Application of electrodedeposited piezo-resitive polypyrrole for a pressure-sensitive bruxism sensor

Onno Akkermans†,1, Mitch Spronck†,1, Theo Kluskens2, Fred Offerein1, Ketie Saralidze3, Jos Aarts4, Pegah Keshaniyan1, Erik Steen Redeker*1, Hanne Diliën1, Bart van Grinsven1, and Thomas J. Cleij1

1 Maastricht Science Programme, Maastricht University, Postbus 616, 6200 MD Maastricht, The Netherlands
2 MUMC+, Department MKA, Postbus 1686, 6201 BR Maastricht, The Netherlands
3 Biobased Materials, Faculty of Humanities and Sciences, Maastricht University Brightlands Chemelot Campus, Urmonderbaan 22, 6163 Geleen, The Netherlands
4 IDEE, Faculty of Health, Medicine and Life Sciences, Maastricht University, Universiteitssingel 50, 6229 ER Maastricht, The Netherlands

Received 30 September 2015, revised 19 January 2016, accepted 21 January 2016
Published online 13 February 2016

Keywords awake bruxism, piezo-resitive effects, polypyrrole, pressure sensors

* Corresponding author: e-mail erik.steenredeker@maastrichtuniversity.nl, Phone: +31 46 70 21 801, Fax: +31 43 38 83 570
† These authors contributed equally to this work.

This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

This paper presents the application of the conducting polymer polypyrrole in a pressure sensitive sensor. Polypyrrole was electrodeposited on copper plates using phytic acid as a dopant and cross-linker. A combination of different polymerization durations and potentials were tested to find the polymerization conditions for thin polymer layers and homogenous surface coverage. The morphology of the surface of the polypyrrole films was examined with scanning electron microscopy to study the formation of hollow sphere beads. The polymer layers were sandwiched between two copper sheets to create pressure sensitive sensors and the piezo-resitive effect was tested. For this, increasing forces were applied to the sensors and the resistance was measured. It was found that the polypyrrole layers were pressure sensitive to pressures relevant for bruxism events and had a thickness that is suitable for application in a splint for the detection of awake bruxism.

An SEM image of polypyrrole hollow sphere beads at 20 kV and 1000× magnification.

1 Introduction Bruxism is a condition which can be defined as: “a repetitive jaw-muscle activity characterized by clenching or grinding the teeth and/or by bracing or thrusting of the mandibles, which can occur during sleep (sleep bruxism) and wakefulness (awake bruxism)” [1]. An event of clenching is considered bruxism when the force that is applied exceeds 5 N and lasts for more than 2 s. However, mean forces of detected sleep bruxism events of 220 N (s.d. 127 N) with a mean duration of 7.1 s (s.d. 5.3 s) are reported [2].

It is believed that sleep and awake bruxism do not share the same causality; the latter is related to psychosocial and psychopathological factors, while no such relation is found in sleep bruxism [3]. This form of bruxism is characterized by grinding of the teeth as opposed to awake bruxism, which is expressed in clenching and occurs in approximately 20% of the population [4].

Several types of pressure- or piezo-sensitive material exist. Piezoelectric material produces a voltage when
mechanical strain or pressure is applied, whereas piezo-resistant material exhibits a change in electrical resistance. Although interesting piezoelectric alternatives like, for example, so-called ferroelectrets (porous piezoelectric films of e.g., polypropylene) exist [5], we present the application of the piezo-resistant polymer polypyrrole for the development of a pressure-sensitive sensor to detect awake bruxism. The advantage of using polypyrrole is that (i) information is already available regarding the biocompatibility of the material. This is a highly desirable feature for medical purposes; (ii) the range of resistance provides an easy read-out and fits exactly in the voltages which we would like to apply (<1 V); and (iii) the chosen material needs to cover very irregular surfaces in a very thin sensitive layer. By using an electrochemical deposition method, polypyrrole can be polymerized and deposited in very thin layers in situ, directly in the desired shape, which is easier than molding the polymer into shape after polymerization.

