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Application of non-equilibrium plasma polymerisation in the conservation of cellulosic supports used in cultural heritage

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Non-equilibrium plasma found efficiency as an environmental friendly, non-destructive alternative for the treatment of different materials, many of them belonging to the cultural heritage, in some proper operations such as: atomic-level cleaning and decontamination. The creation of pin-hole free, thin and conformal films via plasma polymerization by deposition of plasma polymers (PP) onto a multitude of supports to grant them resistance, vapour barrier or gas transport properties, it is also known. In the paper, the non-equilibrium plasma is applied for the deposition of poly(ethyl acrylate) (PEtA) thin films on natural aged papers as items of private collection, with the consolidation and protective aim. (PP) PEtA thin film deposited on aged paper is evaluated by ATR-FTIR spectroscopy, colour/gloss measurement, contact angle and AFM.

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1. Introduction

For the conservation profession the principles of reversibility, minimal intervention and scientific objectivity are fundamental. Although at practical level there are difficult to contend them, in the conservation practice is trying to find scientific methods for non-destructive inspection, testing, evaluation and treatment of objects with historical relevance.

It is well known that non-equilibrium plasma technologies, which are involved in many industrial processes from aerospace to life sciences, offer efficient routes for the modification of natural or synthetic polymeric materials, but for non-destructive operations, too. These technologies have been successfully applied to enhance or replace wet finishing processes in several domains such as biomedical and mechanical applications, optic, paper, textile and automobile industries, food packaging, etc. These extended applications are due to the fact that surface modification may be accomplished through surface activation, ablation, etching, cross-linking, functionalization, film deposition or by some combination of these effects [1].

As a result, non-equilibrium plasma may find efficiency as an ecological, non-destructive alternative for the treatment of different items belonging to the cultural heritage, in some proper operations, such as: atomic-level cleaning and decontamination. The creation of pin-hole free thin films via plasma polymerization by deposition of plasma polymers (PP) onto a multitude of supports to grant them: corrosion resistance, etching, enhanced wear resistance, biocompatibility, adhesive bonding, altered wetting properties such as creation of either hydrophobic, oleophobic or hydrophilic surfaces, and providing unique vapour barrier or gas transport properties, is currently applied in different domains, too [2-7]. Non-equilibrium plasma processes are low energy ones, the species created have little penetrating energy, thus the modification is a customized reengineering, limited to the surface typically no deeper than a few molecular layers (the first 1 – 10 nm), without affecting the bulk properties. The ability to generate new surface characteristics by maintaining the mass properties of materials has a great importance in the tailoring of new applications for them [8 - 10]. Ultra-thin sensitive materials, like many cultural heritage items are, can be easily modified in non-equilibrium plasma without deteriorating the bulk properties of the treated material.

Thus, the authors of the study have applied the plasma polymerization technique in the synthesis of plasma polymer (PP) thin films with conductive properties [11] or with the aim of obtaining magnetic nanocomposites with entrapped ferrite [12]. At the same time, we used non-equilibrium plasma in the treatment of organic supports (of cellulose and protein nature) in the cultural heritage items for their decontamination [13]. With this occasion it is underlined that plasma does not imply a degradative effect, the integrity of the cultural heritage item being preserved.

Paper artefacts (documents, books, prints, maps, etc.) form a vital part of our patrimony, probable the most important carrier for religious, artistic and scientific records, bringing information about human beings from ancientness. The process analysis is often difficult because of restricted sampling, the value of historical substance and its integrity being rarely outweighed by the gained information. As one of the more vulnerable support, the alterations of paper are more than a mere aesthetic problem regarding not only the visual appearance of the objects (stains, patinas, etc.), but often correspond to a deep modification of its chemical and physical structure, at macro- and microscopic levels.

Through physical, mechanical and chemical processes, the multitude of ambient factors (UV light, IR light, high humidity, temperature, micro-organisms, dust and dirt, stagnant air, and darkness) by their complementary action can damage items of cultural heritage. Thus, foxing is a term used to describe a large range of damage and discoloration in old paper used in books and manuscripts from the sixteenth to the twentieth century, as a result of fungal, chemical or physical degradation [14]. The "aging" with yellowing of paper, is due to depolymerisation promoted by pH of cellulose fibres – the main constituent of paper.

The degradation pathway and the rate of carbohydrate chain scission take place in an acidic (more aggressive) or alkaline environment. The latter process is much slower and the lifetime of traditionally moderately alkaline paper (produced prior to ~1850) is thought to be several millennia. This is in contrast with acidic paper produced between 1850 and 1990: some documents from this period are not expected to survive another century. The bad circumstance is that it is estimated more than 70% of documents in Western libraries are acidic [15].

