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Influence of silver/silver chloride electroless plating on the Shore hardness of polyurethane substrates for dry EEG electrodes

Abstract: Dry electrodes enable a shorter preparation time for infant EEG. Since infant skin is more sensitive than adult skin, soft electrodes are required to reduce the mechanical stress for this sensitive skin. Thus, soft electrodes are crucial for eventual repetitive and long-term use like in neonatal intensive care units. A biocompatible polyurethane (PU) can be produced in low hardness resulting in a soft and flexible electrode substrate. Silver/silver chloride (Ag/AgCl) electroless plating provides a conductive, electrochemically stable coating but the process may alter the mechanical properties of the electrode substrate. In this study, we assess the hardness of PU material before and after Ag/AgCl plating. The test sample design for Shore hardness measurement is based on ISO 7619-1:2010. Sample production consists of a 3D print master model, silicone molding, PU casting, and finally electroless plating. UPX 8400-1 (Sika AG, Switzerland) is used for the sample substrates. Test samples are produced with 7 different Shore hardness (range A40-A95) and 14 samples (each hardness: 1 uncoated and 1 coated). The hardness measurements are carried out with a lever-operated test stand Shore hardness tester model with a digital hardness tester (TI-AC with HDA 100-1, KERN & SOHN GmbH, Germany). It is shown that there is a hardness increase (Shore A) due to Ag/AgCl coating with a grand average of 1.1 ± 0.7 ($p < 0.05$). The largest increase of 2.1 ± 0.2 is seen on the initial

lowest Shore hardness sample (Shore hardness: 43.4 ± 0.1). The absolute increase of hardness due to the Ag/AgCl coating decreases with increasing substrate hardness. It is concluded that there is no strong hardness increase of PU substrates due to Ag/AgCl plating. Therefore, the material is suitable as a soft electrode for repetitive and long-term use in infant applications.

Keywords: hardness test, ISO 7619-1, electrodes, EEG, infant, neonatal intensive care unit, neurophysiological monitoring.

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1 Introduction

EEG monitoring is well established in pre- and full-term infants especially for seizure detection [1]. However, clinically used wet EEG electrodes for neonates usually require a long time for preparation (i.e. scalp preparation and gel application) while dry electrodes enable shorter preparation times [2]. Since infant skin is more sensitive than adult skin, soft electrodes are required to reduce the mechanical stress for this sensitive skin [3], [4]. Thus, soft electrodes such as wet or hydrogel electrodes are currently used for eventual repetitive and long-term use like in neonatal intensive care units (NICUs) [1], [3], [5].

A biocompatible polyurethane (PU) can be produced in low hardness resulting in a soft and flexible electrode substrate. Silver/silver chloride (Ag/AgCl) electroless plating provides a conductive, electrochemically stable coating to the substrate [6], [7]. However, the process may alter the mechanical properties of the electrode substrate. In this study, we quantify the possible hardness changes caused by the Ag/AgCl plating of substrates with different Shore hardness.

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2 Methods

2.1 Sample preparation

For a Shore A hardness test, the test piece's thickness is 6 mm based on ISO 7619-1:2010 [8]. For comparative purposes, the thickness for each sample should be uniform [9]. The diameter of the sample should be sufficient to allow measurement at least 12 mm away from any edge [8]. We choose a diameter of 5 cm. A master model is created using a PolyJet Objet30 Prime printer (Stratasys Ltd., USA). Afterwards, a silicone mold is created with ESSIL 291 (Sika AG, Switzerland) under vacuum conditions to reduce defects [10]. The silicone mold is subsequently cured inside an oven. Then, the master model is removed from the silicone mold and PU UPX 8400-1 (Sika AG, Switzerland) is cast. Depending on the weight ratio between polyol, isocyanate, and extender, the hardness of the PU can be varied. Two samples are created for each weight ratio, resulting in a total of 14 samples with 7 weight ratios.

2.2 Ag/AgCl electroless plating

Ag/AgCl is the gold standard material for EEG electrodes [11]–[13]. This material is therefore selected for the electrically conductive coating of the test samples. The samples are coated with Ag/AgCl using an electroless plating method as described in [6], [7]. In summary, the electroless plating of the samples consists of three main processes: I. The first process is the silver deposition treatment, during which the silver seeds are embedded in the substrate surface to improve the surface affinity for silver. II. A silver film is grown on the sample's surface through a Tollens like plating process. III. The test samples are chlorinated. In total, 7 samples are plated to represent each of the 7 weight ratios of the PU. Test samples before and after the plating are shown in Figure 1.



Figure 1: Test samples according to ISO 7619-1:2010 with 6 mm thickness and 5 cm diameter: uncoated sample (left) and Ag/AgCl coated sample (right).

