piezobrush® PZ3: endurance test of standard module

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Abstract

The subject of this study is a long-term endurance of the standard nozzle module used as a plasma generator in the handheld device piezobrush® PZ3 and in the industrial integration unit piezobrush® PZ3-i. The results of an endurance test of 10 piezobrush® PZ3 standard modules equipped with a plasma liner made of polybutylene terephthalate (PBT) are presented. The setup for the endurance test and the applied evaluation methods are described. The modules were 37 weeks (more than 6000 h) under operation, stopped briefly for measurement of electric parameters and activation area. All standard modules passed the test without significant deterioration of performance. The variation of the activation area, electric parameter, and morphology of the module is examined and discussed.

Keywords: piezobrush® PZ3, CeraPlas® F, piezoelectric direct discharge (PDD), activation image recording (AIR), activation area, high density polyethylene (HDPE), free surface energy (FSE)

Contents

1 Introduction

piezobrush® PZ3 released in 2020, is a handheld device designed for use in a laboratory or workshop. The replaceable modules are optimized for different materials and surface shapes. The standard module (see Figure 1) is used for the treatment of electrically non-conducting surfaces such as polymers, glass, or ceramics. It is produced by TDK Electronics GmbH and specified in [10]. Recently, the industrial version of the piezobrush, the piezobrush® PZ3-i was introduced. It is dedicated to use many hours per day in industrial production. The long operation time applications require not only an extended lifetime but also small temporal variations of the process performance. A larger number of the piezobrush® PZ3-i units can be organized in a matrix allowing for large area surface processing. For such multi-module applications, the small piece-to-piece performance variation is essential. To determine a realistic operation time, the long-time and piece-to-piece variation of the process characteristics, relyon plasma GmbH has conducted an extended endurance test of the standard modules under conditions prevailing during typical applications. To get statistically valid conclusions, the set of ten modules was tested. This whitepaper summarizes the results of this test.

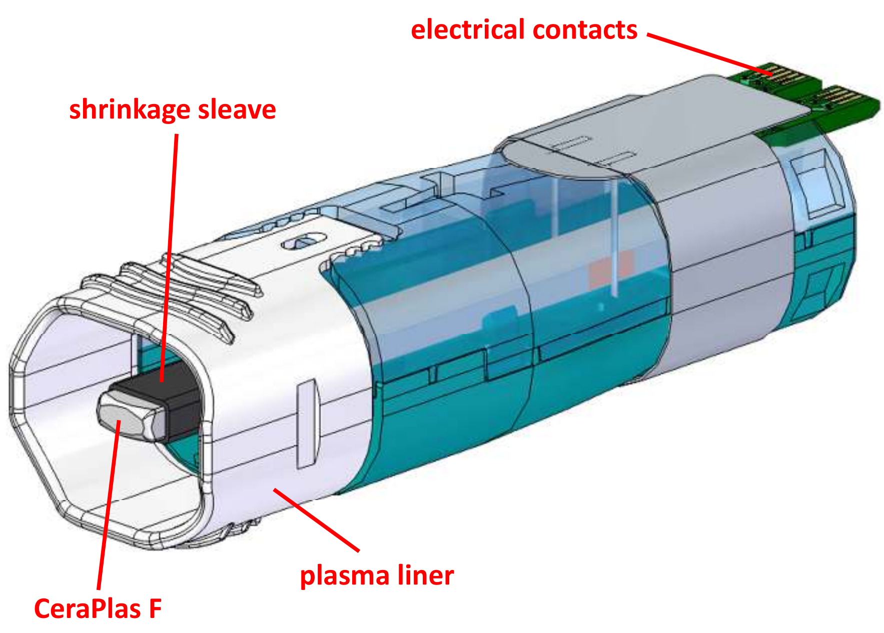


Figure 1: The mockup of the piezobrush® PZ3 standard module.

2 Setup for endurance test

2.1 Standard module

The core component of the standard module is the CeraPlas® F depicted in Figure 1. It is generating a high voltage in the range of > 10 kV on its tip, resulting in the ignition of piezoelectric direct discharge (PDD) [7]. Along the CeraPlas® F, the gas flow is sustained. In the case of piezobrush® PZ3, it is ambient air propelled by a fan. For piezobrush® PZ3-i either compressed dry air (CDA) or nitrogen is used. The gas flow has two purposes: (i) cooling of the CeraPlas® F and (ii) transferring the excited species and chemical radicals produced in the PDD toward the substrate surface.

