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Synthesis via low pressure non-equilibrium plasma process and UV aging performance of polyacrylic films

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Plasma technology offers an innovative and ecological, potentially tunable route to selectively and controllably change the physics and chemistry of the outer surface of a material by deposition of pinhole free, conformal thin films. In the paper, low pressure non-equilibrium plasma is used for the deposition of thin films from a homologous series of alkyl acrylates from methyl to butyl, on planar supports of organic nature (standard paper sample) with the protective aim. To validate the plasma polymer films applicability for paper sheet micro consolidation and protection, they are UV accelerated aged and the structural and morphological aspects are monitored by FTIR spectroscopy, atomic force microscopy, contact angle and color/gloss measurements.

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1. Introduction

Due to the surface characteristics for example hydrophilicity, a great number of materials of organic and inorganic nature with high physical-mechanical and thermo-physical properties are known to lack environmental stability. The material can be affected by light, temperature, microorganisms and moist taken together. To obtain a good protection, the surface hydrophobic polymeric films can be coated onto the surface.

The potential users of specialty films for applications on different substrates sum up their needs for some requirements and features: durable protection of the aesthetics, easy to apply to the substrate, effective cost, UV stability and opacity (color and gloss retention, UV protection of the substrate underneath), chemical resistance (surface integrity and ease of cleaning), mechanical property, and adhesion, low surface tension (low dirt pick up, low soiling), barrier properties (moisture protection), etc.

Among the preferences for the film able to meet these requirements the acrylics family offers the good balance of advantages / limitations, such as: flexibility, good film forming, excellent aesthetics (transparency, lack of color, low gloss), good adhesion to a variety of substrates, non-wettability, reversibility for long time, lower cost, vs. fading and chalking under long term UV exposure, insufficient solvent resistance, low barrier properties. But the limitations are mostly due to the modifiers present in the acrylic films that may influence. The acrylic polymers and copolymers are widely used as formulations of protective coatings in the technical field with the aim of conferring different hydrophobic degrees to the surfaces [1].

The use of acrylic polymers in the domain of cultural heritage items restoration and conservation is accepted as consolidants, protective coatings, adhesives, and varnishes, for supports such as wood, metal, stone, textiles, and paper. In particular, the prevent of paper artifacts decay by micro-consolidation and total final protection is a serious problem for numerous libraries, collections and museums [2-10].

Alongside the traditional procedures applied in the conservation and restoration domain, the application of low pressure non-equilibrium plasma for cleaning, decontamination, activation, crosslinking, etching and protective plasma polymer film deposition has recently given clear evidence for the potentiality of this efficient technology. Regarding to the paper support, the main advantages of the plasma treatment are the dry nature of the process and the possibility of combining different effects, such as the biological agent eradication, the conservation and consolidation of deteriorated specimens by the deposition of superficial layers [11- 14].

The plasma polymerization as a solventless, single all-dry process has important advantages: ● the reactive species do not penetrate below 10 nm of the surface and thus did not alter the bulk composition [15]; ● it is very fast and economic technique for direct dry deposition of homogeneous, thin and adherent, conformal and pinhole free films; ● it can be performed at room temperature; ● it is suitable for deposition of functional coatings over surface complex topology with planar and curved surfaces; ● it allows high homogeneity due to the strict control of the treatment conditions (plasma gas, flow rate, vacuum, etc.). The polymer does not incorporate additives, such as catalysts, surfactants, etc., and therefore a cleaner polymer product can be expected to be obtained [16-19].

After the conservation act is applied, e.g. by polymer film deposition, is essentially to reproduce the effects of subsequent ageing to see if the treatment has stabilized /destabilized the treated material. Correspondingly, the conservation materials require to be aged to see if they will extend undesirable characteristics on ageing, *e.g.* brittleness, discoloration, shrinkage, acidity, etc. The accelerated weathering tries to anticipate what will happen under the natural use conditions and thus, to estimate and predict the polymer life-time, the maintenance and the replacement actions. Because all the environmental variables cannot be exactly reproduced, a problem that has been discussed for a long time is that it does not exist a good correlation between the simulated accelerated aging tests and the real exposure degradation [20-22].

The radiation in the ultraviolet (UV) and visible is the primary factor in the polymer weathering. Other stimuli like temperature, moisture, pollutants, mechanical stresses, and biological attack can contribute to the aging phenomenon, but usually the weathering process begins with a photochemical event.

In our laboratory, previous studies [23-26] investigated and developed a more appropriated technique for conservation of different supports belonging to the cultural heritage items, by thin films' deposition in the conditions of low pressure non-equilibrium plasma polymerization.