Polypyrrole is a multi-purpose conductive polymer; its synthesis is relatively easy, it has good environmental stability, high conductivity and is, above all, biocompatible [6–9]. It was first synthesized in 1963 through pyrolysis of tetraiodopyrrole and subsequently tested for its electronic properties [10–12]. Years later, conductive polypyrrole films have been synthesized for a variety of applications including molecularly imprinted polymer (MIP) sensors [13–19], copper protection [6, 20], OLEDs [21], super-capacitors [22], wearable electronics [23], and pressure-sensitive sensors [24, 25].

Polymerization of pyrrole results in a stiff and brittle material due to its rigid conjugated ring system. Therefore, it was doped with phytic acid, a cheap, non-toxic compound naturally present in plants, animals, and soils and widely used in food and medicine [6, 26–28]. Phytic acid has a dual role: it acts as a dopant and cross-linker of polypyrrole [29]. During mixing, an emulsion of micellar-like structures is formed due to the phase separation between the organic and aqueous components [24]. During polymerization, these micellar structures are maintained, resulting in hollow polypyrrole spheres. These hollow structures can be compressed when force is exerted on them, resulting in a change in electrical resistance. Due to their structural elasticity, the spheres return to their original shape when the pressure is released. This piezo-resistive effect and elasticity of polypyrrole forms the basis for its use in a pressure-sensitive sensor.

The sensor system is based on a thin film of polypyrrole sandwiched between two small copper plates. The polymers were deposited in situ directly on the copper by using electroplating. To create polymer layers that are thin enough to be used in a splint but still have a structure and thickness sensitive to pressures relevant for bruxism events, different polymerization durations and voltages were tested. The morphology of the resulting electropolymerized polypyrrole layers was analyzed with scanning electron microscopy (SEM) and the sensors were tested for their piezo-resistive effect and applicability for pressure-sensitive bruxism detection.

## 2 Materials and methods

### 2.1 Materials

**Pyrrole (98%)** and phytic acid (50% w/w in H2O) were purchased from Sigma–Aldrich and sodium hydroxide (97%) was purchased from VWR. Copper tape (12 mm width) was purchased from 3M.

### 2.2 Electropolymerization

The polymerization basically followed the procedure reported by Lei et al. [20] with some minor modifications. Briefly, the copper tape was cut into rectangular 20 mm by 12 mm sheets. A two-electrode electrochemical cell was prepared by submerging half of the pre-cut copper sheet (exposure area 10 mm by 12 mm) into 50 ml electrolyte solution containing 0.5 M pyrrole and 0.1 M phytic acid in water. The pH of the electrolyte solution was increased to pH 4 with sodium hydroxide. A graphite stick was used as the counter electrode. The polypyrrole polymerization and deposition was performed under different potentials and for different durations (Table 1).

After polymerization, the copper sheets were removed from the electrolyte solution and left to air-dry for at least 2 h. The polypyrrole layer was then converted to a pressure sensitive sensor by sandwiching it between two copper plates with a second sheet of copper. Wires were attached to both top and bottom copper sheets to complete the rectangular sensor of 120 mm². For every polymerization condition, five replicate sensors were prepared.

### 2.3 Piezo-resistive effect of the sensors

To test the piezo-resistivity and sensitivity of the different sensors, they were individually placed on a platform that could be elevated against a force measurement unit (Fig. 1). The vertical sample displacement was done manually, by turning the knob of the lift. The spindle has a measurement of M2, meaning that a turn of 360° would lead to a vertical displacement of 2 mm. Each sensor was tested three times. The sensors were attached to a power source and an amplifier and the sensor sensitivity was recorded at 0.5 V with a sample rate of 200 Hz.

### 2.4 Scanning electron microscopy

The morphology of the surface of the polypyrrole films was examined with SEM. Copper sheets with exposed polymer were placed on a carbon tape and sputter-coated with gold. Pictures were taken with a SEM (Philips XL 30, M4I, Maastricht University, Maastricht, the Netherlands), at an operating voltage of 20 kV.

