An evaluation of non-equilibrium plasma polymerized polypyrrole films for the conservation of metallic items belonging to cultural heritage

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Low pressure non-equilibrium plasma polymerization is an emerging route for the preparation of a variety of pinhole free, conformal thin films, deposited on different substrates, using a room temperature, clean, environmentally benign process. The aim of our research was to develop effective protective coatings fitting the specific requirements of heritage preservation to prevent, or at least slow down, further corrosion of preserved metallic objects. The coatings were deposited by plasma polymerization of pyrrole on Romanian old coins. The resulting plasma polymers deposited on metallic supports are characterized by FTIR spectrophotometry, AFM, optical microscopy and colour changes.

1. Introduction

Low-pressure non-equilibrium plasma polymerization is today accepted as an emerging and versatile process for the formation of entirely new materials starting from organic precursors and an important technique to provide molecular level tailoring of a variety of materials' surfaces for specific applications. It is a well developed technique for the preparation of a variety of functional organic films on substrates with the aim of surface and interface engineering for improving adhesion, hydrophobicity, hydrophilicity, printability, corrosion resistance, selectivity, or for surface etching or cleaning.

The main principle of the plasma polymerization technique is that the ionized and excited molecules and radicals created by the high frequency electrical field bombard and react with the surface of the substrate. These activated molecules may etch, sputter, or deposit on the substrate surface. As a result, the surface properties of substrates are modified. Advantages of plasma polymerization include the fact that pinhole free, conformal thin films can be deposited on most substrates, using a room temperature, clean, environmentally benign which does not release wastes or appreciable atmospheric emissions and energy efficient procedure of coating.

Due to these characteristics, the plasma technique can be used for surface modification and thin film deposition for almost all substrates, including metal and alloy plates, polymer films, paper, glass, porous materials and particulate matter, for application ranging from adhesion to composite materials, protective coatings, printing, membranes, biomedical applications, etc.

Different techniques to improve the control over the film chemistry and surface modifications have been studied, most of them based on decreasing the input energy during the reaction; by using a pulsed high frequency plasma instead of the traditional continuous wave plasma, Timmons et al. [1] reported more selective chemistry of films, leading to less cross-linked and more "conventional polymer – like" structures.

In the field of surface engineering of metals, aspects of corrosion protection as well as aesthetic properties are of real interest. In many cases, the film has to adhere on the oxide covered metal surface even under humid and corrosive conditions. In this case, thin plasma polymers must act as adhesion-promoting, corrosion-resistant, thin interfacial films. In recent years, several authors have proven that metals can be effectively protected against corrosion by deposition of thin plasma polymers [2-6]. Suitable plasma polymers are known to be able to protect metals.

Yasuda et al. have developed the process of cathode plasma polymerization leading to films strongly bound to the metallic substrates [7]. The authors already showed the excellent corrosion protection of these films.

At the same time, the protection of oxidizable metals against corrosion is one of the most investigated applications, since largely used chromates, phosphates and galvanically deposited coatings, have been limited because of ecological concerns [8-12]. In this situation, the plasma polymerization with film deposition from organic monomers appears to be an attractive approach to increase the corrosion resistance of metallic materials.

Conjugated polymers such as: polypyrrole, polyaniline, polythiophene, and their derivatives as coatings have been studied and reported to be used with good results in the corrosion-control of iron and iron-based alloys [13-16], zinc, copper or copper based alloys [17-22]. Several types of interactions between an active metal (such as Al, Fe or their alloys) and an oxidized (thus, electronically conducting) conjugated polymer are possible, including electronic interactions (non-redox), electrochemical interactions (redox) and chemical interactions (involving polymer and/or dopant anions). As a result, the corrosion behaviour of the metal may be influenced by any or all of these interactions, depending on the nature of the metal substrate, the characteristics and the coating deposition method of the conjugated polymer and the manner of metal surface preparation [21].

An important concern of museum restoration and conservation community is the preservation of historical

items taken out of excavations and kept in museums or in depots. In the case of metallic items, one problem is to stop or to limit surface corrosion or its alteration by the ambient atmosphere. After extraction from the environment where they reached equilibrium, these items can be damaged or even completely destroyed by corrosion. To preserve the item, one solution is to isolate it from the environment with a protective organic coating, by respecting the specific requirements of conservation.