This paper is one in the series that deals with the synthesis and characterization of low pressure non-equilibrium plasma polymerized films, as protective and consolidation layer. The plasma polymerized films based on homologous acrylics from methyl to butyl derivatives deposited on a paper sheet specimen are UV accelerated aged in "close-to-real" environmental conditions and analyzed with reference to the polymer structure and surface morphology, by FTIR spectroscopy, AFM, contact angle, color and gloss measurements.

2. Experimental

2.1. Materials

The monomers: methyl acrylate, (MeA), ethyl acrylate (EtA) and butyl acrylate (BuA) (99% purity, all 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, the paper sheet (Standard line printer paper of 80 g m $^{-2}$) support of 20×70 mm as specimen is selected.

2.2. Plasma polymerization

The films are obtained using a routine and a system specially designed in our laboratory already published [27]. The plasma polymerization system consists of a cylindrical plasma reactor (neutral Pyrex glass, L = 30 cm, $\varnothing$ = 5 cm) endowed with an external pair of semicylindrical silver coated electrodes, a liquid nitrogen trap, a vacuum pump, the whole set being connected to a the control - command block.

The electrodes are connected to a radio-frequency capacitive-coupled glow discharge system, which operated at 1.2 MHz and delivered up to 200 W. In order to keep constant the HF (high frequency) glow discharge parameters during the treatments, the generator is equipped with a master oscillator with adjustable frequency within the range 1.2–1.5 MHz and a load tuned power amplifier. For the experiment, the following energetic parameters considered to be quite moderate, are used: power in the discharge 100 W, electric field intensity in the discharge 20 – 50 V cm $^{-1}$, frequency 1.2 MHz.

The control-command block adequately connected to pressure and temperature sensors permits to establish the gas pressure and monomer flow within the reactor. The total pressure in the reaction vessel is adjusted to less than 0.399 mbar with a partial pressure of 0.133 mbar. The temperature in the reaction area does not exceed 35 ^{o}C.

After the paper sheet is placed on the support piece into the plasma reactor between the electrodes in the discharge zone, the chamber is evacuated to less than 0.399 mbar. The monomer in the liquid form is in the flask connected to the plasma reactor and embedded in the thermostatic bath, heated for the monomer evaporation. For deposition, only monomer vapors are flushed into the plasma reactor at steady flow conditions. The coatings are all prepared from the pure monomer, no carrier gases being added.

As soon as the system is regulated to the assigned power, the glow discharge is initiated in the space of the plasma reactor. The plasma exposure is conducted for 600 sec. The average deposition determined gravimetrically is: 1.21 gm $^{-2}$ for PMeA [poly(methyl acrylate)] , 1.15 gm $^{-2}$ for PEtA [poly(ethyl acrylate)] and 1.05 gm $^{-2}$ for PBuA[poly(butyl acrylate)]. Then, the paper sheet specimen coated with plasma polymer film is kept in the vacuum desiccator to be analyzed.

2.3. UV Accelerated aging test

The samples of plasma polymer deposited on paper sheet are irradiated in air, in a rotative accelerated weathering device, equipped with a middle pressure mercury lamp HQE −40 type, 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 mW·cm^{-2} measured with a portable instrument with 109 LCD display PHOTO-RADIOMETER Model HD2302.0, DeltaOhm Italy. The more energetic radiations (λ< 300 nm) not found in the sunlight spectrum at earth's surface, are eliminated with a borosilicate glass filter.

The film samples are mounted on the rotative device and are positioned at the distance of 60 mm from the lamp. By using a fan, the temperature inside the irradiation chamber is kept at 25 ^{o}C and the RH at 55%. The accelerated photo ageing of plasma polymer films is extended up to 100 h with the light source having wavelength of 365 nm. The films are withdrawn from the device at regular intervals (5, 10, 15, 20, 45, 70 and 100 h) and subjected to spectroscopic, colorimetric and gloss analyses.

2.4. Characterization

2.4.1. FT-IR spectroscopy

FTIR Spectra are recorded on a spectrometer Bruker VERTEX 70 (with reflection device Golden Gate Diamond crystal), using the Opus 5 FTIR Software, in the wavenumber range from 3500 to 550 cm^{-1}, accumulating 64 scans in absorbance mode with a resolution of 4 cm^{-1}. The spectra are processed with Origin v 7.0.

2.4.2. AFM surface analysis

AFM measurements are performed in air at room temperature using a scanning probe microscope solver pro-M platform (NTMDT, Russia), in the tapping mode. A rectangular silicon cantilever NSG10 (NT-MDT, Russia), with a typical force constant KN = 11.8 N/m and 156 kHz oscillation frequency is used.

The scan area is 10 μm × 10 μm, while for the image acquisition and image analysis, the latest version of the NT-MDT NOVA software is used.