## 3 Results

### 3.1 Electropolymerization

Polymerization was performed according to Table 1. Figure 2 shows the

| Table 1 Overview of the polymerization conditions and the corresponding sensor codes. |
|---|---|---|---|---|---|
| time | 2.5 V | 5.0 V | 10.0 V | 15.0 V | 25.0 V |
| 1 min | A | C | E | G | I |
| 5 min | B | D | F | H | J |
different polypyrrole films that are deposited on the copper. When polymerization was performed at 2.5 V for 1 min (sensor A), an incomplete polymer layer was deposited rendering this polymerization condition not appropriate. Dental splints for the treatment of bruxism are usually between 2 and 4 mm thick. Sensor J yielded a polymer layer of approximately 3 mm and was, therefore, deemed too thick for the current application. In addition, the brittle and rugged surface made it nearly impossible to efficiently attach the second copper sheet. Sensors B-I did, however, result in complete and homogeneous polymer deposition and suitable polymer layer thickness (<1 mm). These sensors were, therefore, further characterized and tested for their piezo-resistive effect and pressure sensitivity.

3.2 Piezo-resistive effect of the sensors Figure 3 shows the measurements for the resistance of sensor D. When the plateau was elevated, pressure was applied on the sensor, thereby changing the resistance. For the application in mind, the sensor preferably responds to small changes in pressure at lower forces. The resistance-force curve shows non-linear relation with a rapid decrease in resistance, even when small forces (<2.5 N) are applied. When higher forces were applied, the resistance exponentially decreases, reaching a plateau at forces >25 N. This type of pressure sensitivity is preferred for the application in mind and the non-linearity can be a benefit in order to provide sensitivity over a large range in pressure/force. Sensors with similar piezo-resistive patterns were C, G, H, and I.

To test the reproducibility of the piezo-resistive effect, repeated loading–unloading cycles were applied to the same sensor. It was observed that the electrical resistivity is reversible with the applied pressures and that intra-sample variability is low (Fig. 4).

3.3 Scanning electron microscopy SEM analysis was carried out to study the morphology of the different sensors (Fig. 5). As can be seen, no clear polymer layer or polymer beads could be observed for sensors A and sensor B. Figure 5C, E, 5, and I shows that although polymerization for 1 min results in polymeric spheres, the spheres were not closed completely. Polymerization for 5 min (Fig. 5D, F, H, and J), however, did yield closed structures.
Figure 6A shows that the microscopic structure of the polymer layer is almost identical for all sensors. Generally the size of the microspheres ranges between 50 and 100 \(\mu\text{m}\).

4 Discussion and conclusion The change in resistance that is observed in Fig. 4 is likely caused by an increase of contact area between individual spheres. The exponential decrease that is observed could be associated with increasing contact area of the spheres or increased contact area between the conducting polymer spheres and the electrodes [24, 30]. Before pressure exertion, there is no close contact area between the spheres or with the electrodes, so the resistance is maximal. However, upon pressure application the contact area increases, giving rise to a decreased resistance.

As more pressure is exerted, contact areas between the spheres cannot be increased much more and, therefore, the decrease in resistance will be much smaller than the initial decrease.

As an event of clenching is considered bruxism when the force that is applied exceeds 5 N and lasts for more than 2 s [2], it can be concluded that the sensors C, D, G, H, and I are suitable for our application.

Furthermore, from the SEM analysis, it can be stated that 5 min is probably best because the spheres are completely closed and because they resemble the “cauliflower” morphology.
observed in other research [6, 20, 24]. Closed spheres would intuitively have a higher contact area when sandwiched between two electrodes, resulting in a different resistance. However, we observed that both the open and closed morphology of the microspheres provide similar piezo-resistive patterns. Further investigation into this phenomenon is, therefore, required.

In conclusion, different sensors were electropolymerized, tested for the piezo-resistive effect, and characterized by SEM analysis. These sensors are easy and cheap to make while it only takes a very short time to do so. The functional layer of these sensors was thin enough to be implemented into a splint while still having high sensitivity at application relevant pressures. It can do so because the polymer can determine moments of contact and, therefore, awake bruxism.

Acknowledgements We would like to thank the Province of Limburg, The Netherlands and the NWO Top Sector Chemistry Student Competition for providing financial support for this research.