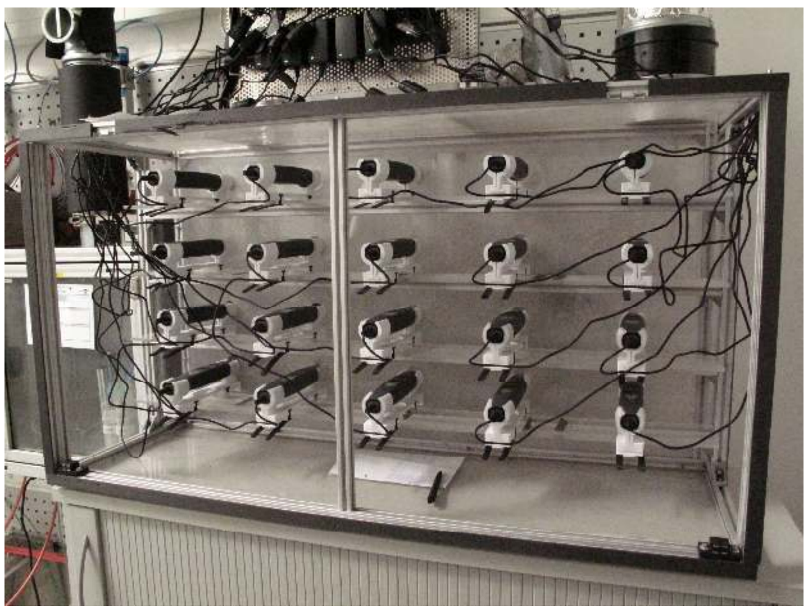


Figure 2: The cabinet for endurance test is equipped with 20 piezobrush® PZ3 fixed in digitally printed holders designed for operation with ten standard and ten near-field modules.

2.2 Endurance test cabinet

The endurance tests involving the piezobrush® PZ3 units are performed in a cabinet shown in Figure 2. It allows for a simultaneous test of 20 piezobrush® PZ3 modules. Depending on the module to be tested, different 3D-printed piezobrush® PZ3 holders are applied. In the test described here, the endurance test cabinet is equipped with ten holders for standard modules operated without substrates. For the operation of the piezobrush® PZ3 units, standard piezobrush® PZ3 AC-DC converters are used. They are placed above the cabinet, as shown in Figure 2. All piezobrush® PZ3 are set on continuous operation mode [8].

2.3 Gas extraction

Each standard module generates about 80 mg/h of ozone and comparable amounts of other oxidizing species [6]. The extraction of the gaseous plasma products is applied to avoid the elevated concentration of ozone in the endurance test room and the exposure of the devices to corrosive medium. The gas extraction is performed by use of a central extraction system Deduster 5000 D280 of P.Ries GmbH working with the frequency of 35 Hz corresponding to 0.46 kW electric power. The piezobrush® PZ3 locked in the holders are inserted in the holes in the transparent backside wall of the endurance test cabinet (see Figure 2). The extraction system is able to produce the underpressure causing the increase of the gas flow through the piezobrush® PZ3 and improving the cooling of the CeraPlas® F devices. This would create test conditions less severe, than in a typical application. To avoid such unwanted influence on the test results, the bypass for airflow is created: the diameter of the holes in the backside wall of 40 mm is larger than the width of the piezobrush® PZ3 of 30 mm, and an additional open slot of $2{\times}56$ cm^2 is provided.

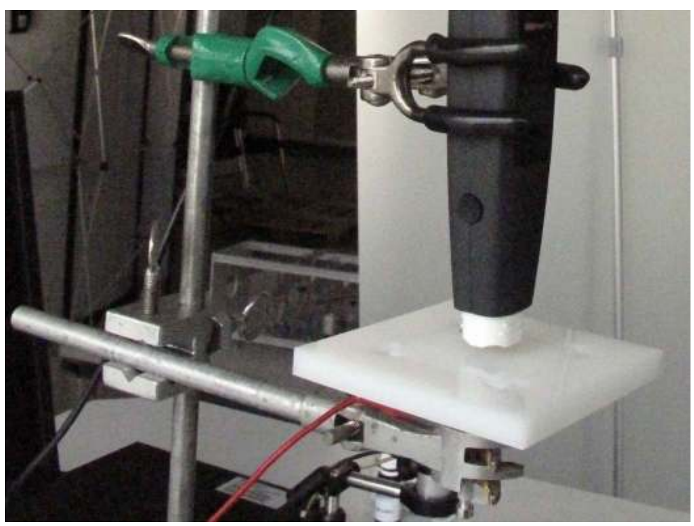


Figure 3: The HDPE substrate positioned on the HDPE substrate holder under the standard module of the piezobrush® PZ3 prepared for plasma treatment.