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

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

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.

2.4.3. Contact angle measurement

It is performed in the sessile drop mode using bidistilled water as test liquid, on KSV Instruments CAM101 Optical Video System 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. Small droplets of about 0.009 ml of distilled water are placed on the sample’s surface with a micropipette. 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.

2.4.4. Surface color and gloss measurements

The surface color changes due to accelerated aging are measured using a color 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.

When the color is expressed in CIELAB color space, L* defines lightness, a* denotes the red/green coordinate and b* the yellow/blue coordinate [28]. The CIELAB L*, a*, b* parameters are measured at six locations on each specimen and average value is calculated. L*, a* and b* values are used to calculate the overall color changes ΔE (Eqn. 2) using a procedure outlined in ASTM D2244 (providing Standard Test Method for calculation of color differences from instrumentally measured color coordinates):

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \tag{2}$$

where ΔL* represents the brightness relationship between light and dark, Δa* represents the relationship between green and red and Δb* represents the relationship between blue and yellow (Δ means the difference between the samples before and after being aged).

The gloss variation on the surface of samples is measured with Horiba IG-320 Gloss-Checker apparatus. The gloss values are determined comparing the intensity of the luminous reflection on the sample surface with the value registered for standard surface (polished black glass, an accessory of apparatus). The surface gloss retention of the films at an angle of incident/reflection of 60^o is calculated with Eqn. (3), where G_i and G_f represent the initial and current gloss values [29].

$$Gloss\,retention \quad (\%) = (Gi/Gf)100 \tag{3}$$

3. Results and discussion

This chapter is subdivided into three sections. In the first part the film deposition by plasma polymerization is discussed, with the evidencing of the relation plasma parameters – preserving the chemical structure of the monomers. In the second part the surface morphology of the plasma deposited films is presented and in the third part the evaluation of the UV accelerated aging is made.

3.1. Chemical structure analysis

As it is known, the plasma polymerization is a radical-dominated process with chemical vapor deposition of the macromolecular compound. The basic growth mechanism is known as rapid step-growth polymerization (RSGP). Also, the low-pressure non-equilibrium plasma polymerization is a highly system-dependent process. For a given monomer, the properties of plasma polymer are closely related to the design factor of the reactor, the location of the substrate in the reactor, the frequency of the electric power source, etc. [30]. This is an all-dry polymerization technique which involves the reactions between the radical-generating species and a monomer with unsaturated bonds to create monomer radicals which are adsorbed on the substrate surface where they polymerize. Gaseous monomers are fed into the active plasma zone, where activation and dissociation processes take place. The recombination of these reactive species, which are mainly radicals and their reactivation, determines the plasma polymerization. Also, the surface takes part in the plasma polymerization by recombination, yielding deposition and etching processes which lead to ablation and redeposition. Rivaling deposition/etching effects get to the plasma polymer film [31-33].

Unlike the conventional polymers, the plasma polymers are generally formed in an extremely tight and three - dimensional network, with an irregular chemical configuration and the chemical structure of the monomer is not necessarily preserved through the process of fragmentation and recombination within the plasma environment.

The most important factor that influences the deposition rate and the properties of plasma polymers is the energy input level of the plasma polymerization process which determines the extent of dissociation and the atom scrambling in the monomer molecule. The better control of film structure can be associated to the W / FM Yasuda parameter [J / kg monomer] (the ratio of W - the input power to F - the monomer flow rate and M - the molecular mass of the monomer), introduced by Yasuda [31]. At high value of W/FM, meaning at high discharge power, the plasma phase is monomer deficient inducing the scission of almost all precursor bonds. On the contrary, at low value of W/FM, meaning at low discharge power, like we used in this work, the plasma phase is energy deficient. The fragmentation of the precursor is low, leading to high retention of the monomer structure. Thus, there are minimized the ordinary irregularities in the structure, leading to less crosslinked and more “conventional polymer-like” configuration. This aspect is important and was underlined [26], if the reversibility of the film deposition on the support surface belonging to the heritage item is considered.

The operational parameters in our experiment at low wattage power of 100 W sustained by the external electrodes and 1.2 MHz frequency, lead to the preservation of the monomers’ chemical structure and the functional groups during the polymerization of acrylate monomer with deposition on the paper support. Thus, the solubility test in: acetone, 2/1 acetone/methanol and 2/1 methanol/tetrahydrofuran of the plasma synthesized thin films revealed the similar behavior with the conventional polymers, with no evidenced crosslinking.

The FTIR spectra (Fig. 1) for each of the investigated plasma polymer (PMeA, PEtA, PBuA) confirm the main frequencies of the absorption bands for the conventional polyacrylics structure, known in the literature [2,3].