Organic coatings are one of the most important ways of protecting metals against corrosive agents, thanks to their diffusion barrier properties to atmospheric oxygen or water [23-25]. They have been used for a long time in conservation, in particular to protect outdoor sculptures against weathering, atmospheric pollution or inappropriate interventions [26, 27]. Many times, water represents the most aggressive factor responsible for weathering, so that it is necessary to reduce the rate at which water and any pollutants transported by it, come in contact with the surface of the item. This can be realized by using a protective surface treatment with a polymeric resin [28-30]. At the same time, in the domain of conservation, plasma treatments have already been used (particularly hydrogen plasma to reduce the oxidized surface) in cleaning applied to the preservation of archaeological iron [31,32]. In this domain, they must also satisfy specific requirements such as reversibility and aesthetic aspect (they must be as invisible as possible). These requirements imply that an ideal and universal protective coating does

not yet exist for conservators and that research in this domain is still important.

Our previously papers [33,34] have evidenced promising results on plasma polymer thin films' deposition in low-pressure non-equilibrium plasma on different supports belonging to the heritage items with the aim of their conservation and consolidation.

In this paper, our results are focused on the low-pressure non-equilibrium plasma polymerization of pyrrole with thin film deposition for corrosion protection of metallic supports as old Romanian coins. The polypyrrole films are characterized by FT-IR spectrophotometry, atomic force microscopy, optical microscopy and colour changes.

2. Experimental

2.1 Materials

Romanian original coins (1883, 1906, 1910, 1914, 1944 years) belonging to private collection, with known chemical composition of the alloy and details on the normal viewing positions, given by authorized information in Table 1 [35], are treated for cleaning and polypyrrole PPy film deposition in the condition of non-equilibrium plasma.

Pyrrole (reagent grade Aldrich, 98%) is purified by distillation under nitrogen atmosphere and only freshly distilled monomer is used in the experiments.

Table 1. Romanian coins used in the experiments [35].

S1: 25 mm diameter, 5 g, copper 95%, tin 4%, zinc 1%, year 1883	S2 : 19 mm diameter, 2.5 g, copper 75%, nickel 25%, year 1906.
S3 : 27 mm diameter, 10 g, silver 83.5%, copper 16.5%, year 1910	S4 : 18 mm diameter, 2.5 g, silver 83.5%, copper 16.5%, year 1914
S5 : 32 mm diameter, 12 g, silver 83.5%, copper 16.5%, year 1944	

2.2 Plasma polymerization

Plasma polymerization equipment and general procedure employed in operation were previously described [36,37]. After the samples are introduced into the plasma reactor, the reaction chamber is pumped down to 0.133 mbarr partial pressure before the monomer of pyrrole is introduced. Then, the samples were cleaned by a hydrogen plasma for 600 sec. Immediately after this cleaning step, the flow of monomer in the reactor at steady flow conditions is controlled by a needle valve, to assure a total pressure of 0.399 mbarr. The coating is deposited from the pure monomer, no carrier gases being added. Power up to 200 W from high frequency (1.2 MHz) oscillator power supply is capacitive coupled to the reactor by means of a pair of semicylindrical electrodes disposed around it. As soon as the system was regulated to the assigned power, a glow discharge is initiated in the space of the plasma reactor. The plasma exposure is conducted at room temperature, for 600 sec. As a result of this treatment, it is gravimetrically estimated an average deposition of $2.5 \ g \cdot m^{-2}$ polymer on the coin' surface. Finally, the treated samples are kept in the vacuum desiccator, until there have been analyzed.

2.3 Characterization

FTIR Spectroscopy. The composition of the plasma polymer films is evidenced on a spectrophotometer DIGILAB Scimitar Series-USA, in the transmission mode with a resolution of 4 cm^{-1} and 32 scans.

AFM Surface Analysis. AFM measurements are performed in air at room temperature, in the Tapping Mode using a Scanning Probe Microscope (Solver PRO-M, NTMDT, Russia) with commercially available NSG10/Au Silicon cantilevers. The manufacturer's value for the probe tip radius is 10 nm, and the typical force constant is 11.5 N/m. The cantilever is oscillated close to the resonance frequency (254.249 kHz) over the area to be scanned (20 μm x 20 μm, 30 μm x 30 μm, 40 μm x 40 μm, 60 μm x 60 μm). The scans were done without any sample surface treatment. The corrugation height of a film was obtained using the cross-section analysis and the reported values are averages taken from scans on different regions of the films.

The Root Mean Square (RMS) roughness parameter, Sq (Eqn.1), is extracted from the Nova software provided:

$$S_q = \sqrt{\frac{1}{MN}\sum_{j=1}^{N}\sum_{i=1}^{M} z^2(x_i, y_j)}$$

(1)

where M is the number of columns in the surface and N is the number of rows in the surface. Off-line image analysis on quantification of surface properties using the surface roughness parameter was obtained.

