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Original article

Positive findings for plasma polymer (meth)acrylate thin films in heritage protective applications

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ABSTRACT

Plasma technology is an innovative environmental friendly process that can be an option to the conventional methods for materials' processing. Nonequilibrium low pressure plasma found efficiency as a nondestructive method for the treatment of different materials, many of them belonging to the cultural heritage, in some proper operations such as: atomic-level cleaning, decontamination, thin film deposition. In the paper, the low pressure nonequilibrium plasma is applied for the deposition of plasma polymer poly(methyl methacrylate-co-ethyl acrylate) P(MMA-co-EtA) thin films on natural aged paper, with the consolidation and protective aim. To verify the plasma polymer applicability for paper protection and consolidation, the film is aged accelerated by UV radiation and the structural and morphological changes are evaluated by FTIR spectroscopy, color/gloss measurement, contact angle and AFM.

1. Introduction

An important part of the cultural heritage consists of graphic supports including papyrus, parchment and paper, which are stored in archives and libraries. The deterioration of written cultural relics is attributed to several causes, such as microbial contamination, oxidation, acidification, and others. Therefore, it is desirable to focus research activities on the conservation and restoration techniques to develop appropriate treatments. Subsequently, the process of these items' conservation and restoration including the use of special preserving polymers [1–6], should be based on fundamental scientific principles: reversibility, inertness, maintenance of the integrity of the objects (aesthetic appearance and compatibility with the substrate).

Alongside the conventional procedures applied in the conservation and restoration of heritage items, the application of low pressure nonequilibrium plasma as an environmental benign technology for cleaning, decontamination, activation, crosslinking, etching and protective plasma polymer film deposition, has recently provided clear evidence for its potentiality [7]. The plasma polymerization process has important advantages: the reactive species do not penetrate below ~ 10 nm of the surface, it is very fast and economic technique for direct dry deposition of homogeneous, adherent, and pinhole free films, it can be performed at room temperature, it is suitable for treating complex shapes, both planar and curved surfaces of heritage items, to conserve and protect them, it allows high homogeneity due to the strict control of the treatment conditions (plasma gas, flow rate, vacuum, etc.).

Also, the literature describes some attempts on plasma treatment in the conservation of paper and other cellulosic materials. Generally, they include initial results of efforts to remove mold spores and other stains on paper, suggestions to use plasma in paper deacidification and strengthening of brittle paper, and indications that a low-temperature plasma treatment by glow discharge of hydrogen can improve the strength of aged papers [8]. Thus, Vohrer et al. [9] underline an overall increase in paper stability of up to 20%, by the removal of microbial contamination combined with an increase in paper strength by using the plasma-based treatment of naturally aged groundwood paper. In another study, Laguardia et al. [7] demonstrates the efficiency of paper microbial sterilization and consolidation by means of plasma treatment, as a function of various gas mixtures, pressure, power, and treatment time.

Previously we studied the thin films' deposition by nonequilibrium plasma polymerization of some vinylic and pyrrole monomers with the aim of protection and consolidation in the conservation domain [10].

The aim of the paper is to continue the investigations by the synthesis and characterization of low pressure nonequilibrium plasma polymerized films based on poly(methyl methacrylate-co-ethyl acrylate), as protective and consolidation layer for natural aged paper. The method is suitable for the improvement of the mechanical resistance and the wetting behavior of the degraded paper artifacts. The homopolymer PMMA is brittle and stiff (Tg ~ 105 °C) while PEtA is too sticky (Tg ~ – 24 °C); as a consequence, they

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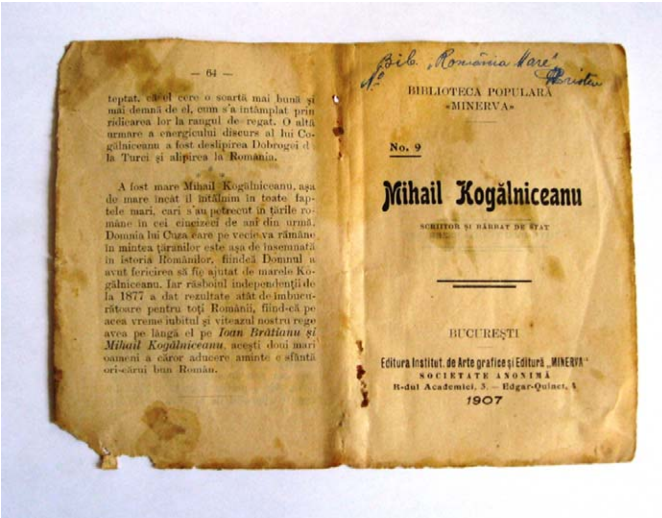

Fig. 1. The selected old paper sample.

are not suitable for cellulose supports. This aspect lead to the selection of the specific mixture of the monomers in the weight ratio of 70/30 MMA/EtA; the copolymer has elasticity and good consolidating properties, its glass transition of ~ 10 °C being just below the service temperature. The plasma polymer poly(methyl methacrylate-co-ethyl acrylate) film deposited on natural aged paper, is an unconventional replica of Rohm & Haas commercialized copolymer in aqueous dispersion Primal AC33. The plasma polymer film is UV accelerated aged in “close-to-real” environmental conditions and analyzed from the viewpoint of its structure and surface morphology, by FTIR spectroscopy, AFM, contact angle, color and gloss changes.