Typical oscillations found in the molecules are recorded as peaks in the area of the spectra between 3500 – 550 cm $^{-1}$: in the area referred to as the "functional group region" (1600 – 3500 cm ¯1) primarily composed of peaks corresponding to the stretching motions of the functional groups and the region referred to as the "fingerprint region" (550 – 1600 cm $^{-1}$) where the peaks commonly overlap. Thus, in Fig. 1, 2957 cm $^{-1}$ and 2873 cm $^{-1}$ were the characteristic stretching peaks of C-H in CH_3 and CH_2, respectively; 1731 cm^{-1} was stretching vibration peak of carbonyl C=O; 1455 cm^{-1} was distortion vibration of -COO – overlapped by peaks at 1448cm^{-1} and 1380 cm^{-1} interpreted as the bending vibration of -CH_3 and - CH_2, respectively; peaks at 1164 cm^{-1} and 1240 cm^{-1} come from the stretching vibration of C - O in the ester group; 957 cm $^{-1}$ was the stretching vibration of C – C; 843 cm $^{-1}$ was the stretching vibration absorption peak of C = O in the acrylic group. No absorption at 1650 cm^{-1} indicates the absence of C=C in the film, i.e., the absence of unreacted monomers, which confirms their polymerization.

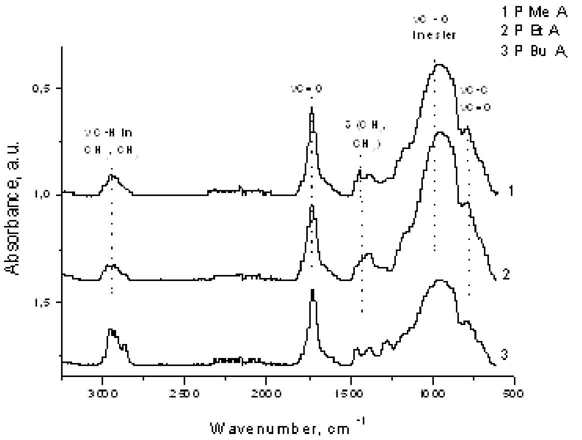


Fig. 1. FTIR spectra (3500 – 550 cm^{-1} range) for plasma polymer films deposited in the specified operational parameters (frequency 1.2 MHz, discharge power 100 W, time 600sec, pressure <0.399 mbar).

3.2. Surface morphology of the plasma deposited films

The surface modifications of the paper specimens coated with acrylic plasma polymerized films were analyzed by two complementary methods: Atomic Force Microscopy (AFM) technique and the contact angle method. Atomic force microscopy (AFM) is a powerful characterization tool for polymer science, capable of revealing surface patterns with superior spatial resolution, in a simple and non-destructive way. The method can create topographical maps of surface consisting of three-dimensional images of the ultra-structure at molecular level, in real time, under atmospheric conditions, and without the necessity to fix samples. It was used to image morphology and topography of the plasma polymer films coated on the paper substrate and to obtain detailed information about the microrelief and roughness, comparative to the reference paper sheet.

The results obtained by the AFM technique are restricted mainly to 3D images of the samples (Figs. 2 a - d). In Fig. 2a the AFM 3D image shows the paper morphology features with fibers organized in a random way, uneven, with peaks and valleys and a root mean square RMS roughness of 113.8 nm (Fig. 3). The plasma films deposition on the paper substrate induces an evolution of the morphology, with small cone-like structures unevenly covering the whole surface (Figs. 2b-d). These structures either are filling the pores or coating the cellulose fibres (PEtA in Fig. 2c) or particular surface morphologies are obtained after plasma polymerization (PMeA and PBuA in Figs. 2 b, d). Thus, the PMeA film on paper AFM 3D image reveals numerous deep ridges running all over the surface sample in an almost parallel fashion (Fig. 2b) while the surface of PBuA film consists of a random distribution of globular features (grains or nodules), associated or even forming some kind of chain structure (Fig. 2d).

