

Protection of Archaeological Artefacts by Deposition of Parylene and SiO_x Thin Films

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The treatment process of archaeological artefacts is usually divided into two main steps. A surface corrosion removal is the first step that is performed by low pressure hydrogen plasma. Its chemically reducing atmosphere allows a careful removal of corrosion without damaging the artefact surface details. After the procedure, the surface is highly reactive and inclines to oxidation. To prevent this process, it is necessary to protect the surface with a barrier film preventing the penetration of oxygen (as well as the other corrosion agents) to the surface.

This study focuses on possibilities of the archaeological artefacts (copper, iron, brass and bronze) protection by a thin film deposition of SiO_x and Parylene thin films. Parylene (poly-para-xylylene) is used in a wide range of applications, particularly as a coating for biomedical implants and microelectronics. Parylene coatings are chemically inert, conformal and transparent with excellent barrier properties [1] but relatively small adhesion. These all properties determine parylene to be a perfect material for protection of archaeological artefacts. Parylene coatings are prepared by the standard chemical vapor deposition (CVD) method [2].

SiO₂-like high density films are widely used in contemporary industrial technologies because they have very good barrier properties and excellent adhesion improving also the mechanical properties of the substrate [3]. Plasma enhanced chemical vapor deposition (PECVD) enables the preparation of SiO_x based thin films with higher flexibility due to incorporated organics groups.

SiO_x layers were deposited by PECVD in a low pressure reactor with capacitively coupled plasma discharge (13.56 MHz). Mixture of Hexamethyldisiloxane with oxygen was used as a precursor of plasmachemical reactions.

The coatings were characterized by various methods in order to obtain information about their thickness (ellipsometry), chemical structure (FTIR) and elemental composition (XPS), surface morphology (LCSM, SEM) and barrier properties (OTR). Standard corrosion tests were performed to determine the effectiveness of corrosion protection. The results were compared with those on samples treated by conventional conservation procedures.

1 Introduction

The traditional process of preservation of artefacts is a long term procedure. Ageing destroys untreated artefacts and we lose our cultural heritage. This study focuses on an alternative way how to save the artefacts before their destruction. Plasmachemical treatment appears to be an effective and fast way of restoration and preservation of archaeological metallic artefacts. Once the surface of the artefact is cleaned, it is highly active and oxidizes easily. To prevent the oxidation, thin film deposition of Parylene or SiO_x layer is performed.

Polymers represent materials of the future, due to their low density, flexibility, softness, inertness and low cost of production. The possibility of selective modification of the surface, while keeping bulk characteristics unchanged, has

greatly increased the applicability of polymers [4]. Polymers, in our case Parylene C and pp-HMDSO, are widely used as a protection of archaeological artefacts because of these properties.

Poly-para-xylylene, also known as Parylene, is a vapour deposited polymer first discovered by Szwarc in 1947. Later, Gorham found a much more efficient route to the vapour deposition of Parylene through the vacuum pyrolysis of di-para-xylylene. He found that at temperatures above 550 °C and the pressures below 1 torr, the dimer is quantitatively cleaved into two monomer units (para-xylylene). These units are adsorbed onto a surface at room temperature and they spontaneously polymerize yielding high molecular weight, linear Parylene thin films [5].

Parylene is one of the most well-known chemical vapor deposited (CVD) thin film polymers. It is used in a wide range of applications, particularly as coatings for biomedical implants and microelectronics. Its desirable properties include chemical inertness, conformal coatings and excellent barrier properties [1]. Although over twenty types of Parylene have been developed, only three the most common types are mentioned: Parylene N, C and D.

Parylene N is a basic member of the group. It is a completely linear, highly crystalline material. Parylene C is produced from the same monomer (as Parylene N) modified only by the substitution of a chlorine atom for one of the aromatic hydrogens. Parylene D is produced from the same monomer modified by the substitution of the chlorine atom for two of the aromatic hydrogens [6].

