishape HiperEtch 09S Type 40 paste, Merck) and used as the substrate and transparent electrode. A 5 wt % ZnO nanoparticle/ethanol dispersion from Avantama (15 nm particles, stabilized with organic ligands, product 7022, work function 4.3 eV) was used as the ink for the gravure printed electron transport layer and it was either plasma treated or utilized as such. The plasma process was performed for the printed and dried ZnO film in the R2R line at a speed of 2 m/min, using a N2/Ar (1/3) mixture and 200 W power in atmospheric pressure. As the R2R plasma process is not performed in vacuum and the plasma unit is open to air, there is always some (unknown) amount of oxygen also present, which might have an effect on the plasma process.

A mixture of regioregular P3HT (no. 4002-E, Rieke Metals) and PCBM (purity 99.5%, Nano-C) was dissolved in 1,2-dichlorobenzene in a weight ratio of 1:0.63 (P3HT:PCBM) and used as the ink for the gravure printed photoactive layer. A ready PEDOT:PSS paste (EL-P5015, Agfa) was used to screen print the hole transport layer and the top electrodes were screen printed with an Ag paste (XPVS-670) from PPG. The modules were printed in atmospheric R2R environment, using gravure and rotary screen printing technologies, as described in previous publications.\textsuperscript{27,28} Printing speeds and drying temperatures were the following, respectively, 1.5 m/min and 140 °C for ITO etching, 8 m/min and 120 °C for ZnO and P3HT:PCBM printing, 2 m/min and 130 °C for PEDOT:PSS and Ag printing. After the R2R printing process, the modules were cut and laminated as sheets inside a N2 (g) glovebox with a pressure sensitive adhesive (EL-92734 from Adhesive Research) and a UV-blocking flexible barrier film (ATCJ from Amcor, wavelengths below 360 nm are blocked), using a copper tape for making the contacts.

The encapsulated OPV modules were stressed under accelerated aging conditions in Atlas XXL+ weathering chamber and frequently electrically characterized during 7000 h (offline measurement, AM1.5). The voltage range for the measurements was from −1 to 14 V. The aging conditions were 65 °C and 50% RH under constant sunlight at an exposure irradiance level of 42 W/m² (300−400 nm), according to the ISOS-L-3 protocol.\textsuperscript{7}

Electrical simulations for a single solar cell were made to study the S-shape phenomena in the IV curve. A spice model for the simulation was created with Analog Devices LTspice simulator.
Surface properties of the R2R printed ZnO layer were studied with contact angle measurements and X-ray photoelectron spectroscopy (XPS). Contact angles of the photoactive ink (P3HT:PCBM in 1,2-dicholobenzene) were measured on top of the R2R printed ZnO layer with and without the postprinting plasma treatment on PET-ITO using CAM 200 from KSV Instruments. XPS measurements were performed using a Thermo Fisher Scientific ESCALAB 250Xi (Thermo Fisher Scientific, U.K.) XPS system. A monochromatic Al Kα (1486.6 eV) X-ray source was used in the measurements. High-resolution elemental spectra were recorded with a 20 eV pass energy with the base pressure of the analysis chamber set to $2 \times 10^{-9}$ mbar. A charge compensation system using low-energy electrons and argon ions was used to compensate the charging of the nonconducting samples.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to take the cross-section images of the OPV module. The sectioning from the encapsulated modules was carried out using a Leica UC7 ultramicrotome under cryo conditions at $-100 \degree C$. The thin (70 nm) sections were imaged using a 300 kV JEOL JEM-3200FSC TEM operated at liquid nitrogen temperature. The microtome smoothed surface of the remaining encapsulated module was sputter coated with 10 nm of platinum and imaged using a JEOL JSM-7500F SEM.

## RESULTS AND DISCUSSION

Table 1 shows mean values (calculated as an average from three modules) for short circuit current ($I_{SC}$), open circuit voltage ($V_{OC}$), fill factor (FF), and power conversion efficiency (PCE) for modules with both ETL options (i.e., ZnO with and without postprinting plasma treatment). Data was collected right after processing, after encapsulation, after 1 h light soaking and after 47 h exposure under sunlight, humidity, and elevated temperature, with the same stressing parameters used in the 47 h exposure as in accelerated testing. The corresponding IV curves are shown in Figure 2. The data shows that the original performance is quite similar both with and without postprinting plasma treatment for ZnO. In our previous study,21 we used 40 nm sized ZnO particles, and removal of the (insulating) ligands had a clear improvement effect on both adhesion and the electrical performance. However, here we used an improved formulation with smaller 15 nm particles, and the original electrical performance was good with and without the postprinting plasma treatment. The modules without plasma treatment were actually slightly better than the plasma treated ones. We can also see that the PSA encapsulation process has a negative effect on the performance, and especially in the plasma treated modules, we also see an S-shape in the IV curve. The drop in performance due to lamination is partly related to the barrier films, which block part of the spectrum. In addition, the S-shape in general has been linked to many different phenomena at the OPV interfaces.29-31 In cases of PSA lamination of inverted ZnO-containing structures, the origin of the S-shape is proposed to relate to absorption of oxygen on the ZnO nanoparticles26 and subsequent decrease in ZnO conductivity and increase of ZnO work function, which leads to energy barriers at the ETL/acceptor interface.31 As expected, we see that light soaking helps to
recover the module performance: An hour of light soaking improves the performance close to the original values. In addition, 47-h sunlight exposure in the weathering chamber at elevated temperature and humidity increases the performance even above the original values, reaching a PCE over 3% for both sample groups. These results are in line with the study by Lilliedal et al. where the effect of postproduction treatments on the S-shape was reported in detail.32