2. Experimental

2.1. Materials

The monomers methyl methacrylate (MMA) and ethyl acrylate (EtA) (99% purity, both purchased from Sigma–Aldrich USA) are used after purification by passing them through an inhibitor removal column (Aldrich, for removing hydroquinone and hydroquinone monomethyl ether). For the plasma treatment by thin film deposition study, it was selected as specimen model a natural “aged” paper (Fig. 1) from an old printed matter (private collection, title page from the volume “Mihail Kogalniceanu” dated: 1907) with great fragility and of felted consistency, yellowed, with colored stains randomly distributed throughout the page, from the proximity of the cover. The experiments are made with the owner’s consent.

2.2. Plasma polymerization

Plasma polymerization is conducted in the laboratory installation with a capacitive coupled plasma source and after a presettled protocol, presented before [11]. For the plasma polymer deposition in this work, the installation operated at: frequency 1.2 MHz, discharge power 200 W, electric field intensity 30–40 V/cm, total pressure 0.399 mbarr in the system, at room temperature for 600 sec. The monomers MMA: EtA ratio in the feeding flask is 70: 30 wt %. To avoid the spontaneous aging process of the plasma polymer film upon exposure to ambient oxygen, the coated paper samples are kept in the vacuum dessicator to be analyzed. The deposited film of plasma polymer based on MMA: EtA on paper substrate is about 1.2 g m^{-2}, determined gravimetrically, by weighing the samples with a precision electronic balance (A&D Co. Ltd. HR 200).

2.3. UV Accelerated aging test

The films of plasma polymer (MMA-co-EtA) deposited on paper samples with the same surface area, were irradiated in air, in a rotative accelerated weathering device, equipped with a middle pressure mercury lamp HQE −40 types, having a polychrome emission spectrum in the range of 300–540 nm, peaking at 365 nm, a wavelength transparent to window panel glass and thus, preferable for testing materials related to conservation. The light intensity is ~ 30 mWcm^{-2} measured with a portable instrument with LCD display PHOTO-RADIOMETER Model HD2302.0, DeltaOhm Italy. The more energetic radiations ($\lambda < 300$ nm) not found in the sunlight spectrum at earth’s surface, were eliminated with a borosilicate glass filter. The film samples were mounted on the rotative device and were positioned at the distance of 60 mm from the lamp. By using a fan, the temperature inside the irradiation chamber was kept at 32 °C and the RH at 55%. The accelerated photo ageing of plasma polymer films was extended up to 100 h with the light source having wavelength of 365 nm. The films were withdrawn from the device at regular intervals (5, 10, 15, 20, 45, 70 and 100 h) and subjected to spectroscopic, colorimetric, gloss and contact angle analyses.

2.4. Characterization

2.4.1. FT-IR spectroscopy

FTIR Spectra were recorded on a spectrometer Bruker VERTEX 70 (with reflection device Golden Gate Diamond crystal), using the Opus 5 FTIR Software, in the range 4000 to 600 cm^{-1}, at room temperature, in the transmission mode with a resolution of 4 cm^{-1}. The signal-to-noise was improved by co-adding 64 scans/spectrum.

2.4.2. Contact angle measurement

It is performed in the sessile drop mode using bidistilled water as test liquid, on 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. The contact angle is obtained using the sessile droplet profile analysis technique, under controlled conditions of room temperature and humidity. Each value is the average of 40 measurements.

2.4.3. AFM surface analysis

AFM measurements are performed in air at room temperature using a Scanning Probe Microscope (Solver PRO-M, NTMDT, Russia). A monolithic silicon cantilever (NSG10/Au Silicon), with a force constant of 11.5 Nm^{-1} and a resonance frequency of 254 kHz was used to work in tapping mode. Representative scans of the film surface (scan physical size is 10 μm × 10 μm) are obtained for each sample. The Root Mean Square (RMS) roughness parameter, Sq, is extracted from the Nova software provided (Eqn. (1)):

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

where M is the number of columns in the surface, N is the number of rows in the surface and z represents the difference between the average height of the investigated area and height of each point having x_i and y_j coordinates.