Hexamethyldisiloxane (HMDSO) is another suitable monomer for preparing thin films. The main advantages of these films are good barrier properties and they are transparent, colorless, flexible, soft and inert [4]. Thanks to silicon atom inside, they can form various thin films capable to bind to glass and other inorganic substrates. Additionally, organic parts of the precursor ensure flexibility and versatility of functional groups leading to practically limitless possibilities of substitutions. Hexamethyldisiloxane (HMDSO) or Tetramethoxysilane (TMOS) are the most common organosilicone precursors in PECVD.

This study focuses on a thin film preparation from Parylene C and pp-HMDSO on archaeological artefacts. These thin films are characterized by various methods (ellipsometry, FTIR, XPS, LCSM, SEM and OTR). We have also performed standard corrosion tests to determine the effectiveness of corrosion protection. The results were compared with those on samples treated by conventional conservation procedures.

2 Experimental

2.1 Parylene

2.1.1 Apparatus

Apparatus for chemical vapour deposition uses, the above mentioned, Gorham process consisted of the following parts: vaporizer, pyrolytic chamber, cooling section and deposition chamber. The vaporizer consists of brass cartridge where the defined amount of Parylene C is placed. The furnace, which is warmed by a resistance wire and thermally insulated by mineral wool, is set on the brass cartridge. The pyrolytic chamber is about 1.5 m long and its inner diameter is 38 mm. The cooling chamber is shorter than the pyrolytic chamber and also has the bigger inner diameter. The

deposition chamber is a vertical cylinder of diameter of 35 cm and a height of approximately 50 cm. Laboratory temperature is kept in this part of apparatus because of condensation of Parylene C on the substrate. Vacuum inside the deposition chamber is up to 10 Pa and it is produced by a mechanical vacuum pump. The last main part of the apparatus is a cold trap with temperature about $-20\text{ }^{\circ}\text{C}$ which serves for removal of the rest of monomer to prevent clogging of mechanical vacuum pump.

2.1.2 Deposition process

The portion of the dimer of Parylene C was specified at 42 g for the thickness of $20\text{ }\mu\text{m}$ after determination of losses on the wall of the deposition chamber. Calculated amount of Parylene C was placed to the vaporizer. Temperature of the vaporizer was gradually increased up to about $120\text{ }^{\circ}\text{C}$ when the process began. Temperature was being increased by about $1\text{ }^{\circ}\text{C}$ per 10 minute because of equal evaporation of the dimer. The whole process was finished at about $180\text{ }^{\circ}\text{C}$. Because of the vacuum gradient, molecules of the dimer went through the pyrolytic chamber which was heated to temperature of about $680\text{ }^{\circ}\text{C}$. The dimer was fragmented into reactive monomer particles. Monomer particles came into the cooling section which served for decreasing of the gas temperature. The temperature of this part of the apparatus was $150\text{ }^{\circ}\text{C}$. The inside temperature of the deposition chamber wasn't controlled but it did not exceed $40\text{ }^{\circ}\text{C}$ during the process. 3-(trimethoxysilyl)-propyl methacrylate was added into the reactor by a syringe before the process beginning. Deposition rate of the layer was measured indirectly by an oscillator attached to the reactor during the whole process. By decreasing the oscillator frequency, polymerization rate of monomer particles was estimated. The temperature of the vaporizer was controlled according to these measurements. Pressure in the deposition chamber was kept constant at the value of 10 Pa. The whole process of the deposition lasted for 4.5 hour.