The UV-induced increase in performance is common for zinc oxide containing solar cells where UV light is needed to remove oxygen from the ZnO layer and to recover the modules after PSA lamination.26 However, the PSA lamination itself does not lead to oxygen absorption, especially when processed under nitrogen, but it might act as a barrier to trap the previously absorbed oxygen molecules inside the modules. Without the barrier film and measured in an N2 glovebox, oxygen is more easily released from the ZnO layer, which can result in very fast recovery of the S-shape upon illumination, making it too fast to be detected by the IV measurements. In addition to removing oxygen from the ZnO layer, UV light is known to degrade the active layer. This degradation is slower than the oxygen release effect, resulting in the initial increase in performance, followed by a slower decay. The further PCE increase at 65 °C, 50% RH, and under sunlight might be partially also due to temperature-induced improved adhesion and charge transport at the P3HT:PCBM/PEDOT:PSS interface, which usually needs an extra annealing step for achieving the best interfacial contact.33

Interestingly, the plasma treated modules need more time to recover from the encapsulation process when compared to the modules without plasma. In addition, when comparing the results to our previously published data27 with the same layout and a very similar process but using ICBA instead of PCBM as

![Figure 4. S-shaped IV-curve of damaged solar cell reproduced with simulation model.](image)

Figure 5. Current density ($I_{SC}$), open circuit voltage ($V_{OC}$), fill factor (FF), and power conversion efficiency (PCE) of the different modules as a function of time under sunlight, 65 °C temperature, and 50 RH% humidity. The data have been normalized relative to the initial performance before encapsulation.
the acceptor, we see clear differences in the intensity of the effect of encapsulation and light soaking. With ICBA, we need 174 h of light exposure to recover the modules after PSA lamination. With PCBM, already 1 h is enough. Thus, we made an electrical simulation of the module’s equivalent circuit in order to clarify the electrical defect caused by the lamination process. Electrical simulation was made based on the equivalent circuit of an undamaged solar cell (Figure 3a) and a degraded solar cell (Figure 3b). Based on the model, we propose that the S-shaped IV curve can be modeled with a partially semiconducting interface as presented in Figure 3b. When an additional diode and resistor are placed in parallel in the equivalent PV circuit, the solar cell becomes less conductive when the direction of the current is reversed and the diode starts blocking the current.

The simulation result is presented in Figure 4 where an S-shaped IV curve was successfully reproduced. Based on the simulation, adding just a resistor does not result in the S-shape. Thus, the S-shape, i.e., the effect oxygen absorption/trapping due to PSA lamination, cannot be explained solely with changes in the ZnO conductivity.

The work function of ZnO is known to be sensitive to surface functionalization, e.g., by humidity, hydrocarbons, and oxygen, and it can either increase or decrease depending on the functionalization material.30,34−36 Oxygen absorption will increase the absolute value of the work function, and the presence of hydrocarbons will lower it, implying that removing the organic ligands by plasma will increase the ZnO work function. For efficient electron injection, the conduction band minimum (CBM) of ZnO needs a close alignment with the active layer acceptor’s LUMO level.37,38 An increase of the energy level in the ZnO can lead to a partially semiconducting interface (Figure 3b) and induce an S-shaped IV curve in inverted OPVs if the difference between the acceptor LUMO level and the ZnO CBM becomes too large.31 The significant difference in recovery time between ICBA and PCBM can be explained with the different energy levels of the acceptors. As the work function of ZnO increases during encapsulation/oxygen trapping, the ICBA molecule, with a lower LUMO level, suffers more from the energy level shift of ZnO and thus the barrier for electron transfer becomes significant after trapping of oxygen during lamination. Simultaneously, it needs heavier light soaking to decrease the ZnO CBM back to an appropriate level vs ICBA LUMO level. For PCBM with a higher LUMO level, the effect is not as strong. The same applies to the plasma ON and plasma OFF samples. Removing the ligands with plasma treatment increases the ZnO work function, which makes the plasma treated modules more sensitive to the PSA lamination (i.e., oxygen trapping) as there is already originally a larger energy gap between the acceptor LUMO level and the ETL CBM.