Optical Microscopy. Optical microscopy images are acquired on a Reflected light brightfield microscope Leica DM 2500 (Leica Microsystems Wetzlar GmbH), magnification across the sample surface: 50X, with a 3.3 Mpix Leica DFC320 R2 digital camera (resolution 2088 x 1550 pixels) mounted on the trinocular head. The photo is later converted into digitized gray scale data for analysis.

Colour and gloss measurements

Colour changes are measured with Pocket Spec QA TM model system, that evaluates L*, a*, b* coordinates according to the standard established by the International Committee of Illumination (CIE). In the L*a*b* chromaticity diagram it is provided a numerical representation of three-dimensional colour space where L* represents the lightness axis, a* represents a red (+a) – green (-a) axis and b* represents a yellow (+b) - blue (-b) axis. The changes of colour can be computed from differences in L*, a* and b* values before and after the film deposition on the metallic coin. A useful parameter is ΔE_{ab} (Eqn. 2), calculated as the square root of the sum of the squares of differences in L*, a* and b* values, using a procedure outlined in ASTM D2244 (providing standard test method for calculation of colour differences from instrumentally measured colour coordinates):

$$\Delta E_{ab} = (\Delta L^2 + \Delta a^2 + \Delta b^2)^{1/2}$$

(2)

where ΔL, Δa and Δb are the difference of initial and final values (before and after the film deposition) of L*, a* and b*, respectively.

3. Results and discussion

3.1 Chemical structure

As it is already discussed before, the experiments with plasma polymer film deposition on metallic support have been realized in the experimental conditions (power 200 W) which contribute to increased film chemistry controllability.

Fig. 1 shows the FT-IR spectrum of plasma polymerized PPy film on the surface of metallic supports presented in Table 1 in the established experimental conditions.
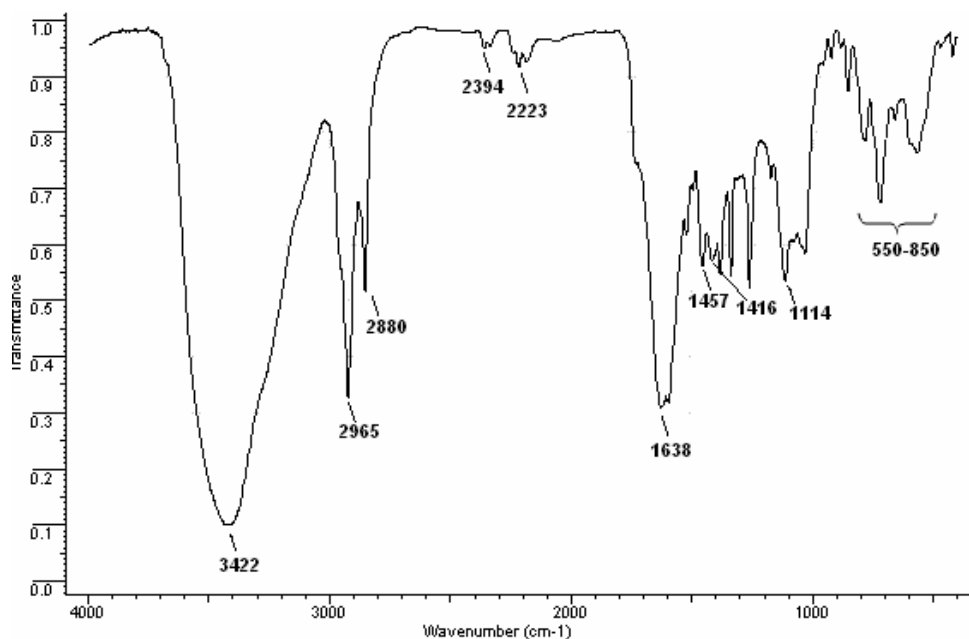
Fig. 1. FT-IR spectrum of plasma polymer film based on PPy.

The vibration spectrum for plasma polymer obtained by us coincides rather well with the results of other authors [38], as it is presented in Table 2. At the same time, in this spectrum are present the reported absorption peaks for the monomer pyrrole [39, 40] (Table 2).

Table 2. The main frequencies of pyrrole ring and the assignments
for monomer (Py) and plasma polymer (PPy).

Frequency, cm^{-1} PPy (present study)	Frequency, cm^{-1} Py reported [39,40]	Frequency , cm^{-1} PPy reported [38]	Assignment
3422	3400	3400	N-H stretching
1457	1460	1450	In plane vibration of ring
1416	1420	1420	In plane vibration of ring
1114	1140	1130	Breathing of ring [x]
1032	1046	1040	C-H in plane bending
784	838	790	Out of plane distortion of ring
721	768	730	C-H out of plane bending
661	647	-	In plane deformation of ring
566	565	600	N-H out of plane bending

x) - From Refs. [39, 41], ring breathing vibration is a totally symmetrical expansion and contraction movements that do not involve angle changes but shows IR absorption because the charge distribution over the ring is not symmetrical and a change in dipole occurs during the breathing.