The use of polymeric materials for the consolidation and protection of artefacts with historical and artistic value is usually accepted. The area of application is extensive and includes various objects made of different materials, such as wood, stone, textiles and paper. For both aesthetic and conservation reasons of paper, polymeric materials have been applied only in a few cases when traditional restoration methods were not sufficient to improve the mechanical resistance of the degraded artefacts. For cellulose-based materials, only a small number of new products and new techniques have been developed and applied [16,17]. Currently, no polymeric material exists whose properties are tailored especially for the conservation of paper. The applied polymers are an assimilation of the existent ones on the market. Some of the main requirements for the use of these polymers is that their application on a paper artefact does not damage the support and to be reversible (to be washed by solvents, e.g.). More even, these materials should be characterized by physical-chemical properties like flexibility, transparency, lack of colour and long-term durability [18].

Acrylic polymers used in conventional applications on heritage items [19, 20], show high filmability, good adhesive properties, and moderate water repellence, and so their use makes it possible to achieve two objectives simultaneously, that is, consolidation and protection, leading to improvement of the restoration treatment. Their action is given by the continuous film that sticks between the cellulose fibres, filling the spaces to obtain a good consolidating action. It is important to remember that a polymer has better consolidating properties when, at the service temperature, it is just above its *Tg* and so, not in the glassy but in the viscoelastic state [21]. If the polyacrylic chains in the deposited film are in the viscoelastic state, the typical flexibility of cellulose may be retained and the recovery of the mechanical resistance of the degraded objects is achievable. Some studies that report the coating of Whatman paper with poly(methyl methacrylate) [22], due to high glass transition temperature (Tg = 114 ^{o}C) show the coated samples become brittle and stiff. The coating with poly(ethyl acrylate) improve the situation, because its Tg is much lower (-21 ^{o}C), thus maintaining the flexibility of the deposited film and of the cellulosic support, too.

On the basis of this polymer applicability information, in a preliminary study [23] we have reported the experiments for non-equilibrium plasma polymerization with deposition of thin films based on vinyl polymers on a Standard line printer paper, with the goal to impart protective properties.

In this work, the plasma polymerization technique is applied for deposition of a thin film of poly(ethyl acrylate) on natural "aged" paper substrates, with the aim of coating and strengthening them. Complementary techniques of analysis (ATR-FTIR spectroscopy, colour / gloss measurement, contact angle and AFM) are used to distinguish that no changing or modifying of physical state, appearance or artistic value of the item is realized.

2. Experimental

2.1 Materials

Natural "aged" paper samples are weakly and yellowed, of 53 g m $^{-2}$: particulate matter from several pages of old books (1907, 1912) from private collection. The monomer ethyl acrylate (EtA) (99%, Sigma-Aldrich USA) is used as received, without further purification.

2.2 Equipment and plasma polymerization

The laboratory equipment designed for plasma polymerization with (PP) film deposition is presented in the photo in Fig. 1.

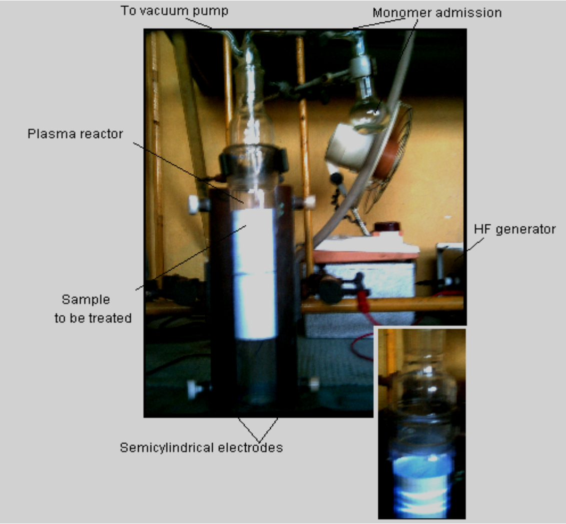

Fig.1. Laboratory experimental equipment for (PP) film deposition. In the medallion the high frequency discharge plasma in the reactor.