The initial measurements revealed that the plasma process has an effect on the energy levels and recovery time after lamination. In addition, we wanted to see if the plasma process has an effect on module lifetime as well. Thus, after the initial measurements and 1 h light soaking, the modules were put under accelerated aging conditions. Figure 5 shows normalized values for $I_{SC}$, $V_{OC}$, FF, and PCE as a function of time and Figure 6 the IV curves at different times during aging at the accelerated conditions. When different modules are compared, the results clearly show that the modules containing the standard ZnO nanoparticle layer (without plasma treatment) suffer a significant performance loss which reaches levels less than half of the initial value before 2000 h have passed. However, if the ZnO layer has been plasma treated, there is significant improvement in lifetime and those modules maintain their PCE values above 50% of the initial value (before light soaking) for more than 7000 h. The modules without plasma treatment show mainly a resistive problem after aging (i.e., no S-shape), which suggests that adhesive failures at the weak ZnO interface are dominating. With plasma treatment, and better adhesion at the ZnO interface, we see also the S-shape after aging, which can lead us assume that the loss in performance is partly due to energy barrier issues at the interfaces.20 Most likely, the highly hygroscopic PEDOT:PSS interface is more sensitive to the humidity exposure but the effect of humidity on the ZnO layer cannot be ruled out as the ZnO work function is known to be dependent on humidity.35,34

In order to better understand the effect of plasma treatment, we studied the samples with cross-section SEM and TEM. The samples were cut with a cryomicrotome, and we saw already during the cutting phase that the samples behaved very differently, as shown in Figure 7. The samples without plasma treatment were easily broken during cutting and there was a large gap between the separated layers. The plasma treated samples showed only a small gap. TEM images in Figure 7...
clearly show that the weakest interface without plasma treatment is the ZnO layer. It looks like part of the ZnO nanoparticles remain on ITO and the structure breaks most likely cohesively inside the ZnO layer and/or at the ZnO/P3HT:PCBM interface. For plasma treated samples, the weakest point is the P3HT:PCBM/PEDOT:PSS interface as the P3HT:PCBM layer adheres to the ZnO during cutting. This observation, and results from the literature,\textsuperscript{19} naturally encourages us to focus in the future on the HTL interface and to improve its adhesion on the photoactive layer.

We performed also contact angle measurements on the R2R printed ZnO layer, with and without plasma, as they give important information about leveling and thus printability of the ink. The measurement showed that the contact angle of P3HT:PCBM ink is very low (~11°) and approximately the same for both films, i.e., there should not be any problems in leveling of the photoactive ink on the ZnO layer, independent of plasma treatment. It can be also assumed that the morphology of the P3HT:PCBM layer is not affected by the ZnO plasma treatment as the ink behaved similarly on both ZnO layers and the initial electrical performance was approximately the same. Thus, the main effect of plasma treatment is the improved cohesive adhesion of the ZnO layer and interfacial adhesion between ZnO and the P3HT:PCBM layer.

So far, we had observed that plasma treatment increases lifetime and adhesion at the ZnO interface. However, we wanted to study the effect of plasma treatment in more detail in order to reveal underlying mechanisms for improved lifetime. Specifically, we wanted to understand if the R2R atmospheric N\textsubscript{2}/Ar plasma treatment would have similar surface defect passivation effects as, e.g., fluorine plasma, demonstrated by Polydorou et al.\textsuperscript{39} Previously,\textsuperscript{21} we have shown via attenuated total reflection-Fourier-transform infrared spectroscopy (ATR-FTIR) and spin-coated >100 nm thick ZnO films that Ar plasma treatment will remove the organic ligands from the ZnO layer. As the imaging depth in the ATR-FTIR method (~1 μm) is much higher than the thickness of the printed ZnO layer (~25 nm), it was not possible to study the actual printed ZnO by FTIR as the substrate bands covered all the bands for the ZnO layer. Thus, we now used XPS to study the elemental composition of the R2R printed ZnO layer, as it is a surface measurement and studies only the top 0−10 nm range of the film. In addition to the elemental
composition, the XPS method also allows the study of the chemical state of each element at the surface, giving important information about possible plasma-induced modifications to the electronic state of the ZnO nanoparticles.