2.2 pp-HMDSO

2.2.1 Apparatus

The apparatus for depositions is designed as a high-vacuum bell jar reactor with pressure of about 10^{-4} Pa . The system consists of a glass reactor with volume of 30 L. It is equipped by two thermal evaporators and a capacitive coupled system of electrodes connected to the plasma generator (working frequency of 13.56 MHz). The system also allows monomer vapour deposition and it is equipped with mass flow controllers. Reactor space is evacuated by a rotary oil pump in the first step, and by a turbomolecular pump, subsequently. It is possible to change the pumping velocity of the whole pumping system continuously by a manually controlled gate valve (DN100) in order to achieve the desired working pressure. The radiofrequency capacitive coupled glow discharge is created between two plan-parallel electrodes with the diameter of 170 mm which are placed in the centre of the reactor. The inlet of working gases is located under the lower grounded electrode. The upper electrode can be settled by substrates (quartz polished on both sides, silicon wafer, a foil or another deposited sample). A radiofrequency voltage is supplied to this electrode from the Cesar generator with an automatic matching network (Cesar 136).

2.2.2 Deposition process

We used a silicon wafer and a PP foil as a substrate. The PP foil was cleaned by ethanol. Liquid hexamethyldisiloxan ($C_6H_{18}OSi_2$) was used for plasma polymerization as a precursor. It was placed in a glass flask and only the vapours of the monomer were flowing into the apparatus. Pressure inside the deposition chamber was $2 \cdot 10^{-3}$ Pa. Then, the chamber was purged with the mixture of the monomer (0.54 sccm) and oxygen (10 sccm). The deposition time was 6 minutes for all samples and power was 50 W.

2.3 Thin film analyses

2.3.1 Confocal Laser Microscopy

Measurement of thickness and surface structure was done by a Confocal Laser Scanning microscopy using the LEXT OLS 3000 Olympus device.

2.3.2 Fourier Transform Infrared Spectroscopy

Chemical structure analysis was done by a spectrometer Nicolet iS10 with OMNIC software. The wave number resolution was 4 cm^{-1} using 32 scans.

2.3.3 Scanning Electron Microscopy

Surface analysis was performed by a Scanning Electron Microscope JEOL JSM-7600F with the resolution of 0.8 nm and magnification of 1 000 000x.

2.3.4 X-ray Photoelectron Microscopy

Elemental analysis of atomic concentration was done by an X-ray Photoelectron Microscope AXIS ULTRA with the source of radiation $Al_{K\alpha}$ and with the possibility of a depth profile measurement by an argon ion beam ablation. The device was able to do quantitative and qualitative elemental analysis in the upper 10 nm of the surface with sensitivity to all elements up to 0.1 atomic percents.

2.3.5 Oxygen Transmission Rate measurement

We have measured foils with the thin layer (Parylene C or pp-HMDSO) as well as clean PP foils. This apparatus is a non-commercial equipment constructed in our laboratory at Faculty of Chemistry. Transmission rate of the PP foil for oxygen was measured. Each measurement was done 3 times. Values in the Table 2 are the average of these 3 measurements.

Total measurement time of one sample was 10 hours. As the first step, we have rinsed the sample for 2 hours. It was necessary for the decrease of residual oxygen which was inside the apparatus.

2.3.6 Corrosion tests

Corrosion tests for Parylene C coated samples were done according to the norm ČSN EN ISO 9227 in a cyclic Salt spray chamber CC450 from the Ascott Analytical Equipment Limited Company. We used four metals (iron, copper, brass and bronze) protected by a thin film of Parylene C. As reference samples, the same samples with the protective coating from copolymer ethylmetacrylate-methylacrylate

PARALOID B44 were used. This copolymer is commonly used as a conservation substance in artefacts restoration.

All the samples were placed into the salt spray chamber. There was an environment of salt fog to imitate natural environment. Salt fog was created from a solution of sodium chloride with concentration of 50 g/L. This solution was mixed in a 1:1 ratio with air at the temperature of 25 °C. The nozzle in the middle of the salt spray chamber was turned up to ensure the best homogeneity of the salt fog. Samples were controlled several times during the test and we made photos in any case of the visible changes in the structure. The inspection was performed after 30, 100, 200 and 300 hours after the beginning of the corrosion test.

A corrosion test for pp-HMDSO layers was performed as an immersion test. We used samples without any protection and samples with the thin layer of pp-HMDSO. One group of samples (samples with protection and without protection) was dipped into pure water and the second group was dipped into the solution of sodium chloride with concentration of 50 g/L. Water and solution of sodium chloride were changed every day and the samples were photographed. Total time of the test was 336 hours.