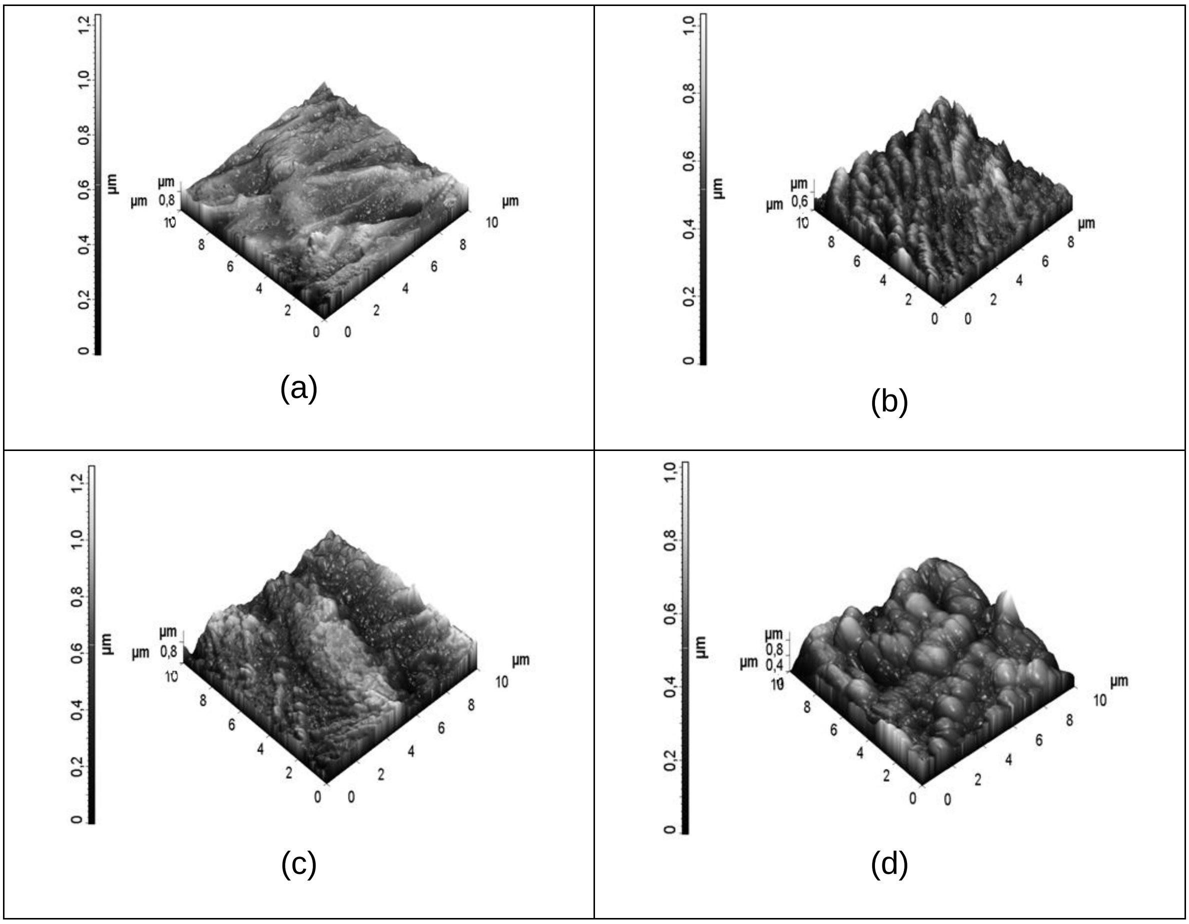


Fig. 2. 3D AFM (10µmX10µm) on the investigated samples:(a) standard paper support; (b) PMeA plasma coated paper; (c) PEtA plasma coated paper; (d) PBuA plasma coated paper.

As comparative with the paper support, the surface roughness of the plasma coated paper is increased, more evidenced for the PEtA coated specimen (Fig. 3). The contact angle of the water droplets onto the plasma films deposited on paper is used to estimate the protective properties against water and its wettability, being presented in Fig. 3.

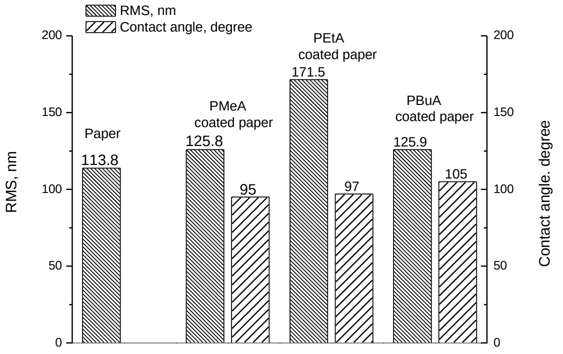


*Fig. 3. RMS (from 10 µm x 10 µm AFM scanned area) and contact angle data for the plasma polymer films deposited on paper substrate. * Water is instantaneously absorbed by paper support.*

Besides the film morphology, the surface wettability of the investigated samples determines the interactions occurring at the interface. For the studied structures of acrylic type (–CH $_2$ – CH-)-COOR, the only difference between the monomers is in the side groups length from methyl to butyl: –$COOCH_3$, –$COOCH_2CH_3$ and –$COOCH_2CH_2CH_2CH_3$, respectively, which explains the hydrophobic nature of the films described by the contact angle data.