3 Activation area evaluation procedure

3.1 Plasma treatment

As a rule, every two weeks of operation all tested modules are removed from the piezobrush® PZ3, examined for damage or wear, measured electrically (see Section 4.2) and their activation area is measured. The last is performed using the activation image recording (AIR) system [5]. In the first step of this procedure, the 50×50 mm^2 substrates made of high-density polyethylene (HDPE) are activated statically, by use of a piezobrush® PZ3 fixed in a laboratory stand, as shown in Figure 3. All modules are inserted one after the other in the same piezobrush® PZ3.

With each standard module, three substrates are then treated. For substrate handling, and metrological reasons, three HDPE blocks with sizes 100 mm × 100 mm × 10 mm and a 2 mm deep hollow for placing the 50×50 mm^2 substrates are used. For substrate treatment, the HDPE blocks are positioned centered on the electrically grounded metal cylinder used for the characterization of the NFN modules. The 10 mm thickness is enough to avoid the electrostatic influence of the metal cylinder on plasma. The distance between the nozzle edge and the substrate is 4.0 mm. This corresponds to the distance between the CeraPlas® F tip and the substrate of 5.5 mm. The treatment time is 10 s. To avoid the thermal drift of the standard module during the activation of the three subsequent substrates, each module is warmed up for 30 s.

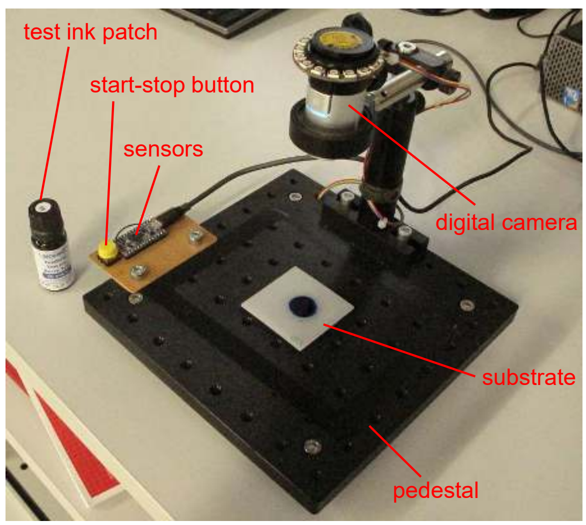


Figure 4: The activation image recording (AIR) system hardware with substrate positioned on the pedestal and the bottle of the test ink used.

3.2 Activation image recording

After treatment, each substrate is positioned on the pedestal of the AIR system (see Figure 4) and the AIR procedure is performed. The activation area is visualized using two droplets of 58 mN/m test ink (ArcoTest) spread using a small brush on the plasma-treated surface directly after plasma treatment. The behavior of the test ink means that the substrate has a higher SFE than 58 mN/m. Otherwise the test ink would not wet the HDPE substrate. The image of the inked area is recorded for a period of about 20 s by use of a digital camera. The area of the images is determined using the AIR-software and stored as a function of time (shrinkage curves). The area reached 10 s after the test ink application is used for the evaluation of the activation performance.

Table 1: The activation area determined for 10 standard modules after 6000 h of endurance test. Substrate material: HDPE. Distance from the CeraPlas® F tip to the substrate: 5.5 mm. Treatment time: 10 s. Power level: 100 %.

conditions:	**open, P=100%, d=5.5 mm, t=10s, HDPE: Rocholl, 58mN/m, V4**					
module-No.	**sample no.**	**S1[mm²]**	**S2[mm²]**	**S3[mm²]**	**mean[mm²]**	**st.dev.[mm²]**
5942-0865	220503-001	558,193	591,868	628,916	593,0	35,4
5942-0898	220503-004	614,722	663,252	625,473	634,5	25,5
5942-0897	220503-007	604,919	637,068	647,741	629,9	22,3
5942-0896	220503-010	611,862	616,594	583,784	604,1	17,7
5942-0895	220503-013	609,373	682,247	566,724	619,4	58,4
5942-0698	220503-016	600,951	627,687	574,177	600,9	26,8
5942-0697	220503-019	598,023	633,18	625,346	618,8	18,5
5942-0656	220503-022	620,782	581,851	617,1	606,6	21,5
5942-0657	220503-025	631,879	601,113	580,681	604,6	25,8
5942-0892	220503-028	644,482	603,181	598,018	615,2	25,5
mean val.:		609,5	623,8	604,8	**612,7**	**27,7**
standard dev.:					**13,19**	