The principal design of the plasma reactor was described earlier [10], with the exception of vertical positioning of the plasma reactor. Generally, the system consists of three main parts disposed around the plasma reactor (neutral Pyrex glass, L = 30 cm, ∅ = 5 cm): vacuum system, monomer and/or gas inlet, and discharge system. On the external walls of reactor there are placed the two semicylindrical electrodes connected to a high frequency (HF) capacitive-coupled discharge system. High frequency generator operating at 1.2 MHz and 0 – 200 W is used. The sample to be coated is positioned into the reactor, or is pendent by loops on a sample holder when there are many different samples to be treated. In each run, prior to the polymerisation process, the reactor is evacuated down to a base pressure of 0.3 Torr. During the reaction, a vacuum gauge is used to measure the pressure inside the plasma reactor. The liquid monomer is placed into a 50 ml round-bottom flask with possibility to be heated for monomer evaporation, just in case. The power of the glow discharge is kept at 200 W, operating at room temperature, in rarefied air, without carrier gases and the discharge time is set at 600 sec.

To avoid the spontaneous aging process of the (PP) PEtA film upon exposure to ambient oxygen, the coated paper samples are kept in the vacuum dessicator to be analysed.

2.3 Characterization

Film deposition determined gravimetrically, by weighing the samples with a precision electronic balance (A&D Co. Ltd. HR 200).

Attenuated total reflection (ATR)-FTIR spectroscopy. The composition of the (PP) films is evidenced on a spectrophotometer DIGILAB Scimitar Series-USA, in the transmission mode with a resolution of 4 cm^{-1} and 32 scans.

2.4 Colour and gloss measurements

Colour changes. Changes in colour due to film deposition were measured using a colour measurement system Pocket Spec QA ^{TM} model relative to a bright white barium sulphate coated disk that displays Red – Green –Blue in values of 255-255-255. CIELAB L*, a*, b* and ΔE* parameters were measured at five locations on each specimen and average value were calculated. In the CIELAB system :

- L* axis represents the lightness (L* varies from 100 for white to zero for black),
- a* and b* are the chromaticity coordinates (a* corresponds to a green/red axis in a range from - 60 to 60: +a* is for red, -a* for green, b* corresponds to a blue/yellow axis in a range from -60 to 60 : +b* for yellow, -b* for blue).

L*, a* and b* values were used to calculate the overall colour changes ΔE_{ab} * (Eqn.1) using a procedure outlined in ASTM D2244 (providing Standard Test Method for Calculation of Colour Differences from Instrumentally Measured Colour Coordinates):

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

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. A low ΔE_{ab} value corresponds to a low colour difference.

Gloss. Surface's attribute of directly reflecting light is measured on a glossmeter Gloss Checker IG-320 Horiba, Ltd.

Contact angle measurement. Is performed in the sessile drop mode using bidistilled water as test liquid, on a KSV Instruments CAM 101 instrument of goniometric type, with automated system for storage the drop images, via digital camera, with PC-based control by appropriate software, acquisition and data processing. There is obtained using the sessile droplet profile analysis technique, under controlled conditions of room temperature and humidity. Each value is the average of 40 specimens.

AFM surface analysis. AFM measurements are performed in air at room temperature, in the tapping mode using a Scanning Probe Microscope (Solver PRO-M, NT-MDT, Russia) with commercially available NSG10/Au Silicon cantilevers. The manufacturer's values for the probe tip radius are 10 nm, and the typical force constant is 11.5 N/m. In the tapping mode, the cantilever is oscillated at a frequency of 254.244 kHz. Representative scans of the film surface (scan physical size is 2 μm x 2 μm) are obtained for each sample. The Root Mean Square (RMS) roughness parameter, Sq, which is the root mean square of the surface departures from the mean plane within the sampling area, is extracted from the Nova software provided (Eqn.2):

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

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 is obtained.

3. Results and discussion

In Fig.2 is evidenced the average deposition of (PP) film in relation with discharge time, as a measure of kinetic process in the non-equilibrium plasma. For the final discharge time the total amount of (PP) deposited film is 2.6 gm^{-2}. The (PP) PEtA deposition is obtained from a competitive process between etching and polymerization underlined by Yasuda and Shi in their studies [24, 25]. In the 600 sec time of discharge it is maintained this gain weight, about unimportant in the first 100 sec and with approximately constant increasing tendency until 600 sec.