The spectrum of plasma polymer contains specific frequencies for the monomer, but also the new bands describing the mechanism occurred during the plasma polymerization process. Thus, NH stretch and NH bend modes in monomer from 3400 cm^{-1} and 1140 cm^{-1} are identified in the polymer spectrum at 3422 and 1114 cm^{-1}. This is indicative of the fact that the NH band is unaffected in the plasma polymerization. Relatively strong bands at 1420 and 1460 cm^{-1} represent ring frequencies in the monomer. Supplementary, the presence of bands at 1457 and 1416 cm^{-1} in the polymer spectrum indicates that the ring structure is not totally affected by plasma polymerization process. The bands characteristic of five member aromatic ring occurring in the range of 550 – 850 cm^{-1} is present in the spectra of monomer and polymer. Again the presence of these bands suggests that the rings are not altogether opened up by plasma polymerization process.

On the other side, pyrrole rings are generally subjected to some destructions during the plasma process, some new bands as compared to the monomer are observed in the spectrum: the bands at 2965, 2880 cm^{-1} are assigned to C-H stretching of sp^3 CH$_3$ and sp^3 CH$_2$ groups [42- 44], while the bands at 2223 and 2394 cm^{-1} are attributed to the stretching of C≡N and/or -N=C=O [45]; the N-H bending in amine is observed at 1638 cm^{-1};

it seems too broad, hence, includes the contributions from C=N imine stretch and possibly C=C alkene stretching [45, 46].

In a previously experiment [36], some pyrrole rings are also remained in the plasma polymer PPy films prepared with a discharge power of 250 W, whereas the other part of rings are decomposed. The conjugation in the chain of 2,5-disubstituted pyrrole rings in the main chain is interrupted by saturated linkages resulted from fragmentation and hydrogenation of aromatic rings.

To compare of our results with those of Kojima et al. [38], it should conclude that the two FT-IR spectra of the plasma polymer have many approaches, excepting the low intensities for some bands of ring for our film because we selected a relatively higher power (200 W) during the

plasma polymerization (the power chosen by Kojima et al. was only 5 W).

In conclusion for our case, the plasma-polymerized PPy film consists of the main chain (aliphatic hydrocarbon) involving nitrogen-containing groups as well as a certain amounts of pyrrole and monosubstituted alkyl pyrrole rings.

3.2 Film morphology

AFM analysis is used as a tool to distinguish the suitability of the deposition conditions of the coating in the plasma polymerization process and to evaluate the topography of the plasma film surface deposited on coins. Fig. 2 shows the 2D and 3D Tapping Mode AFM images of plasma polymer PPy film at different tapping areas.
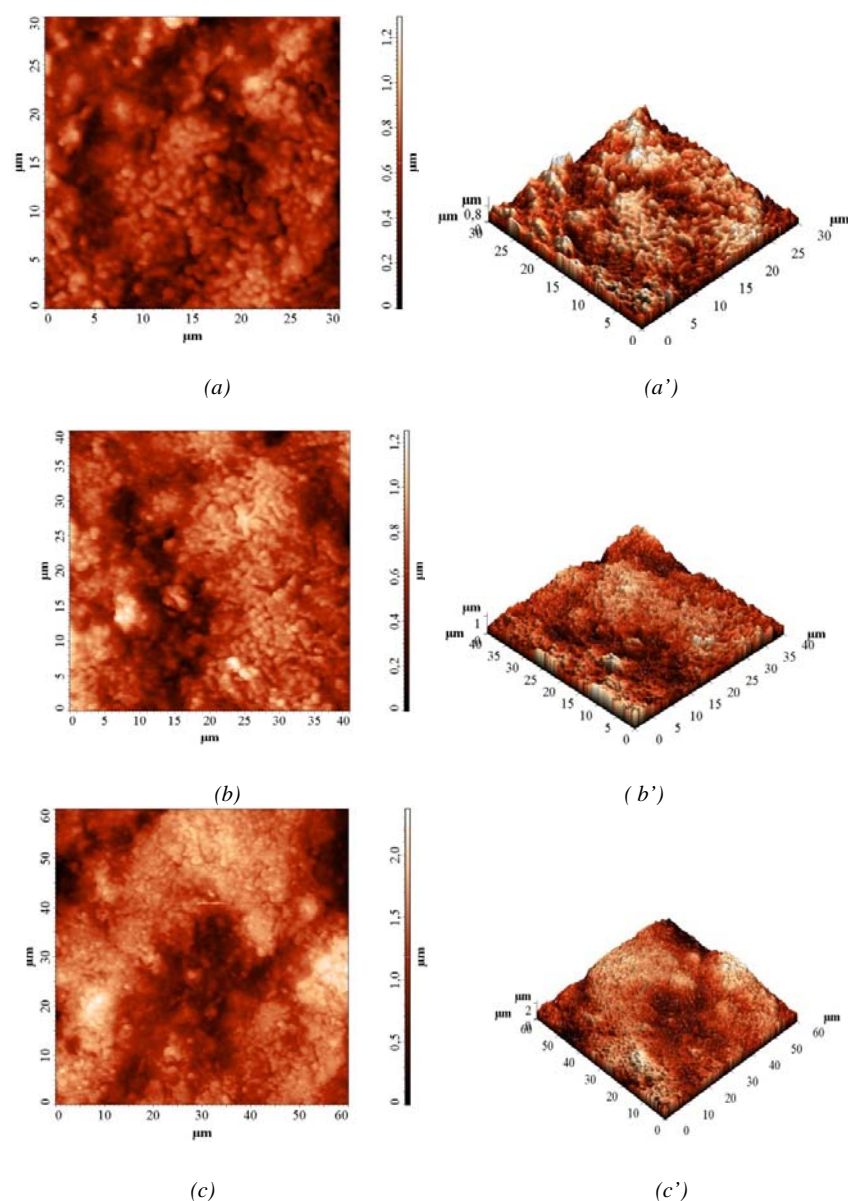