3.3 Activation area

In the Table 1 the activation areas for 10 standard modules after 6000 h of endurance test are listed. For each module, three substrates are activated with the same standard module (results in lines). For each line, the mean value and the standard deviation are calculated. An important parameter characterizing the quality of the measurement is the mean value of these standard deviations. In the presented example it is 27.7 mm^2, which is equivalent to 4.5% of the area mean value. This percentage depends mainly on such factors as the skills of the AIR system operator, quality of the substrate material, and sufficient pre-warming. These factors will be discussed in Section 3.4.

Additionally, the mean values for substrate number related results are calculated and written on the bottom of the table. Three mean values for first, second, and third measured substrate are used to control the module preheating process. Without module preheating, the systematic increase of these three mean values can be observed. With preheating of the nozzle module, no systematic trend in these values can be observed. This is the case in the discussed example. The second value (623.8 mm^2) is maximum, not the third one, and the first one (609.5 mm^2) is higher then the last one (604.8 mm^2).

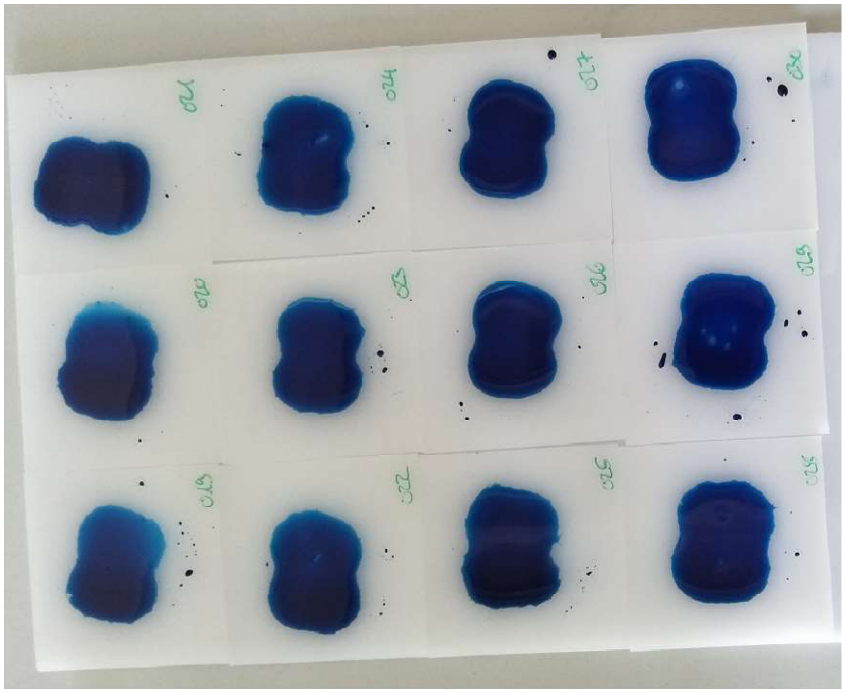


Figure 5: The activation areas visualized by 58 mJ/m^2 test ink on three HDPE substrates per module treated by piezobrush® PZ3 with standard modules 5942-0697 to 5942-0892, as listed in the table in Figure 1 after 6000 h of endurance test.

The most important evaluation parameter is the mean value of the mean values of activation areas determined per module. In our example, it is 612.7 mm^2. This parameter is used for the investigation of the a global trend of the activation area during the endurance tests. This trend is discussed in Section 4.1.

Further important global parameter is the standard deviation of the module-related mean values of the activation area. In the presented example, it is 13.19 mm^2 being equivalent to 2.2%. This parameter gives information about piece-to-piece reproducibility of the activation performance. This parameter should be especially low in a group of standard modules, which should be operated in a matrix of standard modules.

Figure 5 shows the test ink visualization of the activation zones for four standard modules numbered 5942-0697 to 5942-0892, three substrates per module, as specified in the Table 1.