2.3 Hardness measurement

The Shore A hardness test is performed according to ISO 7619-1:2010 [8]. The measurement is carried out with a lever-operated test stand hardness tester model with a digital hardness tester (TI-AC with HDA 100-1, KERN & SOHN GmbH, Germany). The tester is calibrated according to manufacturer instructions.

Afterward, the measurement procedure is carried out for each sample. First, the test piece is placed on flat, hard, and rigid surfaces (glass) as shown in Figure 2. Then, the pressure foot is applied to the test piece as fast as possible but without shock. The foot is kept parallel, and the indenter is normal to the surface of the test piece. Afterward, a reading is taken after 3 seconds of contact between the pressure foot and the test piece. For each test piece, five measurements of hardness are recorded at different positions on the test piece at least 6 mm apart and respecting the minimum distance from the sample's edge. Finally, the mean and standard deviation for each test piece is calculated.



Figure 2: A test sample is placed on the stand hardness tester.

Furthermore, the absolute $\Delta H_{\text{absolute}}$ and relative hardness change $\Delta H_{\text{relative}}$ due to electroless plating is calculated based on equations 1 and 2, respectively, with H_i the Shore A hardness before, and H_t after plating.

$$\Delta H_{\text{absolute}}(\text{Shore A}) = H_t - H_i \quad (1)$$

$$\Delta H_{\text{relative}}(\%) = (H_t - H_i)/H_i \times 100\% \quad (2)$$

3 Result and discussion

Figure 3 proves that less extender in the mixture increases the PU's Shore A hardness. Regardless of the pre-plating hardness, it shows that there is an increase in terms of the hardness due to the Ag/AgCl coating. Absolute ($\Delta H_{\text{absolute}}$) and relative ($\Delta H_{\text{relative}}$) hardness increases with a grand average of 1.1 ± 0.7 and $1.9\% \pm 1.1\%$, respectively, when the plating is applied ($p < 0.05$). Based on Figure 4 and Figure 5, the largest hardness increase due to the plating can be seen on the highest extender ratio sample with an absolute and relative change of 2.1 ± 0.2 and $4.9\% \pm 0.4\%$, respectively. The absolute and relative hardness changes ($\Delta H_{\text{absolute}}$ and $\Delta H_{\text{relative}}$) non-linearly decrease due to the Ag/AgCl coating with increasing substrate hardness. Consequently, the value for the weight ratio 1:1:1 might be an outlier when assuming that the coating has always the same thickness.

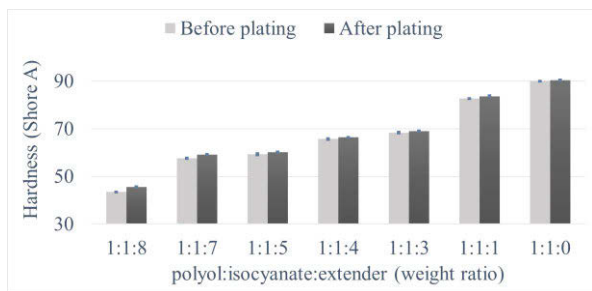


Figure 3: Shore A hardness measurement results before (H_i) and after plating (H_f) with the error bars representing standard deviation.

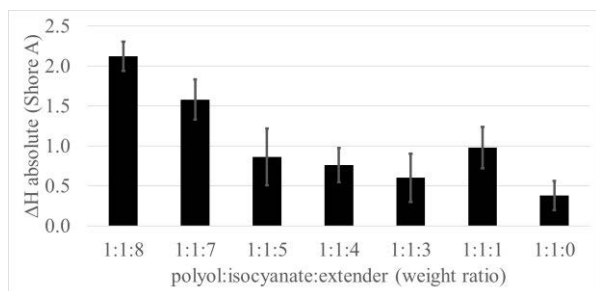


Figure 4: Absolute Shore A hardness changes ($\Delta H_{\text{absolute}}$) due to electroless plating with the error bars representing standard deviation.

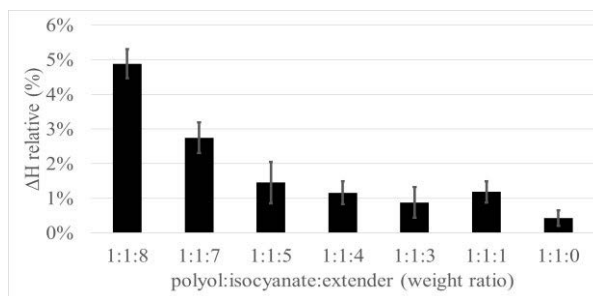


Figure 5: Relative Shore A hardness changes ($\Delta H_{\text{relative}}$) due to electroless plating with the error bars representing standard deviation.

4 Conclusion

It is concluded that there is no strong hardness increase of PU substrates due to Ag/AgCl plating. Therefore, the material is suitable as a soft electrode for repetitive and long-term use in infant applications.

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Conflict of interest: The authors state no conflict of interest.

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