

Investigation on adhesion strength of Parylene-C coatings with different adhesion promotion methods

J. Schorr, F. Blendinger, V. Bucher

Abstract— Delamination of encapsulation materials (here the polymer Parylene-C) is one of the biggest failure mechanisms for active medical implants. This problem is addressed by the application of different pre-treatment and adhesion promotion methods. The methods applied in this research are oxygen and Silane A-174 solution pre-treatment and Silane A-174, titanium oxide and Trimethylsilane as adhesion promoters. The adhesion forces of these methods are quantified after different soaking times in phosphate buffered saline (PBS) solution to mimic environment of the human body.

I. INTRODUCTION

In the modern world of medical engineering there is a vast variety of active implants such as pacemakers, deep brain stimulators, cochlear and retinal implants. Corrosion of the electronics after the implantation is one of the biggest causes for failures and therefore a high amount of research must be done in this field to prevent it. Furthermore, active medical implants usually utilize flexible electrodes for sensing or stimulation. Therefore, a thin flexible encapsulation is necessary to ensure a smooth operation while still ensuring a sufficient moisture, chemical and dielectric barrier. This encapsulation not only guarantees the safety of the patient but also the functionality of the implant after the implantation. A popular choice and the material on which this research is based on is the polymer Parylene-C [1]. One of the biggest drawbacks of the use of this encapsulation material is the poor adhesion on the substrates after the implantation. This poor adhesion in physiological environment leads to delamination and eventually failure of the active implant electronics by water intrusion and corrosion. In conclusion the adhesion can be identified as one of the limiting factors for long-term stability of active implants.

For these reasons efforts have been made to improve and quantify the adhesion of Parylene-C on the substrate. Various methods of adhesion promotion carried out by the means of oxygen plasma treatment and the use of different adhesion promoter layers such as: Silane A-174 (gas-phase), Silane A-174 (Solution), Titanoxide (Atomic Layer Deposition - ALD), Trimethylsilane (Chemical Vapor Deposition - CVD). The substrates with the different pre-treatment methods and the Parylene-C layer on top are subsequently validated via the use of peel test experiments after different times in phosphate-buffered salt (PBS) solution to mimic the environment of the human body.

II. MATERIALS AND METHODS

This chapter describes and outlines the experimental setup for the peel test as well as the different pre-treatment methods. Each sample consists of a glass substrate, the coating Parylene-C and a specific adhesion promoter in between. Adhesion can be generally described as the attractive forces between two materials which have to be overcome to separate them. Adhesion can be distinguished by three main mechanisms: physical bonds (Van der Waals and polar attractions), chemical bonds (Ionic and covalent bonds), mechanical interlocking (surface roughness) [2].

A. Peel Test experimental setup

For the peel test measurements, the FMT-313 universal tensile testing machine from Alluris was used. The load cell FMT-313.B5 (50 N) with a resolution of ± 0.01 N was chosen for these measurements. Furthermore, a separate 3D-printed device was used to keep the samples clamped down and submerged in the PBS solution during the peel test to avoid the drying of the samples.

B. Substrate preparation

The first step is the cleaning process of the new glass slides: the glass slides are submerged in acetone, then in 2-propanol and lastly in deionized water inside of an ultrasonic bath with each step taking 15 min. This process removes all organic and non-organic contaminations from the glass slides by a combination of chemical and mechanical cleaning. These cleaned glass slides are dried using pressurised nitrogen. After the cleaning process, a strip of polyimide foil (Kapton DuPont) with the thickness of either 60 or 12 μm is placed on the glass surface, this serves as a starting point to clamp peel strip with the Parylene-C into the tensile testing machine (Fig. 1).

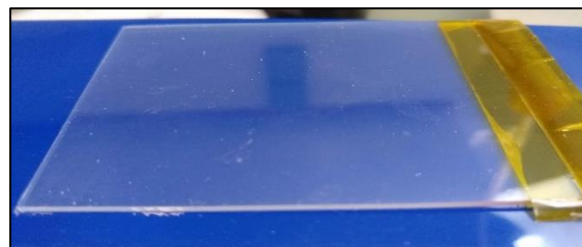


Figure 1: Cleaned and prepared glass slide

The glass slides which are used in this research are standard microscopic glass slides according to ISO 8937/1 and have the dimensions of 76x52x1 mm.