3.4 Factors affecting the measurement

As mentioned in Section 3.3, several factors affect the accuracy of the activation area determination. The skills of the AIR system operator is a subjective influence, which is not discussed any further. Following measures are taken to minimize the unwanted influences.

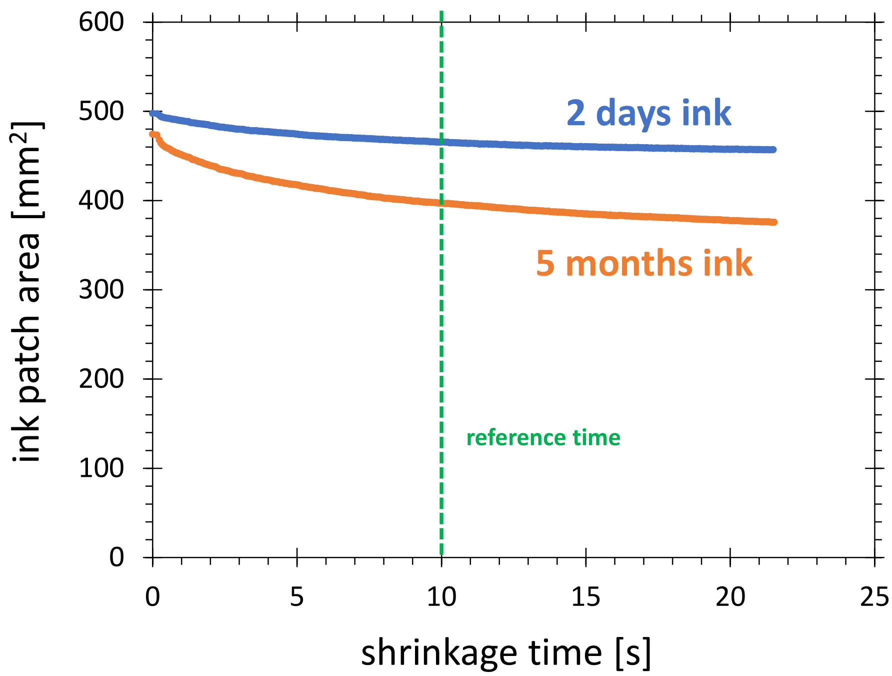


Figure 6: The dependence of the test ink patch area as a function of the time after ink application (shrinkage curve), visualized by two test inks with different storage times. The activation and evaluation procedures are as described in Section 3.

3.4.1 The aging of the test ink.

The test ink 58 mN/m (pure formamide) exposed longer time to air changes its properties and shows a significantly smaller activation area than the fresh test ink. Figure 6 shows the dependence of the test ink patch area as a function of the time after ink application, visualized by two test inks with different storage times: two days, and five months. At the reference time of 10 s the old ink shows 15% lower activation area then the new one. This effect can be explained by hygroscopic properties of the formamide. With the increasing amount of water absorbed by the test ink from the ambient humidity, the ink starts to behave as it would gauge larger surface free energy (SFE). The longer the test ink exposure to the ambient humidity, the larger the error of the visualized activation area.

To avoid the influence of the test ink aging on the activation area results, two rules are followed: *(i)* the test ink bottle must remain closed any time, when not used for ink application, and *(ii)* for each measurement series, the fresh test ink bottle is opened and labeled with a date of opening. Formamide is harmful to people and the environment. To avoid such hazards, the expired ink bottles (two weeks after opening) are collected to be sent for recycling to the vendor.

3.4.2 Varying HDPE properties.

The properties of the HDPE substrates vary from supplier to supplier and from batch to batch. Before starting the endurance test, one supplier was excluded due to a strong deviation of the achieved activation areas resulting from not disclosed additives to the polymer. Only the "natural" HDPE of Rocholl GmbH is used for this study. The substrates of some batches show different surface properties on both sides. One side is sometimes glossy when the other is matt. However, the difference in activation area depending on the side of the substrate was not statistically significant. The substrates are also not completely flat. They show the concave and convex sides. Consequently, depending on the position of the substrate, the effective distance between the CeraPlas® F tip and the substrate surface can vary on up to 1 mm. To avoid such influence, each substrate is positioned with the convex side up during the plasma treatment.