3 Results

3.1 Confocal Laser Microscopy

In Figure 1 you can see a groove in the Parylene C thin film on the silicon wafer. This image was made by the Optical Mode of Confocal Laser Microscope. You can observe blue colour besides darker gray which is Parylene C and lighter gray which is the silicon wafer as a substrate. The blue film is probably some product which was formed from 3-(trimethoxysilyl)-propyl methacrylate. This compound was added before the process beginning in order to get better adhesion of the Parylene C thin film to the surface of the substrate. Analysis of this product will be the object of our further investigations.

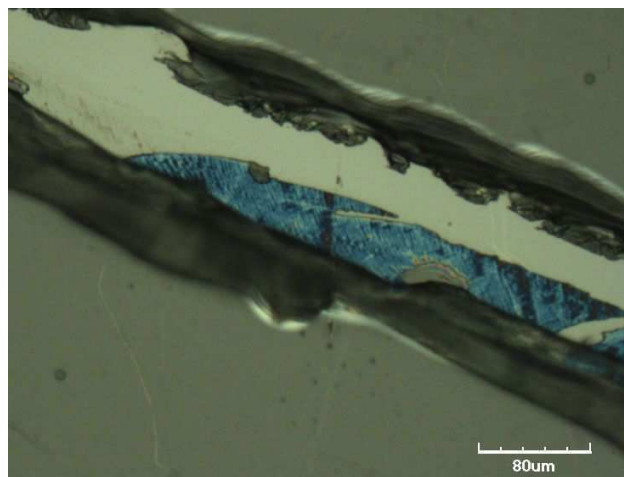


Figure 1: Structure of the groove in the Parylene C thin layer on the silicon substrate

3.2 Infrared Spectroscopy

The FT-IR measurements give information about the coating composition. The obtained spectrum of Parylene C is in Figure 2 and the spectrum of pp-HMDSO is in Figure 3.

In the spectrum of Parylene C, the 1494 cm^{-1} peak represents the aryl carbon vibrational movement (C – C). Peak at 1050 cm^{-1} is attributed to the chlorine bonding to the ring. The 825 cm^{-1} peak is a representative of two neighbouring hydrogen atoms bonded to the ring (CH_2) and the peak at 877 cm^{-1} is a representative of the single hydrogen to the ring (CH) which is neighbouring chlorine and ethyl group in this case. Additional characteristic peak of CH_2 on the benzene ring is at 1452 cm^{-1} . A pair of peaks at 2861 and 2927 cm^{-1} indicates the vibrational movement of the C-H bond in methyl groups and C-H bond vibrational movement in the aromatic ring at 3019 cm^{-1} [7].

There are smaller peaks in addition to the peaks described in the spectrum. These can be caused by noise or various contaminants contained in the deposition precursor of Parylene C or added substances, such as 3-(trimethoxysilyl)-propyl methacrylate.

In the spectrum of the pp-HMDSO, there is the peak at 2330 cm^{-1} which represents the molecule of CO_2 . Peak at 1069 cm^{-1} is a representative of Si-O-Si and the peak at 790 cm^{-1} represents Si-C and Si-O_x bonds [8]. It is probably the Si-O_x bond since the bond Si-C was not detected during the XPS analysis. It means that we have prepared a layer with minimum amount of carbon.