C. Coating and pre-treatment

For the Parylene-C coating the Lab Coater 300 system from Plasma Parylene Systems GmbH (PPS) was used. The recipe used for the Parylene-C coating was already present and produced a thickness of $13 \mu\text{m} \pm 2 \mu\text{m}$ on the prepared glass slides with approximately 15 g of Parylene-C powder. The glass slides are pre-treated with an O_2 -Plasma as part of the Parylene-C coating process which increases the surface roughness of the glass substrates. This increase in surface roughness therefore increases the adhesion of subsequent deposition steps.

To increase the adhesion of the Parylene-C layer on the glass substrate different pre-treatment methods and adhesion promoters were used. It must be differentiated between the pre-treatment with a Silane A-174 solution and the deposition of Silane A-174 out of the gas phase with the Lab Coater 300 system directly before the Parylene-C deposition. The different samples which are prepared with their respective pre-treatment and adhesion promotion method are listed below:

- O_2 plasma pre-treatment and no adhesion promoter. The O_2 plasma treatment is done for 5 min at a pressure of 40 Pa with the power of 300 W and a particle flow of 50 sccm. These samples are then placed in a PBS solution for different times (2 hours and 7 days). These samples will be described as **O₂** in the remaining report.
- O_2 plasma pre-treatment and 0.1 ml Silane A-174 out of the gas phase as an adhesion promoter. Afterwards the Parylene-C layer was deposited. These samples are then placed in a PBS solution for different times (2 hours and 5, 7, 9, 12 days) and will be described as **Si-G** in the remaining report.
- O_2 plasma pre-treatment and deposition of titanium oxide (TiO_x) using atomic layer deposition (ALD) with a thickness of 21 nm as an adhesion promotion layer. Afterwards the Parylene-C layer was deposited. These samples are then placed in a PBS solution for different times (2 hours and 5, 9 days) and will be described as **TiO_x** in the remaining report.
- O_2 plasma and Silane A-174 solution pre-treatment. The solution is prepared with 1 ml Silane A-174, 100 ml deionized water and 100 ml 2-propanol [3]. This solution was left to stand for 24 hours at room temperature. After this time, the cleaned glass slides were placed in the solution for 30 min at room temperature and dried for 30 min after that also at room temperature. All the samples were cleaned with 2-propanol for 15 s to remove the superfluous solution. Afterwards the Parylene-C layer was deposited. These samples are then

placed in a PBS solution for different times (2 hours and 7 days) and will be described as **Si-S** in the remaining report.

- O_2 plasma pre-treatment and deposition of Trimethylsilane (TMS) using chemical vapour deposition (CVD). The Trimethylsilane is deposited for 20 min at a pressure of 0.35 mbar and with a particle flow of 20 sccm (TMS) and 20 sccm (Ar) at a power of 200 W. Afterwards the Parylene-C layer was deposited. These samples are then placed in a PBS solution for different times (2 hours and 7 days) and will be described as **TMS** in the remaining report.

After the Parylene-C deposition on every glass sample they are cut using a scalpel and a 3D-printed template. This results in 5 parallel stripes of Parylene-C with a Kapton-stripe at the beginning and a width of 10 mm.

D. PBS solution

After the pre-treatment and deposition, all the glass substrates were put into a PBS solution for different times (2 hours to maximum 12 days). This PBS solution combined with a hotplate set to 37°C mimics the human body. Therefore, the implantation into the human body can be simulated and the adhesion for different implantation durations can be validated and examined. The PBS solution is supplied by ROTI Fair and has a pH value of 7.4 ± 0.05 .

E. Peel test

To determine the adhesion of the different pre-treatment and adhesion promotion mechanics the 90° peel test according to DIN EN 28510-1:2014 [4] was applied. The peel length is set to 100 mm, with a measuring frequency of 100 Hz and a peel speed of $50 \frac{\text{mm}}{\text{min}}$ (this leads to more than 90000 measuring points). The glass substrate is fixated in the 3D-printed device which is mounted onto the 90° table and the Kapton stripe is clamped down in the tensile testing machine (Fig. 2). Each stripe is peeled at the