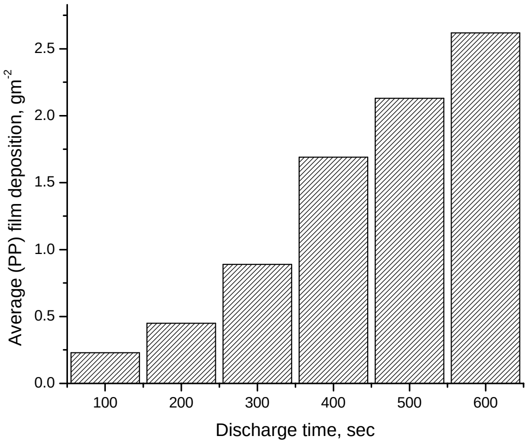

Fig 2. (PP) PEtA film average deposition on "aged" paper vs. discharge time.

While the great interest in plasma polymerisation is reserved on the synthesis of films that contain high concentrations of specific functional groups at the surface, there are also studied different techniques to improve the control over the film chemistry of plasma films. Most of them are based on decreasing the input energy during plasma polymerization. At the same time, by employing high frequency plasma instead of traditional continuous wave plasma, Timmons et al. reported a high control over the film chemistry [26-28]. Thus, there are minimized the ordinary irregularities in structure and composition, leading to less crosslinked and more "conventional polymer-like" structures.

At low wattage power of 200 W and 1.2 MHz frequency in our experiment, there are retained the chemical structure and the functional groups during the polymerisation of ethyl acrylate with deposition on paper substrate. At the same time, the high frequency plasma being initiated and sustained by external electrodes, it is operated at much lower voltage.

The chemical bonding structures of (PP) PEtA films and paper substrate were evaluated by ATR-FTIR spectroscopy (Fig. 3). These films show no crosslinking, the functional groups in the conventional polymer structure being represented and found again in the (PP) PEtA spectrum. There are evidenced the following main characteristic vibrations in cellulose and in (PP) PEtA: OH bending (3330 cm^{-1}) , C=O stretching (1731 cm^{-1}), C-O bond stretching (1251 cm^{-1}), ethyl group stretching C-C (1024 cm^{-1} and 850 cm^{-1}).

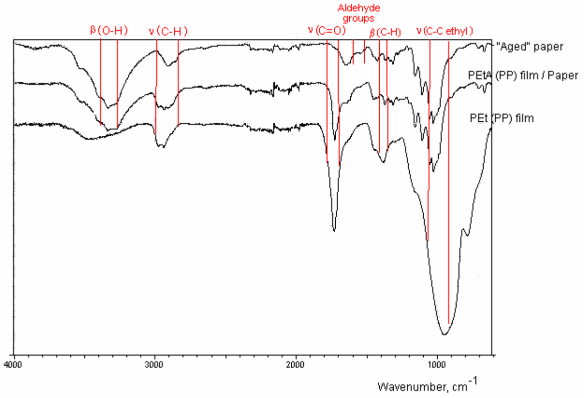

Fig.3. ATR-FTIR spectra of (PP) PEtA films deposited on paper samples in the plasma operational parameters: frequency 1.2 MHz, pressure 0.3Torr, discharge power 200 W and discharge time 600 s.

Therefore, C=O, COC_2H_5, COO, CH_3 groups are formed on the cellulose support by the plasma polymerisation of ethyl acrylate.

Our investigations were focused on two paper samples resulted from old books that are still in good enough condition. Upon visual inspection both specimens of aged paper a1 and a2 in Fig. 4, displayed the yellowing and foxing stains randomly distributed on surfaces.

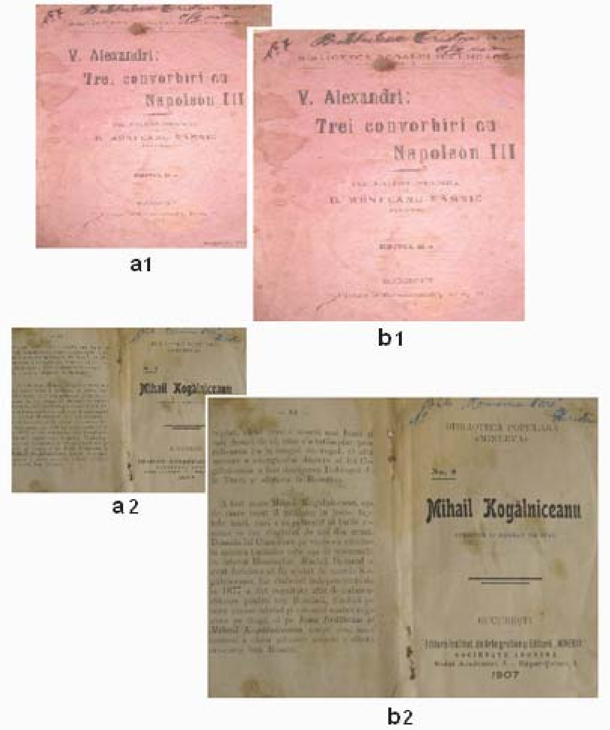

Fig. 4. Initial appearance of natural "aged" paper samples (a1 and a2) and after plasma deposition of (PP) PEtA (b1 and b2).