3.4.3 Influence of the surface pretreatment.

Different preparation procedures for the HDPE surface before plasma treatment are known. For example, they are cleaned by ultrasonic rinsing in iso-propanol for 30 s [9], in distilled water for 20 minutes [4], or in 96% ethanol for 5 min and dried in dynamic vacuum at 0.1 Pa for 10 min [1] or purified by extraction with acetone overnight and stored in a desiccator prior to each plasma treatment [2].

To avoid the influence of solvents and water on the result, no wet treatment of the substrates was applied. To remove the dust particles and residua of sawdust, the surfaces were wiped dry with paper tissue. This treatment must be repeated systematically, because the visualized activation area is on average 5% larger on the dry-cleaned substrates then on the pristine ones.

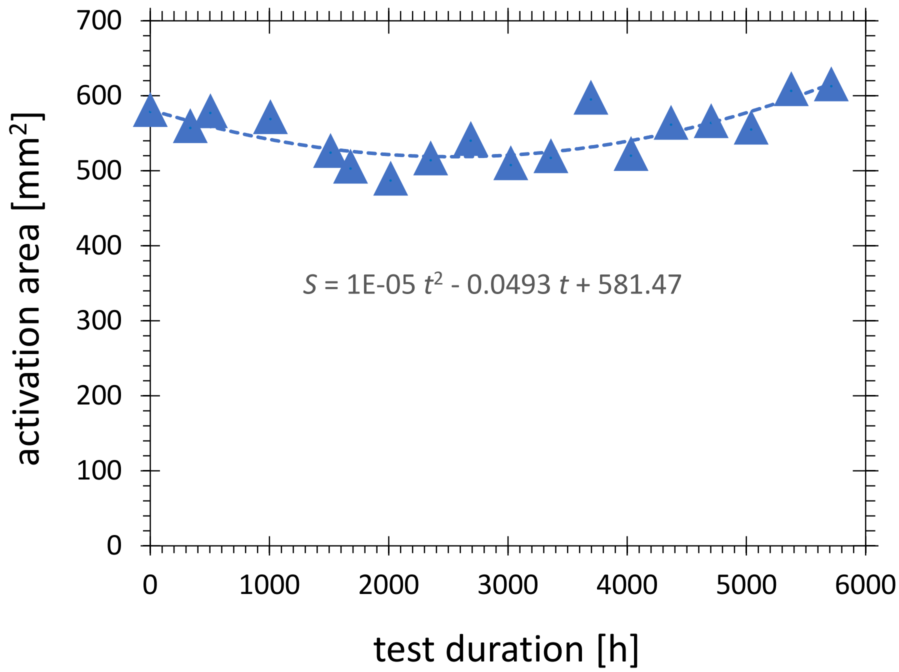


Figure 7: The activation area as a function of endurance test duration.

4 Module aging

4.1 Variation of activation area

Figure 7 shows the activation area measured as described in Section 3.2. The values vary with endurance test duration. During the first 2000 h, the activation area slightly decreases. Starting from about 2000 h the increase can be observed. The maximum value reached after 6000 h is by 26% higher than the minimum. The mean value of module-related standard deviations calculated as described in Section 3.3 is 2.86%.

4.2 Variation of electrical parameters

The testing system linked to a data-base was applied to measure and store the electrical parameters of the CeraPlas® F from the tested modules. Each time when the activation area was determined using the AIR system the module was inserted in the electronic docking station reading automatically the excitation frequency, input voltage and current, power, phase shift and input impedance.

The impedance is selected to monitor the temporal change of the module properties. Its value as a function of the endurance test duration is shown in Figure 8. A clear trend can be observed (see the fitting line): slight increase during the first 2000 h and a monotonous

