An investigation of plasma polymer thin films deposition by low-pressure non-equilibrium plasma

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Plasma polymerisation offers an ecological, potentially tuneable 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 investigation, a low pressure non-equilibrium plasma is useful for the preparation of films from a homologous series of alkyl acrylates from methyl to butyl and methyl methacrylate, deposited on planar supports of organic nature (paper). The resulting plasma polymers are characterized by FTIR spectroscopy, AFM and contact angle.

1. Introduction

Non-thermal plasmas have a gas temperature (heavy particles temperature) slightly higher than room temperature and offer high excitation selectivity and energy efficiency in plasma chemical reactions. They are strongly in non-equilibrium state and can be easily generated at pressure lower than atmospheric pressure. Plasma modification of polymer materials including the thin films deposition by polymerization, too, is a very fast, clean, and environmentally benign and safe (gas-dependant though) method. By appropriate plasma treatments new properties such as optical reflection, adhesion, friction coefficient, surface energy (wettability and water repellence), permeability, surface conductivity and biocompatibility of conventional polymers can be obtained [1-5].

Plasma polymerization was selected as method because of its well known ability to create physically stable coatings on different substrates and with good preservation of functional groups and structure, particularly with the use of high frequency plasma. Under these conditions it is possible to maintain pulsed plasma at very low power levels, which allows the preservation of functional groups.

At the same time, plasma polymerization is a unique technique to fabricate thin polymer films (20 Å - 1 μm) from a variety of volatile compounds without chemical solvents (dry process) and catalysts. Furthermore, plasma polymerized (PP) films can be prepared from monomers that cannot be polymerized by conventional chemical techniques (i.e. methane, ethane, saturated hydrocarbons, organo-metallics). (PP) films are pinhole-free and highly crosslinked and therefore are highly resistant to chemical and physical treatment, and mechanically tough. Furthermore, such films are often highly coherent and adherent to a variety of substrates including conventional polymer, glass and metal supports of planar or even complex 3D shapes. These characteristics of the (PP) films (adhesion, mechanical properties, extent of crosslinking, etc.) are dictated by the choice of kinetic formation parameters such as high frequency power input, plasma pressure, and reaction time [6].

Due to these excellent properties (PP) films have been undertaken very actively in the last few years for a variety of applications such as permselective membranes, protective coatings, biomedical materials, electronics, optical devices and adhesion promoters [7,8].

Among the limitations of (PP) films are the sensitivity to oxidation when exposed to the atmosphere. Because of the nature of the polymerization process, which is largely by a radical mechanism, many plasma polymers contain long-lived radicals. These sites have the tendency to absorb oxygen which may eventually alter the properties of the films. Another less favourable property is that plasma-polymerized films tend to become brittle when deposited in higher film thickness. This phenomenon has been explained by a wedge-type growth mechanism [9].

Many papers concerning the plasma polymerization processes are more descriptive, by referring to the particular characteristics of deposition process in a particular experimental set-up, for a particular set of deposition conditions. Answers are required especially on how deposition parameters influence the resulting properties of the plasma polymers. Other papers have been focused on the ability of standard polymerization model (Bell-Yasuda) to predict the dependence of deposition on Yasuda factor, power, duty cycle and monomer flow [10]. In general, low values of Yasuda factor and power have shown a greater retention of structures from the monomer in the plasma polymers. Similar observations of a high retention of the monomer structure at low values of Yasuda parameter were reported by Inagaki et al. [11] when they used a mixture of carbon dioxide with acrylic acid for depositing plasma polymers.

Previously, we have reported the plasma polymerization of aniline [12], styrene and methyl methacrylate [13] on glass substrate and nanoscale ferrite particles, with aim of conductive and protective thin films deposition.

In this paper, plasma-polymerized (PP) films are synthesized from a homologous series of alkyl acrylates from methyl to butyl and methyl methacrylate, being

deposited on planar supports of organic nature (paper), by plasma polymerization under the same experimental conditions for each monomer. (PP) films are characterized using FTIR spectroscopy, atomic force microscopy (AFM), and contact angle determination.

2. Experimental

Materials

Paper sheet samples of 15x70 mm (Standard line printer paper of 80 g m^{-2}) are the supports for (PP) film deposition. The monomers: methyl methacrylate (MMA), methyl acrylate, (MeA), ethyl acrylate (EtA) and butyl acrylate (BuA) (99%, Sigma-Aldrich USA) are used as received, without further purification.

Plasma polymerization

Plasma polymerization equipment was previously presented [12]. After the sample is introduced into the plasma reactor, the chamber is evacuated to less than 0.3 torr. The monomer from the flask is then introduced at steady flow conditions. The coatings are all prepared from the pure monomer, no carrier gases being added. The plasma reactor is placed between a pair of semicylindrical electrodes connected to a radio-frequency capacitive-coupled glow discharge system, which operated at 1.2 MHz and delivered up to 200 W.

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. After deposition in the plasma reactor, paper sheets coated with (PP) films based on PMMA, PMeA, PEtA and PBuA, are kept in the vacuum desiccator until has been analyzed.

Characterization

(PP) Film Deposition as a measure of plasma kinetic process is determined gravimetrically, by weighing the samples with a precision electronic balance (A&D Co. Ltd. HR 200).

ATR-FTIR Spectroscopy. The composition of the (PP) films is evidenced on a spectrometer Bruker VERTEX 70 (Golden Gate device - Specac), in the transmission mode with a resolution of 2 cm^{-1} and 64 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, 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 constants are 11.5 N/m. In the tapping mode, the cantilever is oscillated at a frequency of 183,228 kHz. Representative scans of the film surface (Scan Physical size is 10 μm x 10 μm and Scan Point size was 256 x 256) 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:

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

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.