(a)   *(a')*

(b)   *(b')*

(c)   *(c')*

Fig. 2. 2D and 3D Tapping Mode AFM image of plasma polymer PPy film at different tapping areas :
a - 30μmx30μm; b - 40μmx40μm; c -60μmx60μm.

2D and 3D AFM images registered on different tapping areas (Fig. 2 a-c, a'-c' and Fig.3 a,b) show the surface topography of the polypyrrole film is compact, but inhomogeneous, existing ordered and smooth domains alternating with nanometer-sized peak-to-valley irregularities of the grooves at various locations on the treated coin, such as nodules or bundles of unclear shapes. There is evidenced the polymer film has good adhesion to metallic surface, "imitating" with accuracy the substrate topology: polished zones alternating with inscriptions and relief images on the coin surface.

As it is underlined elsewhere [34], the non-equilibrium plasma discharge is concentrated especially on peaks; as a consequence, in those high energy peak regions a preferential deposition takes place, with a rounded off of the peaks and the increase of difference between heights and cracks, evidenced in 3D AFM image.

The cross-section analysis in AFM image of plasma polymer PPy film (Fig.3c) shows the peaks' distribution with variable dimensions, revealing a periodicity of peaks in this spectrum.

Local surface roughness is defined, on each analyzed area, as the root mean square deviation of the surface height, from its average value. The RMS roughness is S_q = 108,594 nm for the shown area (20 μm x 20 μm in this case).

(a)

(b)

(c)