The basic effect of surface structure on hydrophobicity has been well known since the initial studies of Wenzel [34] which considered the solid/liquid interface follows the relief of the solid surface. For the paper sheet support the hydrophilicity is notable, the droplet being immediately absorbed, without the capacity for the optical recording of the contact angle by the digital camera.

After the deposition of the plasma films PMeA, PEtA or PBuA on the paper support, the topographic modifications appeared and the average contact angle has increased values, in the range of 95 – 105°. Even if the literature [35] consents the surface roughness of a non-planar substrate may increase the wetting, the quantitative depiction of the phenomenon is still lacking. In a theoretical study, Chow [36] mathematically analyses how the roughness results in local changes in the contact angle. Its conclusion, the greater the surface roughness is, the contact angle decreases while the critical surface tension enhances.

Our observation regarding the deviation in the contact angle by plasma film deposition on paper sheet support is that a correlation with microstructure disorder cannot be made, because the chemical structure of these films has the main influence on the contact angle. It is observed that the voluminous alkyl group in the side chain induces a slightly higher contact angle.

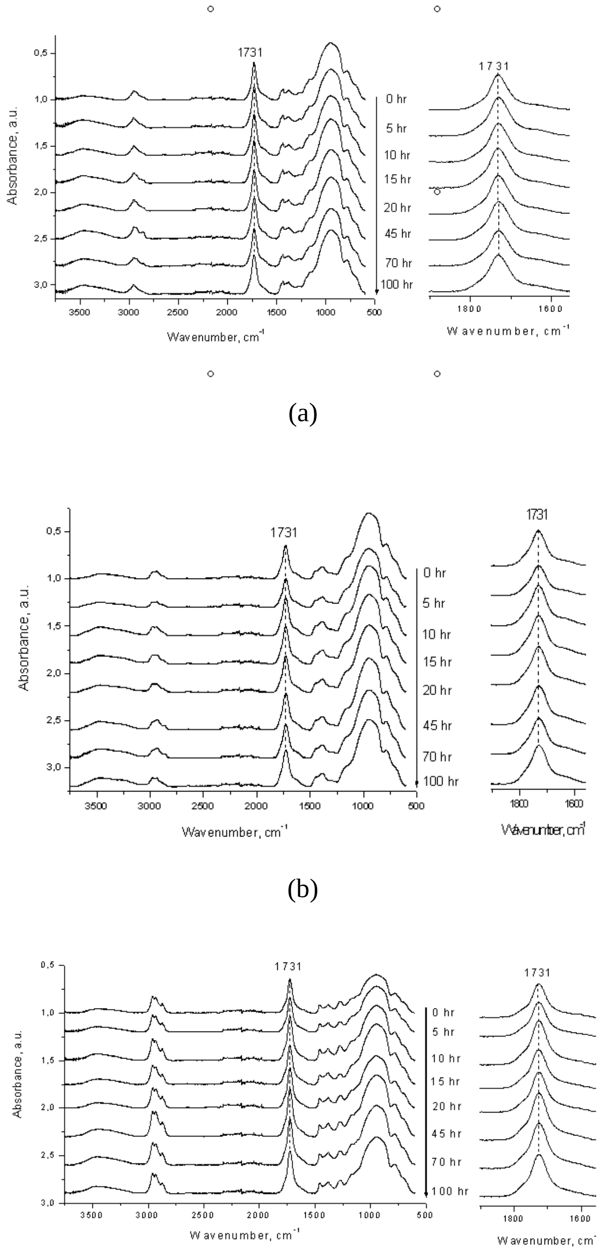
3.3. Assessment of the UV accelerated aging

At the macroscopic scale, the visual inspection indicated that the standard paper specimens with coated plasma polymer do not show any detectable modification until 100 h of UV exposure.

Typically, in the presence of light the degradations are sometimes greatly accelerated if an absorbing chromophore group is present, such as carbonyl groups, hydroperoxides, aromatic rings, conjugated C=C bonds. These species absorb strongly in the near ultraviolet region. The absorption of light energy by sensitive groups can result in the formation of reactive species by bond rupture or in some cases just by the formation of suitable electronically excited states (e.g., singlet oxygen). These species often can accelerate the normal free-radical chain oxidation as well as provide new degradation paths: formation of backbone carbonyl groups, chain scission, production of CO, H_2O and CO_2.

For the acrylic polymers, the photostability is a function of UV wavelength and irradiation time, as it is already mentioned by Chiantore et al. [9]. Also they showed the acrylates units are more reactive towards photodegradation as comparative with the methacrylate ones, and the length of the alkyl side groups determines the ratio of chain scission vs. crosslinking reactions to prevail.