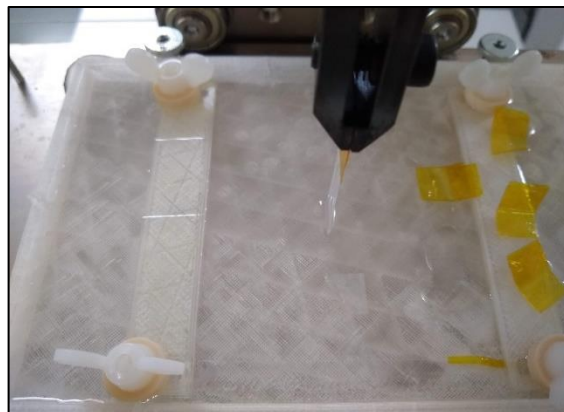


Figure 2: Peel test with the 3D-printed device and glass substrate inside

set speed and the table moves at the same speed ensuring a 90° angle at all times of the peel test.

In the measurement diagram the transition from the Kapton stripe to the Parylene-C can be clearly seen and therefore the values for the calculation of the Parylene-C adhesion are taken after this significant point.

III. RESULTS AND DISCUSSION

The 5 peel stripes of every glass slide are measured, and the adhesion is calculated for the effective peel range of the pure Parylene-C in the range of approx. 10 to 50 mm excluding the Kapton-stripe at the beginning. The Parylene-C stripe is peeled off over a length of 100 mm, the glass slide has a length of 76 mm which means the Parylene-C stripe is completely stripped off it and hangs on the clamp of the tensile tester. This remaining load represents the mass load of the Parylene-C and Kapton stripe and is subtracted from all measurement. The adhesion force (F_{ad}) of the Parylene-C peel stripes is calculated by the measured force (F_m) and the width of the stripe (d). The width of each stripe is 10 mm provided using a template to cut the 5 stripes on each glass slide.

$$F_{ad} = \frac{F_m}{d}$$

The adhesion forces calculated this way are scaled to $\frac{mN}{mm}$ in the remaining report.

One effort has been made to distinguish the effect of post-baking on the adhesion force of Parylene-C because it was described as a method to enhance the adhesion force of a stack of Parylene-C on Parylene-C [5]. The glass slides with the Parylene-C were put into an oven at 180°C for 30 min and afterwards put into the PBS solution. It could be seen that the Parylene-C dried out in the oven which left an inhomogeneous surface with many holes on the glass slide which could not be validated by a peel test.

The determination of the adhesion force for the Si-G (Silan out of gas phase) samples has been proven to be difficult. After 2 days in PBS solution the first samples were measured but the stripes broke off at the transition point from the Kapton tape to the Parylene-C. This can be attributed to a very high adhesion force between the Parylene-C, Silan and glass and therefore the stripes break off under these measurement conditions. After this the other samples are kept inside the PBS solution for a longer amount of time and measured again. Table 1 shows all the measured adhesion forces for the different times in PBS solution. The maximum adhesion force of $137 \frac{mN}{mm}$ is measured after a soaking time of 5 days but the standard deviation of this measurement is rather high (approx. 54 %) and therefore this value must be treated critically. It can be clearly seen that the longer the glass slides soak in the PBS solution the lower the

adhesion force will be. All these measurements have a rather high standard deviation, so they need to be repeated to make a qualitative statement. The problems with the adhesion force and the standard deviation of the Parylene-C with the Silane A-174 (out of the gas phase) could be explained by the Lab Coater 300 system not working properly regarding the Silane deposition.

Table 1: Adhesion forces of Si-G samples at different PBS soaking times

PBS duration	Adhesion force [mN/mm]	Standard deviation [mN/mm]
2 days	broke off	broke off
5 days	137,26	53,66
7 days	0,63	0,59
9 days	2,10	1,16
12 days	4,53	5,91

The measurements for the samples with solely a O₂ plasma pre-treatment are listed in Table 2. A clear decrease in adhesion force can be seen from the soaking time of 2 hours to a soaking time of 7 days. Furthermore, the adhesion forces with just O₂ plasma pre-treatment are significantly smaller ($13 \frac{mN}{mm}$) compared to the samples with Silane A-174 as an adhesion promoter ($137 \frac{mN}{mm}$) which was to be expected.