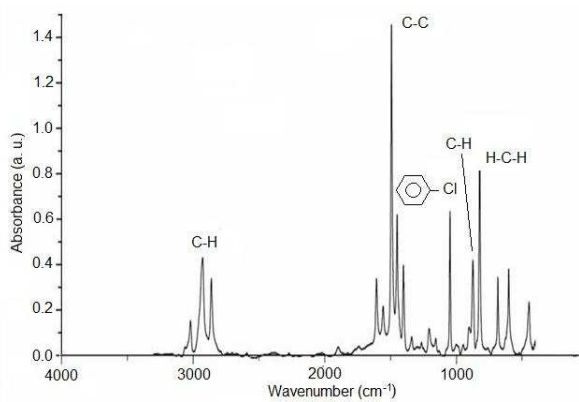


Figure 2: Infrared spectrum of Parylene C

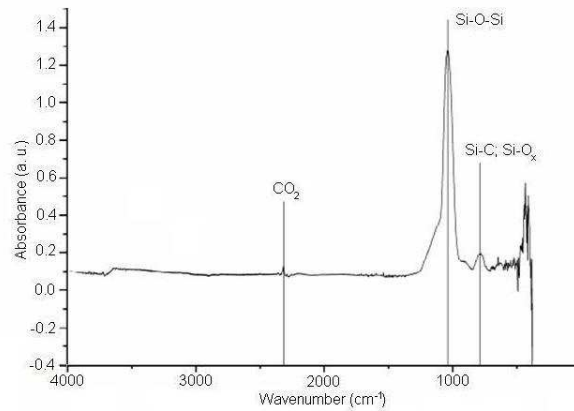


Figure 3: Infrared spectrum of pp-HMDSO

3.3 Scanning Electron Microscopy

Homogeneity of the thin layer of pp-HMDSO was observed by the Scanning Electron Microscope. We wanted to know how the layers look like on the ideal substrate, so that is why we measured thin films of Parylene C and pp-HMDSO on the silicon wafer. All deposited thin layers had homogeneous structure. We can observe some dirt on the surface but these spots were only superficial and they did not interfere to the overall structure of the layer.

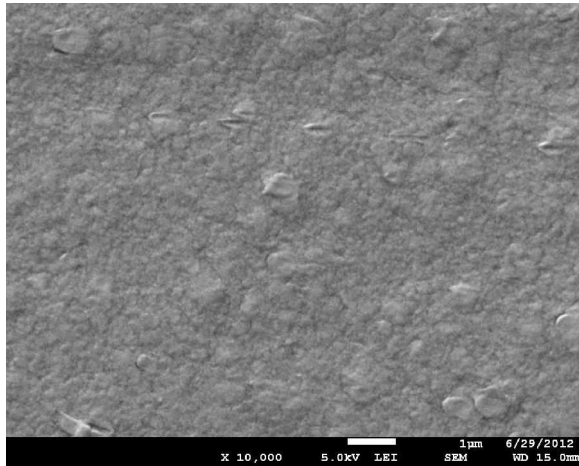


Figure 4: Micrograph of the Parylene C surface, magnification of 10 000

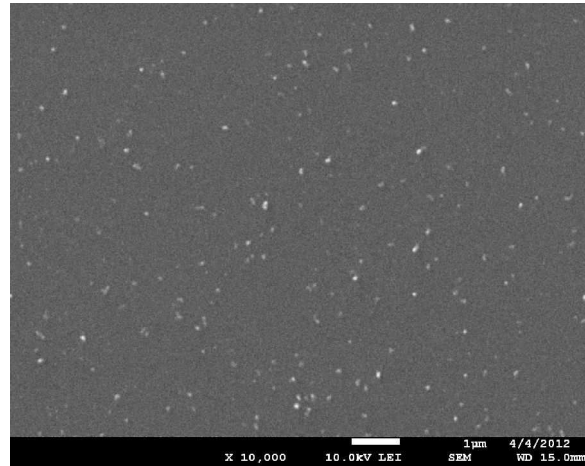


Figure 5: Micrograph of the pp-HMDSO surface, magnification of 10 000

3.4 X-ray Photoelectron Spectroscopy

We used the X-ray Photoelectron Spectroscopy to find out the elemental composition of thin layers of pp-HMDSO. The layers contained C, O and Si. We wanted to know whether the layer contained a lot of carbon because we need a layer which is the most similar to the SiO₂ layer. The layer with a smaller amount of carbon is fragile, but with better protection properties. In contrast to this fact, a layer with a higher content of carbon is much more flexible and does not crack so often, but it has worse protection properties.