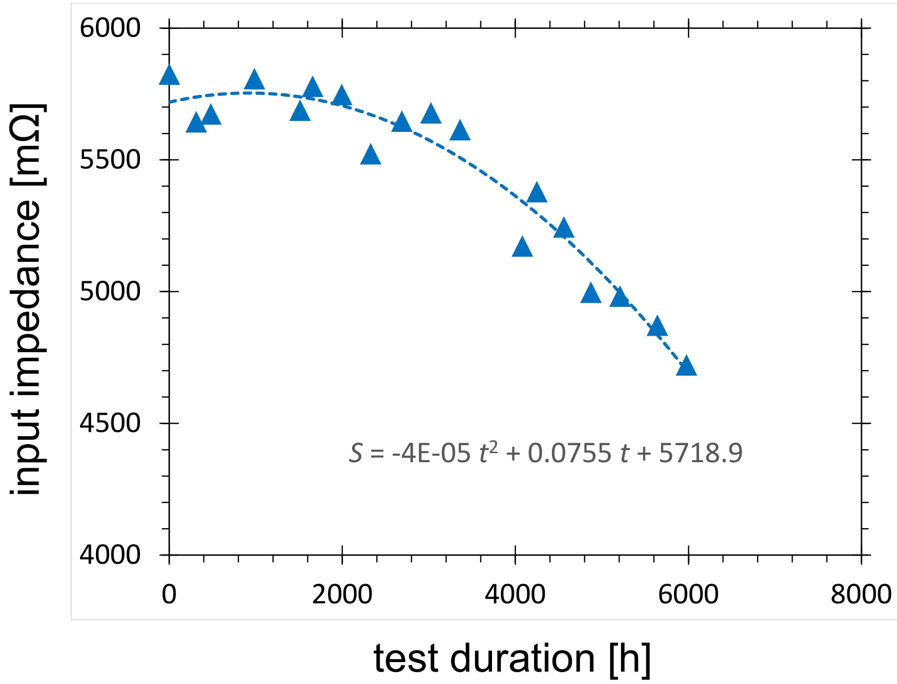


Figure 8: The CeraPlas® F input impedance as a function of endurance test duration. Each point in the diagram represents the average value for 10 modules.

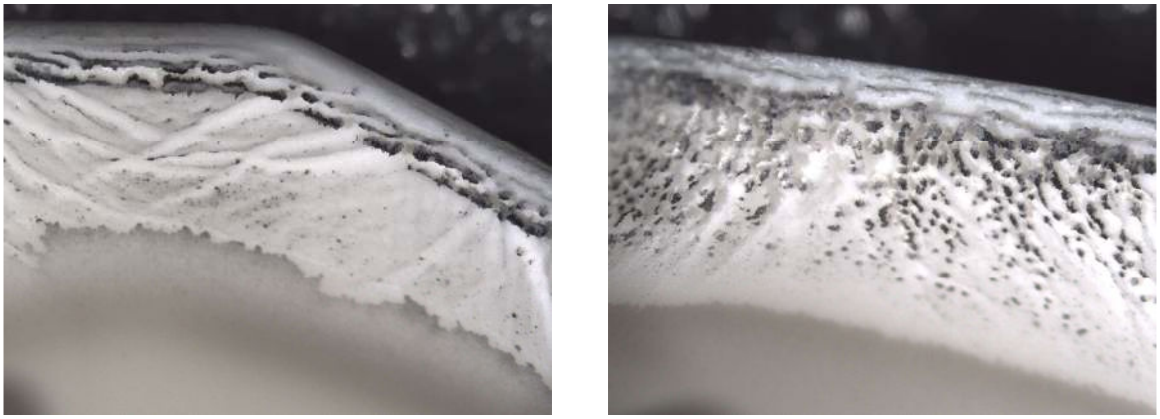
decrease by a total of 19% between 2000 and 6000 operation hours. This trend is opposite to this of the activation area, which is first slightly decreasing and then increasing.

(a) (b) (c)

Figure 9: The inner side of the plasma liner after a) 2000 h, b) 4000 h, and c) 6000 h of the endurance test.

4.3 Changes in module morphology

Figure 9 shows the typical morphology of the inner side of the standard module plasma liner after 2000, 4000, and 6000 operating hours respectively. After 2000 hours, a small amount of black contamination is present. The surface of the PBT remains smooth. After 4000 h of operation, the strong roughness of the PBT surface can be observed. The amount of the black deposit increases. After 6000 h of operation a macroscopic structuring of the PBT surface is present.



(a) (b)

Figure 10: The microscopic details of the standard module plasma liner after 4200 operation hours: a) focused erosion and b) spread erosion.

The microscopic pictures in Figure 10 show two different types of polymer erosion. The polymer PBT consists of hydrogen, carbon, and oxygen only and is partially eroded chemically by oxidation from this material and partially converted into the carbon layer due to the removal of hydrogen atoms from the polymer chains by oxidation [3]. In Figure 10a, the erosion involving both hydrogen and carbon is shown, resulting in macroscopic changes of the polymeric material structure. Figure 10 shows the deep wells with carbon contaminant inside, resulting from the preferential oxidation of hydrogen atoms. It is not very probable, that these structural changes of the plasma liner can affect the electrical and activation performance of the CeraPlas® F that much.