The possible chemical changes of the film surface in the artificial weathering environment were detected by FTIR spectra of specimens before and after exposure for different times (Figs. 4 a,b,c). For the investigated polyacrylate plasma films are made commonly remarks. The main information is that the breaks of molecular groups on the polymer chain did not occur. Also the locations of the characteristic absorption peaks are almost completely the same.



(a)

(b)

(c)

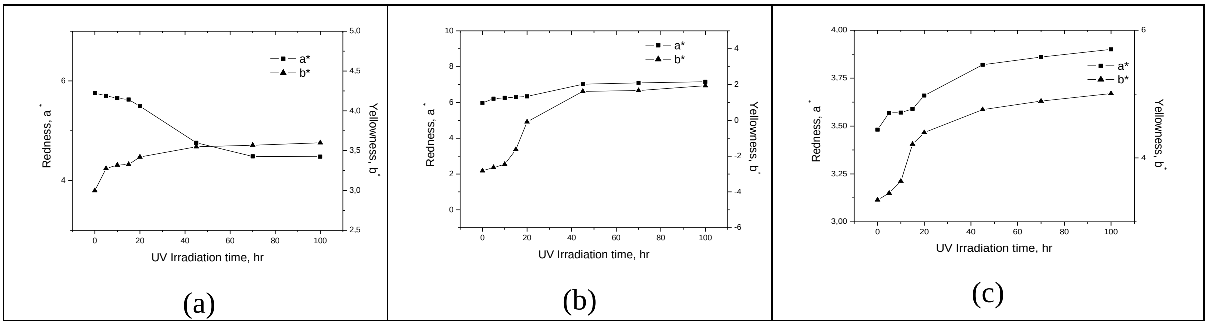
Fig. 4. FTIR spectra of polyacrylic films under UV accelerated aging at different irradiation time: (a) PMeA; (b) PEtA; (c) PBuA

Also, in the “fingerprint” range between 1600 and 550 cm $^{-1}$ is detected a great number of peaks, but there are not observed the displacements of the maximum absorption positions. The main signal that evidences the oxidation reactions’ development during the photodegradation process, with increasing of the UV irradiation time to 100 h, is the progressive increase and broadening at both sides of the peak at 1731 cm $^{-1}$ attributed to C – O stretching. This confirms the progressive formation of new carbonyl groups caused by photo-oxidation after 20 h of UV irradiation. These experimental results are agreed with the hypothesis of the carbonyl groups formation during the photooxidation process [37].

For the polymers’ use in the cultural heritage conservation is essential to preserve in time the color and the gloss of the deposited films. These attributes quantify the weatherability of coatings applied in this domain. The alteration in the surface color of the polymer films exposed to the UV accelerated weathering is illustrated in Figs. 5 and 6. The color changes in the aging procedure are correlated to the formation of new carbonyl groups, like chromophores, caused by the photodegradation process sustained by IR spectroscopy data presented before.

The color indices a * and b* registered the modification under the UV irradiation for all the polymeric films subjected to aging (Figs. 5 a-c). The b* coordinate (the blue – yellow axis) increases in the first 45 hr of UV treatment from 2.99 to 3.59 for PMeA film (Fig. 5a), from - 2.8 to 1.8 for PEtA film (Fig. 5b) and from 3.34 to 4.75 for PBuA film (Fig. 5c), after which a little change is observed. These data signify that the film surface color displaced from blue to yellow, and then remains stable.

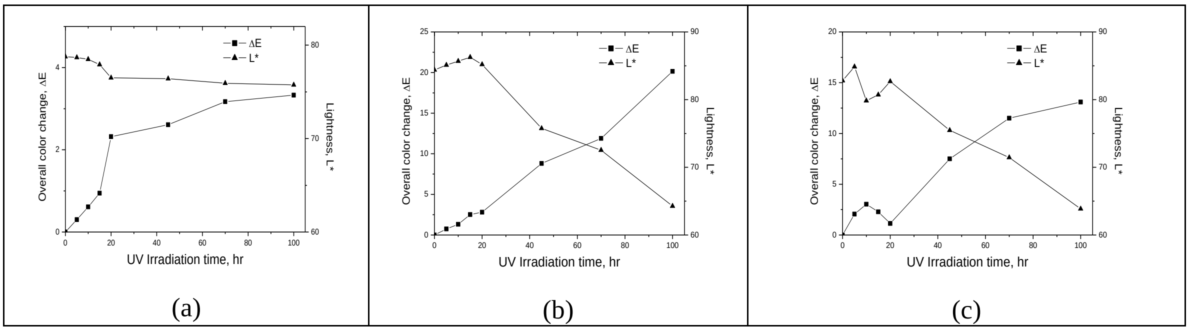
The a* (the green - red axis) value (Fig. 5) for the aged films based on PEtA and PBuA pursues the same trend with b* (Fig. 5 b, c), with gradually increase until 45 h of aging, followed by a plateau until the end of the irradiation time; the exception is a* value for PMeA film (Fig. 5a) that shows a monotonic decrease until 70 h and then remains almost unchanged in the following hours.