As this method detects only a depth of about 10 nm, it detects also carbon adsorbed onto the surface in the form of hydrocarbons. It was determined using the argon beam sputtering that it is the only carbon on the surface. The amount of carbon decreased already by the etching of a small layer. In Table 1 you can see values for concentration of C, O and Si. You can see that the amount of carbon after etching is zero. It means that carbon on the surface came really from dirt and we have prepared a good layer which is similar to the SiO₂ layer.

Table 1: Concentrations of O, Si, C obtained from the XPS measurements

	Concentration (%)		
	O	Si	C
Surface	66	31	3
After etching	67	33	0

3.5 Oxygen Transmission Rate

As you can see in Table 2, the values for Oxygen Transmission Rate measurements are very different. In case of pp-HMDSO, the transmission rate is of the same order as the clean PP-foil. It is in contrast to Parylene C where the transmission rate is about 20 times lower than the permeability of the PP-foil.

Table 2: Transmission rate of the PP-foil

Substrate	Permeability (cm ³ /(m ² ·atm·day))
PP-foil	665
PP-foil with pp-HMDSO	127
PP-foil with Parylene C	32

3.6 Corrosion tests

In Figure 6 you can see iron samples covered by copolymer ethylmethacrylate-methylacrylate PARALOID B44. On the left side (a) there is a sample before the test beginning. You can see patterns on the surface which were formed during the preparation of the coating. It indicates that the surface is not homogeneous but it does not influence the test. Corrosion was formed on the edges of the samples after 30 hours. After 100 hours, the samples were covered by a thin layer of corrosion which was spread from the edges. The corrosion started to peel off the surface after 200 hours. On Figure 6 (b) is the sample after the test stop, it means after 300 hours. The range of the corrosion layer remained approximately the same, but with thicker layer of the corrosion.

Corrosion tests for Parylene C layers on iron substrates showed a very good protection of these substrates. There are any significant differences among artefacts with the thin layer and without the thin layer after the test finish in the salt spray chamber. First signs of corrosion were observed after 100 hours when the samples became darker. Pitting on the edges of the samples was observed. Corrosion was spread very slowly from the edges to the centre of the surface and corrosion oxide layers were very thin. In Figure 7 (b) you can see photo of the samples after the test finish, this means after 300 hours. The samples were darker and the corrosion progress from the edges towards the surface slightly expanded.

Another examined metal was brass. On Figure 8 (a) is a sample with the PARALOID B44 coating at the beginning of the test and in Figure 8 (b) is the same sample after 300 hours in the salt fog. The sample in Figure b is strongly covered by corrosion products. Corrosion is on the whole surface, but the layer is thin. In Figure 9 (b) you can see photo of the brass samples with the thin layer of Parylene C after the test finish, this means after 300 hours. The sample was almost unchanged, only there was slight pitting at some places. Compared to iron, brass is more resistant.

Copper samples with the PARALOID B44 coating became darker after the start of the test. Pitting on the samples was observed after 300 hours in the salt spray chamber. The samples with the thin layer of Parylene C were darker too, but pitting was isolated on the surface and it was less frequent. The surface of the sample stayed relatively smooth.

The last sample was bronze. There were no major changes on the surface of all samples (with PARALOID B44 and with Parylene C) after the corrosion test finish. The only change was a slight darkening of the surface after 300 hours in the salt spray chamber.