(a) (b)

Figure 11: The tip of the CeraPlas® F from the standard module a) before and b) after 6000 operation hours.

The time-dependent changes in morphology can be observed not only on the walls of the plasma liner, but also at the tip of the CeraPlas® F. Figure 11 shows this tip before (a) and after 6000 h (b) of the endurance test.

The first observation is, that a kind of ash is depositing at the corners of the shrinkage sleeve. The white deposit grows on the edge of the shrinkage sleave of the CeraPlas® F, as shown in Figure 11. The probable reason is the oxidation of the shrinkage sleeve polymer due to the discharges reaching from time to time almost to the shrinkage sleeve edge. Since this is a very small amount of the deposit, it is most probably also not the reason of the observed performance variations.

The second observation is, that between the surface of the CeraPlas® F and the inner side of the shrinkage sleeve wall a cavity is created. The loosening of the shrinkage sleeve material can be the result of a dielectric or mechanical fatigue due to the electric and mechanical oscillation of the CeraPlas® F. It results in less damping of the CeraPlas® F mechanical oscillation, and in consequence in increased activation efficiency and lower input impedance.

5 Conclusion

All 10 modules have completed 6000 hours of the endurance test without failure. During the test, the activation area varied between 500 and 600 mm^2. The CeraPlas® F input impedance decreases with endurance test time over 2000 h. After 6000 hours it is by 19% less than the maximum value of 5800 mΩ. Both, the increase of the activation area and decrease of the CeraPlas® F input impedance can be explained with the loosening of the shrinkage sleave, resulting in less mechanical damping of the CeraPlas® F oscillations.

References

[1] Behnisch, J., Holländer, A., and Zimmermann, H. Factors influencing the hydrophobic recovery of oxygen-plasma-treated polyethylene. *Surface and Coatings Technology 59*, 1 (1993), 356 – 358.

[2] Drnovská, H., Lapčík Jr., L., Buršíková, V., Zemek, J., and Barros-Timmons, A. Surface properties of polyethylene after low-temperature plasma treatment. *Colloid Polym. Sci. 281* (2003), 1025 – 1033.

[3] Fricke, K., Steffen, H., von Woedtke, T., Schröder, K., and Weltmann, K.-D. High rate etching of polymers by means of an atmospheric pressure plasma jet. *Plasma Processes and Polymers 8*, 1 (2011), 51 – 58.

[4] Guragain, R., Baniya, H., Gautam, S., und U.M. Joshi, B. P., and Subedi, D. Characterization of dielectric barrier discharge (DBD) produced in air at atmospheric pressure and its application in surface modification of high density polyethylene (HDPE). *Journal of Technological and Space Plasmas 1*, 1 (2020), 27 – 35.

[5] Korzec, D., Andres, T., Brandes, E., and Nettesheim, S. Visualization of activated area on polymers for evaluation of atmospheric pressure plasma jets. *Polymers 13*, 16 (2021).

[6] Korzec, D., Hoppenthaler, F., Burger, D., Andres, T., and Nettesheim, S. Atmospheric pressure plasma jet powered by piezoelectric direct discharge. *Plasma Processes and Polymers 17*, 11 (2020), 2000053.

[7] Korzec, D., Hoppenthaler, F., and Nettesheim, S. Piezoelectric direct discharge: Devices and applications. *Plasma 4*, 1 (2021), 1 – 41.

[8] Korzec, D., Hoppenthaler, F., T. Andres, D. B., Werkmann, A., Nettesheim, S., and Puff, M. Piezobrush® PZ3: Part I: Operation principle and characteristics. `https://www.relyon-plasma.com/wp-content/uploads/2020/11/201024_whitepaper_piezobrush_PZ3_1.pdf`, 27 2020. whitepaper.

[9] Lommatzsch, U., Pasedag, D., Baalmann, A., Ellinghorst, G., and Wagner, H.-E. Atmospheric pressure plasma jet treatment of polyethylene surfaces for adhesion improvement. *Plasma Processes and Polymers 4*, S1 (2007), S1041–S1045.

[10] TDK Electronics AG. Standard module for handheld device piezobrush PZ3. `https://www.tdk-electronics.tdk.com/inf/130/Cold_Plasma/B54321P5100A020.pdf`, June 2019. Code: B54321P5100A020.