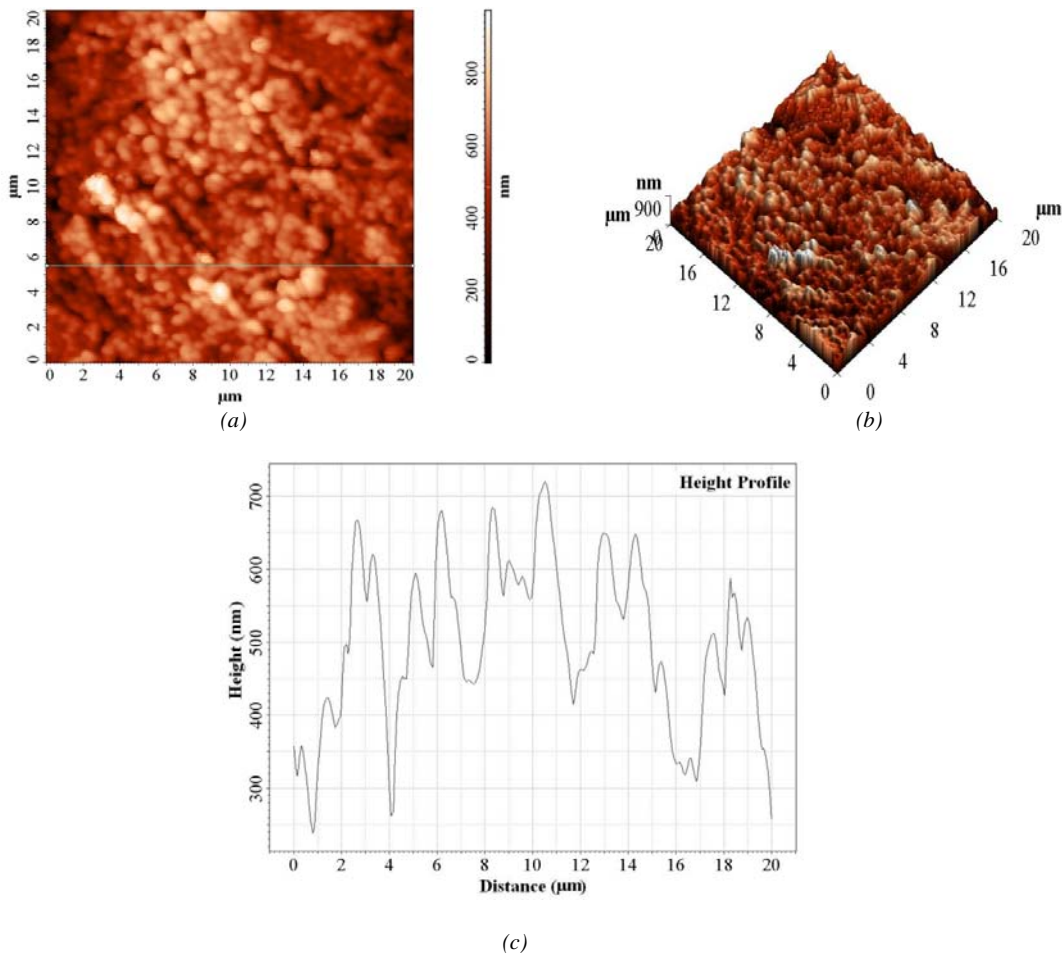*Fig. 3. 2D (a) , 3D (b) AFM image of plasma polymer PPy film:*
tapping area 20 μm x 20 μm and its cross-section analysis (c).

Inspection of the plasma polymer PPy films deposited on metallic surface of coin was performed by optical microscopy (Fig. 4 a and b). As complementary information to the AFM investigation, these micrographs reveal a wavy replica on the pattern coin that follows the relief.
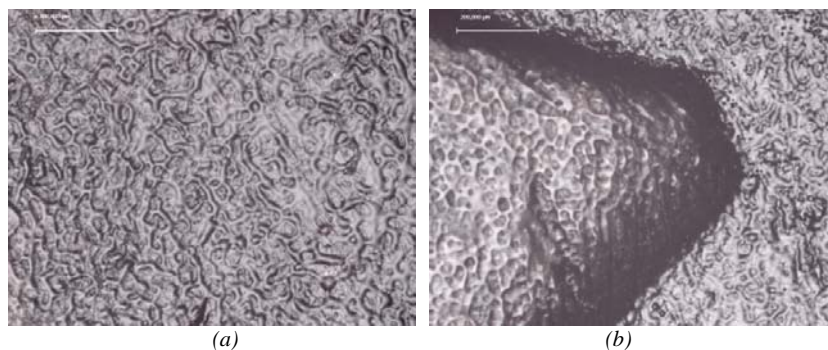
(a)   *(b)*

*Fig. 4. Optical micrographs (magnification 50 X) of plasma polymer PPy film
deposited on metallic coin. : a – flat level area on the coin;
b- area with in relief detail on the coin.*

In Fig. 4b the dark phase represents the edge of a relief shape on which is evidenced the preferential deposition of plasma polymer with a rounded off of the contour on the coin surface.

3.3 Colour changes

By observing with naked eye the plasma treated coins, it is realized a slightly yellowish for the thinnest films deposited on the metallic surface. This colour can be a problem depending on the aspect of the original metal. Indeed, the coating colour will alter the aesthetic appearance of silver or other shiny metals; but, on the other hand, on old metallic items which are always oxidized and black, a yellowish coating remains almost invisible. This affirmation is valid in the case of our study. The CIE Lab system for measuring chromaticity is chosen to record colour differences because it is well suited for determination of small colour differences. In Table 3 there are presented the chromaticity parameters differences (ΔL, Δa, Δb) and overall colour change ΔE_{ab} calculated with eqn. 2 for the five metallic supports denominated S1 – S5 in Table 1.

Table 3. Colour parameters of plasma polymer PPy coated metal comparative to metallic substrate.