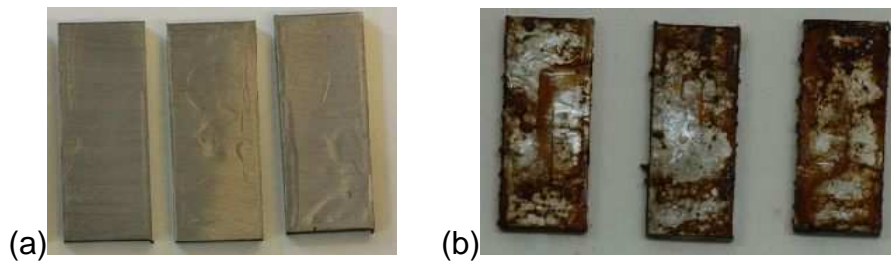


Figure 6: Iron sample covered by copolymer PARALOID B44 (a) before the test beginning and (b) after the test stop

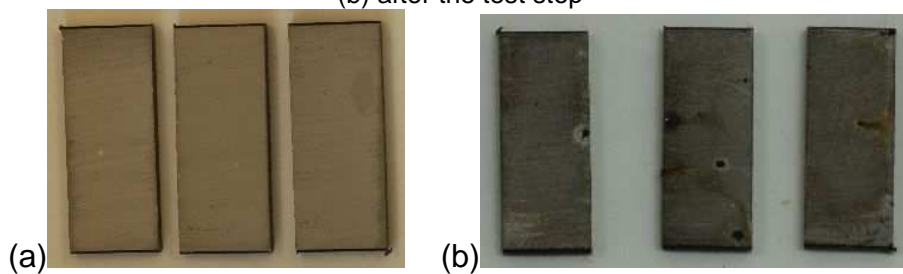


Figure 7: Iron sample with thin film of Parylene C (a) before the test beginning and (b) after the test stop

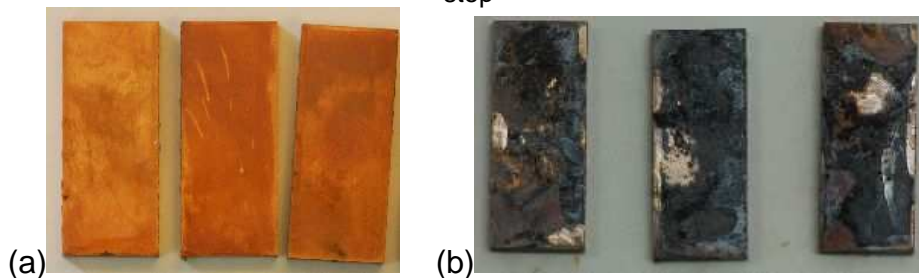


Figure 8: Brass sample covered by copolymer PARALOID B44 (a) before the test beginning and (b) after the test stop

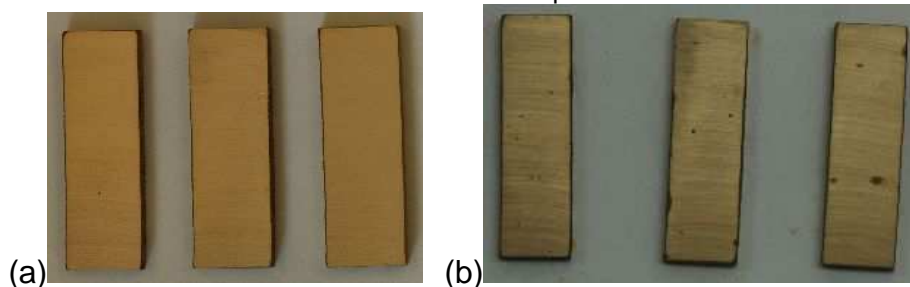


Figure 9: Brass sample with thin film of Parylene C (a) before the test beginning and (b) after the test stop

Samples which were protected by the thin layer of pp-HMDSO had another course of corrosion tests. The time of the testing was about 336 hours. The samples were dipped both in water and in salt solution and they were compared and checked every day. From these tests, it is clear that the most resistant is brass and the least resistant is iron. This is applied to water and salt solution too.

The samples of iron changed after about 4 hours in the test in water, but in case of brass there was any significant corrosion observed for a long time. In the case of copper, corrosion was observed after 48 hours, and changes on bronze were observed in about one day. The Figures (10 b, d) show the metals (iron and brass) after the test finished, it means after 336 hours. The corrosion in the salt solution was much faster and more aggressive.