(a) (b) (c)

Fig 5. a * and b coordinates of polyacrylic films under UV accelerated aging at different irradiation time : (a) PMeA; (b) PEtA; (c) PBuA*

During the aging processes, the lightness L* values depicted in Fig. 6 have the tendency to decrease. This behavior for L value is observed by other authors [38] too, like the increase effect of the visible light dispersion caused by photooxidation process of the film.



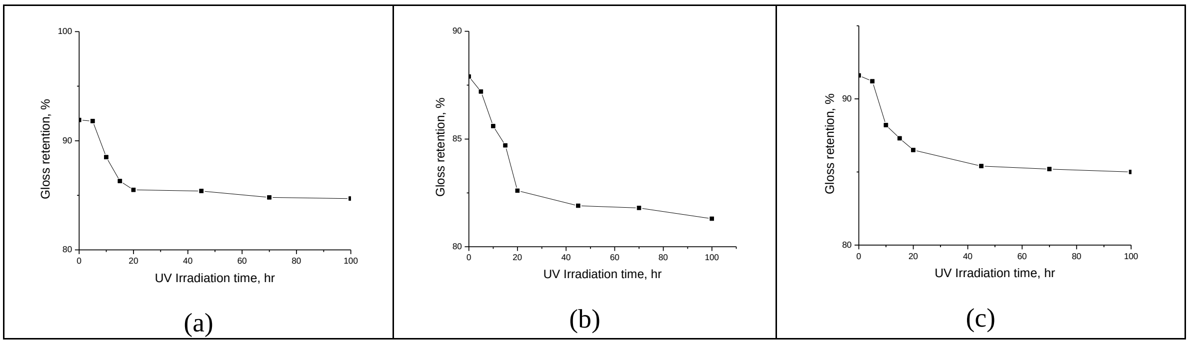
(a) (b) (c)

Fig. 6. L * and ΔE of polyacrylic films under UV accelerated aging at different irradiation time: (a) PMeA; (b) PEtA; (c) PBuA

In the first hours of UV irradiation, L* achieves a peak value followed by an abrupt decrease, more accentuated for PEtA and PBuA films (Figs. 6b, c). For PMeA film the decrease is almost irrelevant.

The overall color change□ΔE represented in Fig. 6 raises continuously for all of the UV irradiated polyacrylic films with the exposure time increasing up to 100 h. The PMeA film presents the smaller raise until 3.3 units of ΔE, while PEtA and PBuA have greater values of 20.1 units and 13.1 units, respectively. From the results it can be concluded that compared with the unaged specimens, the surface of the films turned yellow, the overall color change calculated by Eqn. 2 being correlated with a*, b* and L* evolution.

The gloss is another index for the film aspect evaluation in relation with the application as protective component for the items in the cultural heritage conservation. The gloss estimates the reflection ability of the surface under a particular standard source and using a particular incidence angle [39]. The light in the UV range with λ□= 365 nm induces some modification in the gloss of the plasma polymer films' surface (Fig. 7). It is known the correlation that exists between the surface roughness increase and the reducing of the light reflection capability [40].



(a) (b) (c)

Fig. 7. Gloss of polyacrylic films under UV accelerated aging at different irradiation time: (a) PMeA; (b) PEtA; (c) PBuA

All the plasma polymer films in our experiment show the gradually gloss decrease as a consequence of the surface roughness increase with the exposure time.

4. Conclusion

With the aim of finding for an innovative solution in the protection and consolidation of the paper supports belonging to the cultural heritage, the low pressure non equilibrium plasma polymerization process of a series of acrylate monomers with thin films deposition is applied. The deposition of these films on the paper surface confers new functional properties, in particular stability and low wettability, in order to preserve the paper for the future.

According to the previous presented data, it can conclude that:

- The pre-established plasma parameters allow the synthesis of a "conventional polymer-like" structure, with the preservation of the monomers' functionalities. This aspect is important in relation with the reversibility rule imposed by the application in the conservation domain;

- The accelerated UV aging induces some modifications of the polymeric plasma films followed by FTIR, color and gloss. Until 100 h of UV irradiation, FTIR does not show displacements, appears or disappears of new peaks in the spectra. The increase and broadening at both sides of the peak at 1731 cm^{-1} confirm the progressive formation of new carbonyl groups caused by photo-oxidation after 20 h of UV irradiation.

- The color indices for the plasma deposited polyacrylic films revealed they turned yellow and the gloss decreases due to the UV irradiation time increase.

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