Sample	ΔL	Δa	Δb	ΔE
S1	2.18	0.52	-2.99	4.11
S2	2.0	0.54	-0.16	2.08
S3	2.55	0.41	-1.46	2.97
S4	0.76	0.54	-0.75	1.19
S5	1.12	0.38	- 1.19	1.73

As compared with the reference models (coins S1-S5 in Table 1), the coated coins with PPy films do not show great changes of the chromaticity parameters. Lightness change (ΔL) with greater value results in a film with less luminosity, brightness and transparency. Red / green difference stated by Δa, reflects an unimportant change but with tendency to green of the coin covered by film, while the yellow/blue difference stated by Δb, having negative values show a slight tendency to yellow. The smaller values for ΔE are an evidence for the changes almost undetectable with the naked eye (according the standard ASTM D2244 stipulations).

At the same time, the film of plasma polymer based on polypyrrole deposited on coin is stable when the coins are dipped in solvents, such as acetone or ethanol; it is not destroyed. However, from the conservator's viewpoint the reversibility of the treatment is especially important and the coating layers should be removable without affecting the integrity of the coated item. The plasma polymer based on polypyrrole deposited on coins fulfills these requirements, as it can be totally removed in hydrogen plasma for 30 minutes, by etching phenomena.

4. Conclusions

The polypyrrole films are deposited on metallic supports as Romanian coins, in non-equilibrium plasma polymerization, by using the operational parameters of : frequency 1.2 MHz, total pressure 0.399 mbarr, discharge power 200W and discharge time 600 s. FT-IR analysis evidences the main chain involving nitrogen-containing groups with pyrrole and monosubstituted alkyl pyrrole rings. Topography of films is revealed by AFM and optical microscopy, while the changes in colour of the original coins by film deposition is established by L*a*b* chromaticity diagram.