Colour analysis is without doubt the most frequently used method when diagnosing the effect of a treatment on the physical appearance and the aspect of a heritage item. This case, it is obvious that colour is the most incident term for evaluating superficial changes produced by film deposition. At least five superficial colour shade readings were taken as samples for each test, both before and after (PP) PEtA film deposition on the paper samples. The data obtained were processed according to classical methodology where ΔE_{ab} is estimated, that is the evaluation of the square root of the differences between the various colorimetric system contributions: *CIEL*a*b** (eqn.1). Another approach tried to verify the type of correlation that exists between luminosity (L^*) and the relation between colour terms a^* and b^*. This type of approach tries to eliminate any influence due to luminosity variation, which is the most important one for results obtained with ΔE_{ab}.

Table 1. Colour parameters, gloss, contact angle and RMS of (PP) PEtA/ Coated paper comparative to paper substrate.

Sample	Color parameters according CIELAB			Gloss, in rel. units	Contact angle, degree	RMS ^{x}, nm
	L*	a*	b*			
Natural aged paper	62.64	0.4575	22.8774	2.6	Instantaneously absorption	17,5178
(PP) PEtA/ Paper	59.36	4.7086	22.9361	2.6	97 - 112	36,289

^{x} RMS - Root Mean Square surface roughness evaluated on scanned area (2 μm x 2 μm)

From Table 1, it can be observed that luminosity L* decreases and chromaticity parameters a* and b* increase by (PP) film deposition.

After deposition, L* decreases from 62.64 to 59.36. The a* (redness) increases more rapidly by film deposition, while b * (yellowness) value has slightly increased by the deposition of (PP) PEtA on the natural aged paper. According to Eq.1, overall colour change is $\Delta E_{ab} = 5.36$. Anyway, these values according the standard providing (ASTM D2244) are registered in the domain of those changes not detectable with the naked eye, affirmation we make , too (evidenced in Fig.4, b1 and b2 medallions).

Gloss is often used as a criterion to evaluate the quality of a material, especially in the case of those where the aesthetic appearance is of importance. This category includes the cultural heritage items. It is a subjective term used to describe the relative amount of light reflected to a viewer's eye and produces a lustrous appearance. A visual gloss evaluation includes many subjective sources of error and is not sufficient. Therefore, to be objective, it is necessary to put a measured value on the degree of gloss. The calibration of the instrument we used is made with a polished black glass standard that has gloss 91, in relative units. For the two samples in the study: natural aged paper and (PP) PEtA coated paper, gloss has identical values in relative units of 2.6 (in Table 1). In a comprehensive work accessible on internet [29], Talbert had classified materials by their gloss and from this point of view, the non- or (PP) coated paper samples are flat or matte – practically free of sheen, with gloss less than 15 (relative units). From the viewpoint of a historic item, important is the fact that gloss value is constantly kept at the base value by the coating process.

The presence of the (PP) deposited film on the surface of paper also produces a change in the behaviour against water: from the total and instantaneously absorption of water by the paper sample, the contact angle is placed in the range of 97 – 112^0 for the coated paper sample.

The AFM technique is very a powerful tool to characterize surfaces of materials, enabling us to establish quantities like RMS roughness of the heights and its influence on optical properties. Figures 5 and 6 show typical AFM images (2 μm × 2 μm) for top layers of the natural "aged" paper sample and the (PP) PEtA coated natural "aged" paper by the non-equilibrium plasma polymerisation. The both sample surfaces in AFM images are uneven, with peaks and cracks aleatory arranged on irregular fibrillar structures, more or less evidenced and slight oriented across the image, which it has presuming there are formed during the application of the letterpress printing (technology applied predominantly until the end of 20th century). It is also presented a kind of nodular structure and interconnected cavity channels between the agglomerated nodules, assuming to be macromolecular aggregates in the non-woven cellulosic network of the paper.

By plasma deposition of (PP) PEtA film, surface morphology seems to change: the elastic pellicle created by plasma polymerization of ethyl acrylate follows the topography of the cellulose support, observation made in another study [23] for plasma deposition of polyacrylics on standard papers, too. The results on RMS roughness of the heights are summarized in Table 1. RMS value for the paper coated with (PP) film shows an important increase with about 100% comparative with the reference paper. It is known the non-equilibrium plasma discharge is concentrated especially on peaks, even they are made of insulating materials, like cellulose it is; 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 (Fig. 6).