References
[1] R. de Leeuw (Ed.), Orofacial Pain, Guidelines for Assessment, Diagnosis, and Management (Quintessence Publishing Co., Inc., Chicago, 2008).
[2] K. Nishigawa, E. Bando, and M. Nakano, J. Oral Rehab. 28, 485–491 (2001).
[3] D. Manfredini and F. Lobbezoo, J. Orofac. Pain. 23, 153–166 (2008).
[4] S. Shetty, V. Pitti, C. L. S. Babu, G. P. S. Kumar, and B. C. Deepthi, J. Ind. Prosthodont. Soc. 10, 141–148 (2010).
[5] S. Bauer, R. Gerhard-Multhaupt, and G. M. Sessler, Phys. Today 57, 37–43 (2004).
[6] Y. Lei, N. Sheng, A. Hyono, M. Ueda, and T. Ohtsuka, Corros. Sci. 76, 302–309 (2013).
[7] M. Finšgar and I. Milošev, Corros. Sci. 52, 2737–2749 (2010).
[8] Y. Fan, C. Li, Z. Chen, and H. Chen, Appl. Surf. Sci. 258, 6531–6536 (2012).
[9] A. V. Rao, S. S. Latthe, S. A. Mahadik, and C. Kappenstein, Appl. Surf. Sci. 257, 5772–5776 (2010).
[10] R. McNeill, R. Siudak, J. H. Wardlaw, and D. E. Weiss, Aust. J. Chem. 16, 1056–1075 (1963).
[11] B. A. Bolto and D. E. Weiss, Aust. J. Chem. 16, 1076–1089 (1963).
[12] B. A. Bolto, R. McNeill, and D. E. Weiss, Aust. J. Chem. 16, 1090–1103 (1963).
[13] B. Schweiger, J. Kim, Y. J. Kim, and M. Ulbricht, Sensors 15, 4870–4889 (2014).
[14] M. Peyrovi and M. Hadjmohammadi, Biomed. Chromatogr. 29, 1623–1628 (2015), DOI: 10.1002/bmc.3469.
[15] P. T. Do, P. Q. Do, H. B. Nguyen, C. N. Van, D. L. Tran, T. H. Le, H. N. Le, H. V. Pham, T. L. Nguyen, and Q. H. Tran, J. Mol. Liq. 198, 307–312 (2014).
[16] I. Chernov, H. Greb, U. Janssen-Bienhold, J. Parisi, R. Weiler, and E. von Hauff, Sens. Actuators B 203, 327–332 (2014).
[17] E. Mazzotta, C. Malistesta, M. Díaz-Alvarez, and A. Martin-Esteban, Thin Solid Films 520, 1938–1943 (2011).
[18] N. Maouche, M. Guergouri, S. Gam-Derouich, M. Jouini, B. Nessark, and M. M. Chehimi, J. Electroanal. Chem. 685, 21–27 (2012).
[19] Y. Kong, W. Zhao, S. Yao, J. Xu, and W. Wang, J. Appl. Polym. Sci. 115, 1952–1957 (2010).
[20] Y. Lei, N. Sheng, A. Hyono, M. Ueda, and T. Ohtsuka, Prog. Org. Coat. 77, 774–784 (2014).
[21] I. C. Ciobotaru, E. Matei, C. C. Ciobotaru, and S. Polosan, Synth. Met. 198, 323–328 (2014).
[22] Y. Chen, L. Du, P. Yang, P. Sun, X. Yu, and W. Mai, J. Power Sources 287, 68–74 (2015).
[23] Y. Huang, H. Hu, Y. Huang, M. Zhu, W. Meng, C. Liu, Z. Pei, C. Pao, Z. Wang, and C. Zhi, ACS Nano 9, 4766–4775 (2015).
[24] L. Pan, A. Chortos, G. Yu, W. Wang, S. Isaacson, R. Allen, Y. Shi, R. Dauskardt, and Z. Bao, Nature Commun. 31, 3002 (2013).
[25] S. Brady, D. Diamond, and K.-T. Lau, Sens. Actuators A 119, 398–404 (2004).
[26] F. Crea, C. De Stefano, D. Milea, and S. Sammartano, Coord. Chem. Rev. 252, 1108–1120 (2007).
[27] H. W. Kaufman and I. Kleinberg, Arch. Oral Biol. 16, 445–460 (1971).
[28] L. Oatway, T. Vasanthan, and J. H. Helm, Food Rev. Int. 17, 419–431 (2001).
[29] B. Liu, P. Soares, C. Checkles, Y. Zhao, and G. Yu, Nano Lett. 13, 3414–3419 (2013).
[30] R. S. Timsit, IEEE Trans. Comp. Pack. Technol. 22, 85–98 (1999).