References

[1] Y. Wu, L. M. Han, B. E. Thomes, H. Qiu, W. W. Lee, R. B. Timmons, Mater. Res. Soc. Symposium Proceedings **544**, 77 (1999); M. T. Van Os, B. Menges, R. Förch, W. Knoll, R. B. Timmons, G. J. Vansco, Mater. Res. Soc. Symposium Proceedings **544**, 45 (1999); L. M. Han, R. B. Timmons, J. Polym. Sci.: Part A: Polym. Chem. **36**, 3121 (1998); J. G. Calderon, A. Harsch, G. W. Gross, R. B. Timmons, J. Biomed. Mater. Res. **42**, 597 (1998); L. M. Han, D. Bogdal, R. B. Timmons, Chem. Mater. **10**, 1422 (1998); L. M. Han, W. W. Lee, R. B. Timmons, Mater. Res. Soc. Symposium Proc. **511**, 93 (1998); L. Tang, Y. Wu, R. B. Timmons, J. Biomed. Mater. Res. **42**, 156 (1998); L. M. Han, R. B. Timmons, W. W. Lee, Y. Chen, Z. Hu, J. Appl. Phys. **84**, 439 (1998); J. G. Calderon, R. B. Timmons, Macromolecules **31**, 3216 (1998); J.-H. Wang, X. Chen, J. Calderon, J.-J. Chen, R. B. Timmons, Plasmas and Polymers **2**, 241 (1997); L. Han, K. Rajeshwar, R. B. Timmons, Langmuir **13**, 5941 (1997).
[2] T. F. Wang, T. J .Lin, D. J. Yang, J. A. Antonelli, H. K. Yasuda, Prog. Org. Coat. **28**, 291 (1996).
[3] W. J. van Ooij, J. Test Eval. **23**, 33 (1995).
[4] H. Yasuda, T. F. Wang, D. L. Cho, T. J. Lin, J. A. Antonelli, Prog. Org. Coat. **30**, 31 (1997).
[5] G. Grundmeier, M. Stratmann, Mater. Corros. **49**, 150 (1998).
[6] T. J. Lin, J. F. Antonelli, D. J. Yang, H. K. Yasuda, F. T. Wang, Prog. Org. Coat. **31**, 351 (1997).
[7] W. J. van Ooij, D. Surman, H. K. Yasuda, Prog. Org. Coat. **25**, 319 (1995).
[8] B. del Amo, R. Romagnoli, V. F. Vetere, L. S. Hernandez, Prog. Org. Coat. **33**, 28 (1998).
[9] M. Bethencourt, F. J. Botana, J. J. Calvino, M. Marcos, M. A. Rodriguez - Chacon, Corros. Sci. **40**, 1803 (1998).
[10] T. Ohtsuka, M. Iida, M. Ueda, J. Solid State Electrochem. **10**, 714 (2006).
[11] D. Kowalski, M. Ueda, T. Ohtsuka, Corr. Sci. **49**, 1635 (2007).
[12] D. Kowalski, M. Ueda, T. Ohtsuka, Corr. Sci. **49**, 3442 (2007).
[13] F. X. Perrin, J. Pagetti, Corros. Sci. **40**, 1647 (1998).
[14] J. L. Camalet, J. C. Lacroix, S. Aeiyach, P. C. Lacaze, J. Electroanal. Chem. **445**, 117 (1998).
[15] B. D. Sazou, C. Georgolios, J. Electroanal. Chem. **429**, 81 (1997).
[16] J. He, V. J. Gelling, D. E. Tallman, G. P. Bierwagen, C. G. Wallace, J. Electrochem. Soc. **147**, 3667 (2000).
[17] M. Bazzaoui, E. A. Bazzaoui, J. I. Martins, L. Martins, Mat. Sci. Forum **455–456**,484 (2004).
[18] M. Bazzaoui, L. Martins, E. A. Bazzaoui, J. I. Martins, J. Electroanal. Chem. **537**, 47 (2002).
[19] M. Bazzaoui, E. A. Bazzaoui, L. Martins, J. I. Martins, Synth. Met. **128**, 103 (2002).
[20] M. Bazzaoui, J. I. Martins, E. A. Bazzaoui, T. C. Reis, L. Martins, J. Appl. Electrochem. **34**, 815 (2004).
[21] D. E. Tallman, G. Spinks, A. Dominis, G. G. Wallace, J. Solid State Electrochem. **6**, 73 (2002).
[22] G. M. Spinks, A. J. Dominis, G. G. Wallace, D. E. Tallman, J. Solid State Electrochem. **6**, 85 (2002).
[23] Y. Lin, H. Yasuda, J. Appl. Polym. Sci. **60**, 543 (1996).
[24] C. P. Klages, A. Dietz, T. Höing, R. Thyen, A. Weber, P. Willich, Surf. Coat. Technol. **80**, 121 (1996).
[25] V. Kh. Kudoyarova, A. V. Chernyshov, T. K. Zvonareva, N. B. Dzhelepova, M. B. Tsolov, Surf. Coat. Technol. **100/101**, 192 (1998).
[26] K. F. B. Hempel, Studies in Conservation **13**, 34 (1968).
[27] L. D'Arienzo, P. Scarfato, L. Incarnato, J. Cultural Heritage **9**, 253 (2008).
[28] R. Cioffi, O. Marino, G. Mascolo, Mat. Eng. **2**(2), 263 (1991).
[29] J. Kiuberis, S. Tautkus, R. Kazlauskas, I. Pakutinskiene, A. Kareiva, J. Cultural Heritage **6**, 245 (2005).
[30] M. F. Vaz, J. Pires, A. P. Carvalho, J. Cultural Heritage **9**, 269 (2008).
[31] J. Patscheider, S. Veprek, Studies in Conservation **31**, 29 (1986).
[32] P. Arnould-Pernot, C. Forrieres, H. Michel, B. We´ber, Studies in Conservation **39**, 232 (1994).
[33] M. Totolin, I. Neamţu, D. Filip, I. Stoica, D. Macocinschi, Optoelectron. Adv. Mat. – Rapid Commun. **2**(5), 309 (2008).
[34] M. Totolin, I. Neamtu, Optoelectron. Adv. Mat. – Rapid Commun. **2**(6), 387 (2008).
[35] http://www.geocities.com/romaniancoins/ selector.html
[36] M. Totolin, M. Grigoras, Rev. Roum. de Chimie **52**(10), 999 (2007).
[37] M. Totolin, M. Grigoras, D. Conduruta, J. Optoelectron. Adv. Mat. **9**(4), 881 (2007).
[38] T. Kojima. H. Takaku, Y. Urata, K. Gotoh, J. Appl. Polym. Sci. **48**, 1395 (1993).
[39] R.C. Lord Jr., F. A. Miller, J. Chem. Phys. **10**, 328 (1942).
[40] B. Tian, G. Zerbi, J. Chem. Phys. **92**, 3886 (1990).
[41] R. G. Davidson, T. G. Tumer, Synth. Met. **72**, 121 (1995).
[42] B. Dischler, A. Bubenzer, P. Koidl, Solid State Commun. **48,** 105 (1983).
[43] T. R. Gengenbach, Z. R. Vasie, R. C. Chatelier, H. J. Griesser, J. Polym. Sci., Polym. Chem. Ed. **32**, 1399 (1994).
[44] S. Schelz, J. Eitle, R. Steiner, P. Oelhaffen, Appl. Surf. Sci. **48/49**, 30t (1991).
[45] F. Fally, C. Doneux, J. Riga, J. J. Verbist, J. Appl, Polym. Sci. **56**, 597 (1995).
[46] S. F. Durrant, N. Mareal, S. G. Castro, R. C. G. Vinhas, M. A. B. de Moraes, J. H. Nicola, Thin Solid Films **259**, 139 (1995).

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