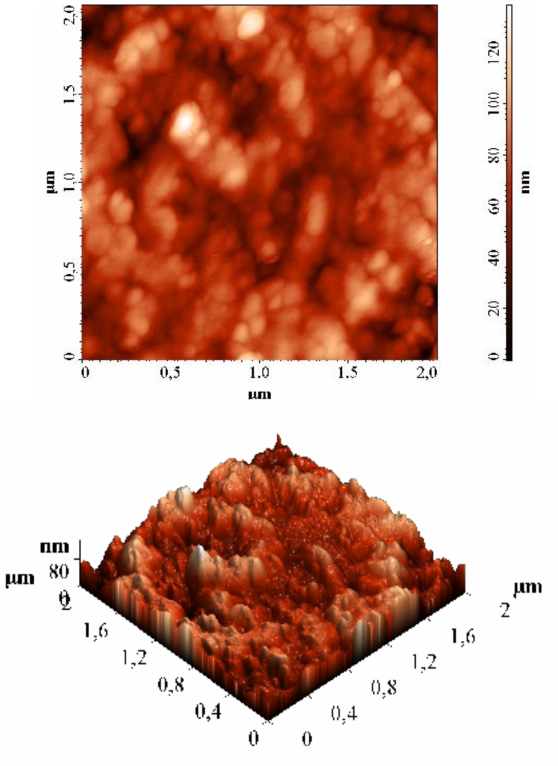

Fig. 5. AFM images (2D, 3D) on natural "aged" old paper

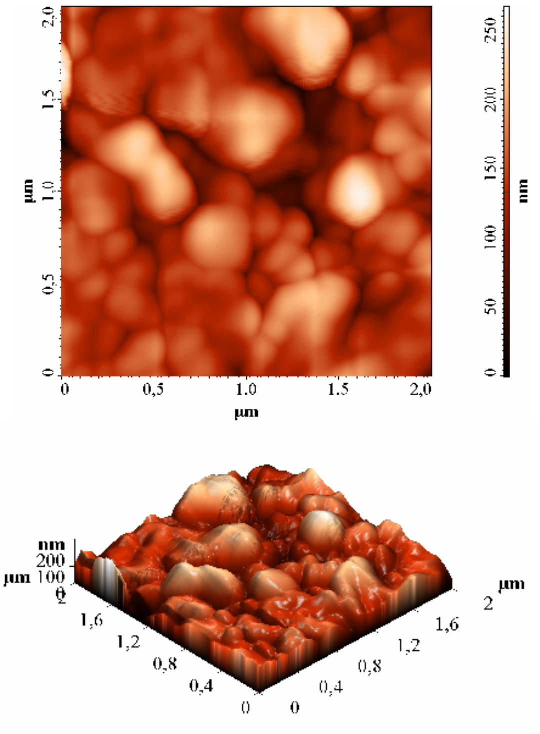

Fig. 6. AFM images (2D, 3D) on (PP) PEtA coated natural "aged" old paper.

Thus, the roughness increases at nanometric level, the thin film being total protective all over the treated surface. The data of RMS roughness is in correlation with color properties, especially with the determined L* (Table 1): with the increase of RMS for (PP) PEtA / coated paper the L* decreased, the fact emphasized by other authors, too [30]. In the case of the cultural heritage items like the samples we used in the study are, this correlation is important in the establishment of non-invasive intervention by non-equilibrium plasma polymerization application.

4. Conclusions

This paper investigates the possibility of obtaining a strengthening and protective film on a support of natural "aged" paper belonging to a private collection, by deposition of (PP) poly(ethyl acrylate) in non-equilibrium plasma, with operational parameters : frequency 1.2 MHz, pressure 0.3 Torr, discharge power 200W and discharge time 600 s.

ATR-FTIR analysis underlines the (PP) PEtA chemical structure with no evident crosslinking obtained in the plasma environment, in the pre-set sparing conditions.

The colour and gloss measurements scientifically complete the subjective information get with the naked eye, that film deposition doesn't change physical state, appearance or artistic value of the treated paper support. At the same time, the contact angle value is an evidence of the fact the deposited film acts as a barrier against water or vapour water.

AFM images reveal at nanometric level the surface topograpgy and the increase of roughness by thin film deposition on paper substrate.

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