Table 2: Adhesion forces of O₂ samples at different PBS soaking times

PBS duration	Adhesion force [mN/mm]	Standard deviation [mN/mm]
2 hours	13,22	3,02
7 days	6,34	2,07

Table 3 shows the measurements of the adhesion force of the samples with a TiO_x adhesion layer. Here the adhesion was measured once directly after the deposition of TiO_x and Parylene-C which resulted in an adhesion force of $1.94 \frac{mN}{mm}$ after 2 hours soaked in the PBS solution an adhesion force of $1.06 \frac{mN}{mm}$ was measured, which was to be expected. The remaining samples were soaked in the PBS solution for 5 days and these measurements resulted in an adhesion force of $11.85 \frac{mN}{mm}$. This high value for the adhesion force was not expected and could be explained by a residue

of Silane A-174 inside of the Lab Coater 300 system during the Parylene-C deposition (the samples were deposited at different days) which means an additional adhesion promotion is present on some samples. To verify this assumption further testing must take place.

Table 3: Adhesion forces of TiO_x samples at different PBS soaking times

PBS duration	Adhesion force [mN/mm]	Standard deviation [mN/mm]
0 hours	1,94	0,33
2 hours	1,06	0,09
5 days	11,85	5,48

In Table 4 the measurements of the samples which were soaked in the Silane A-174 solution are presented. These samples were measured after a PBS soaking time of 2 hours and 7 days. After 2 hours the adhesion force was measured as $86 \frac{\text{mN}}{\text{mm}}$ and after 7 days the adhesion force was $73 \frac{\text{mN}}{\text{mm}}$. The decrease in adhesion force was to be expected. The Si-S samples show a way higher adhesion force at 7 days in PBS solution compared to the Si-G samples ($73 \frac{\text{mN}}{\text{mm}}$ to $0,63 \frac{\text{mN}}{\text{mm}}$). This means Si-S rather than Si-G should be preferably used for an adhesion promotion of Parylene-C on glass.

Table 4: Adhesion forces of Si-S samples at different PBS soaking times

PBS duration	Adhesion force [mN/mm]	Standard deviation [mN/mm]
2 hours	86,10	6,69
7 days	72,82	8,12

The last adhesion promotion method investigated was the use of an TMS layer before the Parylene-C deposition. The results for this adhesion promotion are listed in table 5. This method of adhesion promotion shows comparable adhesion force values to the use of Silane A-174 solution ($72 \frac{\text{mN}}{\text{mm}}$ to $86 \frac{\text{mN}}{\text{mm}}$). The adhesion force decreases with longer PBS soaking times which is to be expected.

Table 5: Adhesion forces of TMS samples at different PBS soaking times

PBS duration	Adhesion force [mN/mm]	Standard deviation [mN/mm]
2 hours	71,54	2,87
7 days	54,42	6,63

All the adhesion force measurements with their respective standard deviations are displayed in figure 3.

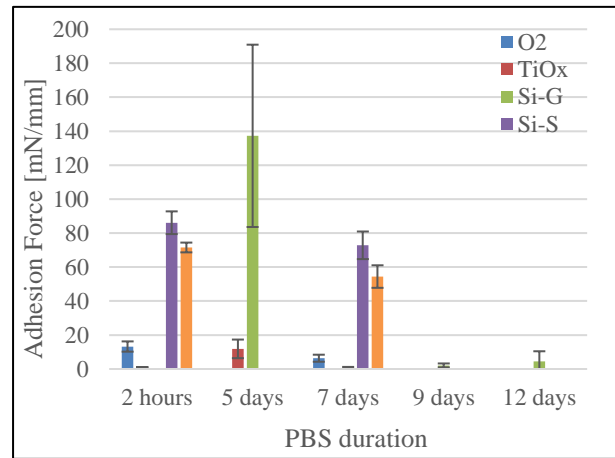


Figure 3: Adhesion forces of the different adhesion promotion methods after different PBS soaking times

IV. CONCLUSION AND OUTLOOK

This report aimed at the research of the solid encapsulation of electronics in active implants and especially on the change of adhesion of these encapsulation materials after submersion in a solution which mimics the human body after implantation. It can be clearly said that Silane A-174, either out of the gas phase or via a solution, is the best method for adhesion promotion. Other methods like TMS and TiO_x could be good alternatives but need to be researched more. Another point which must be further researched is the optimal soaking time of the samples with Silane A-174 out of the gas phase to ensure reliable measurements can be performed and the adhesion force is not too big so the peel stripes will not break off.

In the future the adhesion forces and long-term stability of Parylene-C encapsulation of complex structures could be researched.

V. REFERENCES

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