Table 2 shows the elemental composition of the R2R printed ZnO layer before and after plasma treatment. As seen from the table, the amount of carbon (i.e., ligands around the ZnO particles) decreases during plasma treatment, as expected. In addition, the shape of the C 1s peak (see Figure 8) and the relative atomic percentages of each carbon type (see Table 3) change during plasma treatment, indicating that the main effect of plasma treatment is to break the (ZnO)—O bond that attaches the ligands to the ZnO nanoparticle. The peak positions or shapes of the other elements did not significantly change. Thus, we suggest that the atmospheric N2/Ar treatment does not change the chemical state of the ZnO material, and the main reason for improved adhesion and lifetime is detachment of the organic insulating ligands from the nanoparticles.

Another mechanism to consider for the ligands to be removed from the ZnO is through thermal exposure. In our plasma process, the effective length of the plasma unit is approximately 10 cm, meaning that the ZnO layer is exposed to plasma (and possible plasma-induced heating) for three seconds (Web speed was 2 m/min). However, this short time period is much less than the heat treatment during the drying steps (30 s for the ZnO layer and altogether 5 min at 120–130 °C if all drying steps from ZnO to Ag are included). It is thus clear that the possible heating during the plasma treatment does not have a significant effect on the removal of ligands or sintering of ZnO particles and it is the N2/Ar plasma that removes/detaches the ligands.

To summarize all the studies, Figure 9 shows a schematic of the effect of ZnO work function (Φ) on the IV curve of the OPV module. Oxygen (due to PSA lamination), plasma treatment (i.e., removal of organic ligands), and humidity (during aging) are suggested to increase the absolute value of the ZnO work function, which leads to the S-shape in the IV curve (red) if the energy level differences between ZnO and the acceptor becomes too large. UV exposure has an adverse effect and can decrease the ZnO work function and recover the modules after lamination (green IV curve).

<table>
<thead>
<tr>
<th>name</th>
<th>peak BE (eV)</th>
<th>atomic %</th>
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<tbody>
<tr>
<td>C 1s C—C, C—H</td>
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<td>40.54</td>
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<td>286.29</td>
<td>49.67</td>
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<tr>
<td>C 1s O—C=O, O=O</td>
<td>288.70</td>
<td>9.79</td>
</tr>
</tbody>
</table>

Table 3. C 1s XPS Binding Energy (BE) Peaks and Atomic Percentages of Each Carbon Species for the R2R Printed ZnO Layer with and without Plasma Treatment

Figure 9. Schematic of the effect of ZnO work function (Φ) on the IV curve of the inverted OPV module. Oxygen (due to PSA lamination), plasma treatment (i.e., removal of organic ligands), and humidity (during aging) are suggested to increase the absolute value of the ZnO work function, which leads to the S-shape in the IV curve (red) if the energy level differences between ZnO and the acceptor becomes too large. UV exposure has an adverse effect and can decrease the ZnO work function and recover the modules after lamination (green IV curve).
ICBA was used as the acceptor - leading to the largest difference between the ZnO CBM and acceptor LUMO level. Logically, these modules took the longest time to recover via UV exposure. The effect of humidity during aging is also suggested to contribute to changes in the ZnO work function, even though the highly hygroscopic PEDOT:PSS layer is most likely the most sensitive layer against humidity. However, in case of humidity exposure, the S-shape cannot be recovered by light soaking as it is not possible to remove moisture form the interfacial layers via UV treatment.

**CONCLUSIONS**

We presented a R2R process for organic photovoltaic modules and studied how (i) postprinting plasma treatment for the ZnO nanoparticles (i.e., removal of organic ligands), (ii) PSA encapsulation process (i.e., oxygen trapping), (iii) UV exposure (i.e., oxygen desorption), and (iv) acceptor LUMO level affect the occasionally observed S-shape in the current–voltage characteristics. Also, further interpretation of the experimental results were performed via electrical circuit modeling. We conclude that, for fresh modules, the S-shape in the IV curve is related to an increased energy barrier between the acceptor and the electron transport layer. The energy gap can be controlled, and S-shape removed, by decreasing the absolute work function value of the ETL, e.g., via UV exposure. The energy gap can be controlled, and S-shape removed, by decreasing the absolute work function value of the PEDOT:PSS layer.

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The results emphasize the importance of interfaces and give us guidelines for achieving the best performance and lifetime with a carefully selected ETL material and process. For example, the PSA encapsulating induced S-shape could be avoided by selecting an ETL and active layer accepting material with closely matching energy levels. This would avoid the need for long light soaking, which is not suitable for industrial large-area processing of solar cell modules. In addition, it is clear that in addition to searching for stable materials as such, it is equally important to develop processes and materials that can increase the mechanical stability at the interfaces in order to improve the lifetime of flexible solar cells.

**AUTHOR INFORMATION**

**Corresponding Author**

*E-mail: marja.vilkman@vtt.fi.* Phone: +358 50 3586644.

**ORCID**

Marja Vilkman: 0000-0003-1354-6742

Riccardo Po: 0000-0002-8374-195X

**Author Contributions**

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

**Notes**

The authors declare no competing financial interest.

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