Printed 2D Proton Sensor for In-Situ Measurement in Glue Lines [†]

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Abstract: A screen printed pH sensor was developed using a PANI layer as a proton sensitive material for the in-situ measurements of matrix cross-linking. The sensor showed a linear response in a broad pH range (3–10) and had an evident cross-talk to Cl[−] ions. Preliminary in-situ measurements showed a substantial signal change during the cross-linking process.

Keywords: printed pH sensor; PANI layer; in-situ proton sensing

1. Introduction

Wood industry uses conventional methods (i.e., pulling, bending, and ripping) for the characterization of their products. These methods are normally cost-, material- and time-consuming, ex-situ, destructive and incompatible with the state-of-the-art connectivity and data evaluation procedures that enable the modern industrial Internet of Things (IoT). The performance of wood composites, the mechanical core of many wood-related products, is strongly influenced by the type and degree of cross-linking of the matrix. The in-situ measurement of temperature, proton-concentration and impedance in the press-moulding process can greatly improve the quality of the products. These sensors have to be 2D (easy integration), robust (withstanding the pressures), cheap and have to act as a part of the matrix material without any mechanical or any other influence on the end-product (the sensors will not be removed after processing). The traditional sensor technologies (e.g., silicon-based) do not fulfill most of the requirements stated above; therefore, alternative sensors such as printed ones not only complement the silicon technology but also open new possibilities and applications that were so far not feasible [1].

Printed electronics (PE) enables the development of sensors and smart systems with unique characteristics such as flexibility, conformability, transparency, biocompatibility and the possibility of easy integration and even fabrication of sensing parts over a large area. Moreover, the use of additive processes allows PE devices to be fabricated waste-free and at very low-cost [1]. Printed sensors were identified to be the most suitable sensor-platform for the undistorted, real-time and in-situ measurements of cross-linking kinetics, curing and aging of glue joints, coating and composites. Although some studies already show the high potential of printed sensors for the in-line impedance detection [2], printed pH sensors selectively detecting proton formation can give an in-depth information of the chemical cross-linking.

In the present paper, a screen printed proton sensor based on polyaniline (PANI) has been developed for the in-situ measurement of the cross-linking of glue lines inside the wood composite. The sensors were characterized with standard buffer solutions and first preliminary in-situ measurements were conducted.

2. Materials and Methods

2.1. Sensor Development

A three electrode structure was manufactured via screen printing of Ag (DuPont 5028, Du Pont Limited, Michigan, USA), carbon (SD 2843 HAL, Lackwerke Peters GmbH + Co KG, Kempen, Germany) and insulator (Thermo-Jet®, Proell KG, Weißenburg in Bayern, Germany), as seen in Figure 1a. A proton-sensitive polyaniline (PANI) layer was deposited on the working electrode with the selective electropolymerization, according to the literature [3]. Briefly, printed electrodes were positioned into the 3D-printed holder, as shown in Figure 1b. 0.1 M monomeric aniline prepared in 1 M HCl was deposited over the electrodes and a PANI electropolymerization was performed by cyclic voltammetry (CV) from -0.2 V to 1.0 V using portable potentiostat (μ STAT 4000P, DropSens, Llanera, Spain). After first 12 CV cycles, the depleted solution was removed and a fresh aniline solution was deposited again, followed by another 12 CV cycles. The growth of the oxidation peak at the potential of 0.35 V indicates the formation of the PANI layer.

Figure 1. (a) A three-electrode sensor structure manufactured with screen printing of silver (contact pads, connections and reference electrode) and carbon (working and auxiliary electrode); (b) set-up of the parallel pH calibration measurements in a 3D printed measurement housing.

2.2. Sensor Characterization

The performance of printed sensors was characterized with the parallel pH measurements (Figure 1b) of open circuit potential (OCP) between the working and the reference electrode. Firstly, measurements with standard pH solutions between pH 2 and 10 were performed. The buffers had different elemental structure: pH 2—citric acid, HCl, NaCl; pH 3 and 4—citric acid, NaOH, NaCl; pH 5 and 6—citric acid, NaOH; pH 7 and 8— KH_2PO_4 , NaOH; pH 9 and 10—boric acid, NaOH, KCl. Due to the potential cross-sensitivity of other ions, such as Cl^- , on the PANI layer [4], a second reference buffer solution (McIlvains solution) with fixed elemental structure (Na_2HPO_4 , citric acid) was prepared and used for the calibration measurements.

2.3. In-Situ Measurements

The in-situ measurements were performed according to the scheme in Figure 2. A wooden-substrate was covered with the glue (Primere 10F152, Metadynea Austria GmbH, Krems an der Donau, Austria) and the proton sensor as well as the thermocouple (type K) was positioned on the top of the glue surface. The proton sensor was turned upside down to ensure the direct contact of the glue with the PANI surface. The sensors were covered with another wood part, put into the hot-press and a 40-min cross-linking procedure was conducted with a constant pressure of 20 bars and temperature of 120 °C (ramp: 5 °C/min).

Figure 2. Schematic presentation of the experimental setup for the in-situ measurements of cross-linking.

3. Results and Discussion

Measurements with standard pH solutions (Figure 3a) show a linear response of pH values between 2–4 and 9–10, while the measured values are somehow shifted but retain the same slope between pH 5–8. The latter was assigned to the effect of the Cl^- ions which evidently also react with the PANI surface and increase the signal. A second round of testing using the McIlvains buffer solution free of Cl^- supported our previous suggestion (Figure 3b); the sensor possessed a perfect linear response between pH 3 and 8 ($R^2 = 0.993$) with high sensitivity (70 mV/pH).

Figure 3. Characterization of the printed pH sensor with standard pH buffer solutions: (a) commercial pH buffers with different elemental structure and (b) McIlvains buffer solutions.

For the in-situ testing, the sensor was positioned on the wooden-substrate, as shown in Figure 4a, that was glued to another one with a cross-linking of binder with and without the hardener. The preliminary results (Figure 4b) show the evident signal of the printed sensors with the maximal absolute signal change of 140 mV. Although the signal is evidently influenced by the temperature profile, the additional peak in the case of gluing with hardener suggests the chemical formation of protons after reaching 70 °C. This observation is also in agreement with the cross-linking chemistry, as the formation of the H^+ is initiated above 60 °C.

Figure 4. (a) Integration of the printed proton sensor for the in-situ measurements of cross-linking and the thermocouple; (b) in-situ measurements of pH and temperature during the hot-press gluing process.

4. Conclusions

The 2D printed proton sensor was manufactured using screen printing of the three-electrode structure and subsequent selective electropolymerization of PANI on top of the working electrode. The sensor shows a linear response between pH 3 and 8, and has a noticeable cross-sensitivity to Cl⁻ ions. The in-situ measurements show a significant signal after 15 min hot-pressing procedure which corresponds to the formation of protons during the cross-linking of closed glue joints.

Author Contributions: M.K., J.Z. and T.S. conceived and designed the experiments; F.E. manufactured the electrode structures; M.K. fabricated the PANI layer; M.K. and J.Z. performed the pH calibration experiments; T.S. performed the hot-press measurements; M.K. and U.M. analyzed the data; M.K. and T.S. wrote the paper.

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Conflicts of Interest: The authors declare no conflict of interest.

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