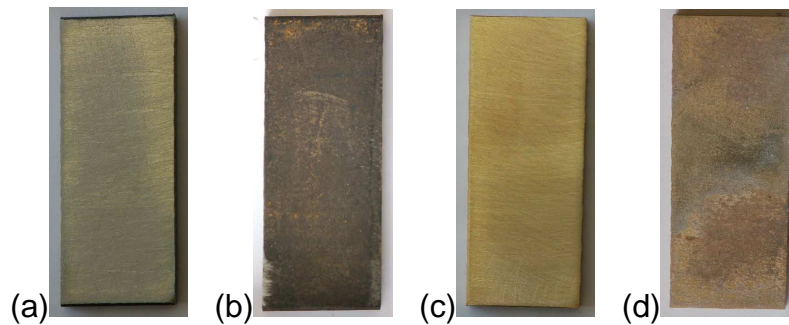


Figure 10: Samples with thin layer of pp-HMDSO, (a) iron sample before the test beginning and (b) after the test stop; (c) brass sample before the test beginning and (d) after the test stop

4 Conclusion

We have compared thin layers of Parylene C and pp-HMDSO which were used for the protection of archaeological artefacts. We chose copper, iron, brass and bronze as samples. Thanks to the Scanning Electron Microscopy we determined that all thin layers had homogeneous structure. Then we examined the permeability of the thin layers on the PP foil by Oxygen Transmission Rate measurements. PP foil itself had a much higher transmission rate than the examined thin layers. The thin film of Parylene C had a four times smaller permeability than the thin film of pp-HMDSO. Elemental composition was investigated by the Infrared Spectroscopy and X-ray Photoelectron Spectroscopy. We determined that thin layers of pp-HMDSO did not contain carbon, which indicated that we had prepared the thin layer really similar to the SiO₂ like layer. The last test was the standard corrosion test. The thin film of Parylene C appeared to be a better protection than the thin film of pp-HMDSO.

Acknowledgements

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References

- [1] Meng, E., Li, P.-Y., Tai, Y.-C., Plasma removal of Parylene C, *J. Micromech. Microeng.*, **18** (2008) 045004 (13pp)
- [2] Fortin, J. B., Lu, T.-M., Chemical Vapor Deposition Polymerization – The Growth and Properties of Parylene Thin Films. Kluwer Academic Publishers, New York 2004, 89 p. ISBN 1 4020 7688 6
- [3] Inagaki, N., Kondo, S., Hirata, M., Urushibata, H., Plasma Polymerization of Organosilicon Compounds, *J. Appl. Polym. Sci.*, **30** (1985), pp. 3385.
- [4] Zanini, S., Riccardi, C., Orlandi, M., Esena, P., Tontini, M., Milani, M., Cassio, V., Surface properties of HMDSO plasma treated polyethylene terephthalate, *Surface & Coatings Technology.*, 200 (2005) 953-957
- [5] Fortin, J. B., Lu, T.-M., Ultraviolet radiation induced degradation of poly-para-xylylen (parylene) thin films, *Thin Solid Films.*, 397 (2001) 223-228
- [6] Specialty Coating Systems, *Parylene Conformal Coating Specifications & Properties*, (available from <http://www.scscookson.com/parylene/properties.cfm>)
- [7] Callahan, R. R. A., Pruden, K. G., Raupp, G. B., Beaudoin, S. P., Downstream oxygen etching characteristics of polymers from the parylene family, *Journal of Vacuum Science.*, 21(4) (2003) pp. 1496-1500 ISSN 0734211
- [8] Patelli, A., Vezzu, S., Zottarel, L., Menin, E., Sada, C., Martucci, A., Costacurta, S., SiO_x-Based Multilayer Barrier Coatings Produced by a Single PECVD Process, *Plasma Processes and Polymers.*, 6 (2009) pp. 665-670 ISSN 16128850