Contact angle measurement. On a KSV Instruments CAM 101 instrument, with automated system for storage the drop images, via digital camera, with PC-based control, acquisition and data processing. There is obtained using the sessile droplet profile analysis technique, under controlled conditions of room temperature and humidity. Bidistilled water is used as test liquid. Each value is the average of 40 specimens.

3. Results and discussion

Through inelastic collisions, monomers are fragmented into activated species or into their constituent atoms. The activated fragments are recombined and rearranged by a rapid step growth mechanism, and deposition occurs due to a loss of kinetic energy upon collision of the activated species with the substrates or walls of the reactor. The loss of kinetic energy is due either to a chemical reaction of the species or increased molecular weight [1]. The repetition of activation / fragmentation and recombination leads to film formation. This concept is significantly different than the mechanism of conventional polymerization [14].

Consequently, polymers formed in plasma generally have complex, highly crosslinked structures due to the large number of reaction pathways available during plasma excitation [15,16].

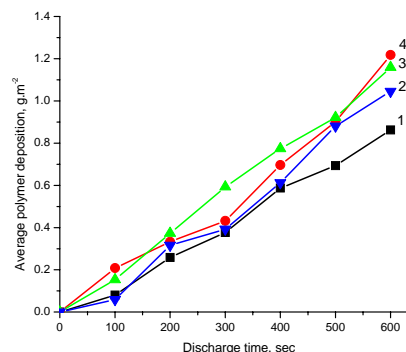Fig. 1 shows the average polymer deposition as a function of the reaction time.

Fig. 1. Polymer average deposition vs. discharge time in plasma polymerization: 1-PMMA; 2-PBuA; 3-PEtA; 4-PMeA.

Although the monomers are different as well as their rate of evaporation (a function of vapours' pressure), it is

observed they have approximately the same growing rate of the films. For 600 sec final reaction time, poly(methyl acrylate) is deposited in the highest average amount of 1.21 g.m^{-2}. For the tested structures in the plasma polymerization, the ordering established by the average polymer deposition is: PMeA > PEtA > PBuA > PMMA. Through careful control of the plasma polymerization parameters, (PP) films can be tailored to contain specific functional groups existent in the monomer structure, which resembles addition polymers from conventional syntheses.

Thus, for the established operational parameters, the solubility test in acetone and ethyl acetate, and the ATR-FTIR spectra (Fig. 2) of the synthesized thin films deposited on paper sheets samples revealed a similar structure with the conventional polymers, with no evidenced crosslinking. In Table 1 the main frequencies of the absorption bands, relative intensities and assignments are reported for reference paper and all the investigated (PP) polymers (PMMA, PMeA, PEtA, PBuA) deposited on paper sheets. The ATR-FTIR spectra of all the samples show a typical broad band in the range of 3330 cm^{-1} corresponding to the OH bending vibration in cellulose.
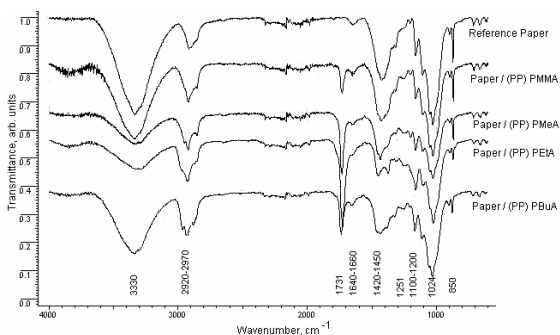

Fig. 2. ATR-FTIR spectra for reference paper and (PP) films deposited on paper by plasma polymerization, in the specified operational parameters (frequency 1.2 MHz, discharge power 200 W, time 600sec, pressure <0.3 torr).

Table 1. Frequencies of absorption bands, relative intensity and assignments for the investigated polymers.

Frequency, cm^{-1}	Relative intensity [x]	Assignments [xx]
~3330	broad	ν (O-H)
~ 2920 - 2970	S	ν (C-H aliphatic)
1731	S	ν (C=O)
~ 1640 - 1660	W	Aldehyde groups in cellulose
~ 1420 - 1450	S	β(C-H aliphatic)
~1251	W	ν (C-O ester)
~ 1100 - 1200	S	δ(C-H aliphatic)
~1024	S	ν (C-C ethyl)
850	W	ν (C-C ethyl)

x – S is strong; W is weak

xx – ν is stretching; β is bending; δ is bending out-of-plane

For all the analyzed samples, the presence of C=O group is confirmed by the characteristic sharp carbonyl stretching peak at 1731 cm^{-1}, while the band at ~1251 cm^{-1} confirms the presence of C-O bond (stretching) and the band at ~1024 cm^{-1} confirms the presence of the ethyl group (stretching C-C).

AFM technique can be used to study the topographies (morphology and roughness) resulted after (PP) film deposition comparative to the reference paper sheet; it can provide both qualitative and semi-quantitative information. The method can create topographical maps of paper consisting of three-dimensional images of the surface ultra-structure at molecular level, in real time, under atmospheric conditions, and without the necessity to fix samples [17,18].

Fig. 3-7 evidenced AFM measurements performed on untreated and plasma treated paper sheets. In Table 2 there is presented the Root Mean Square surface roughness evaluated on scanned area (10 μm x10 μm) on all the investigated samples.
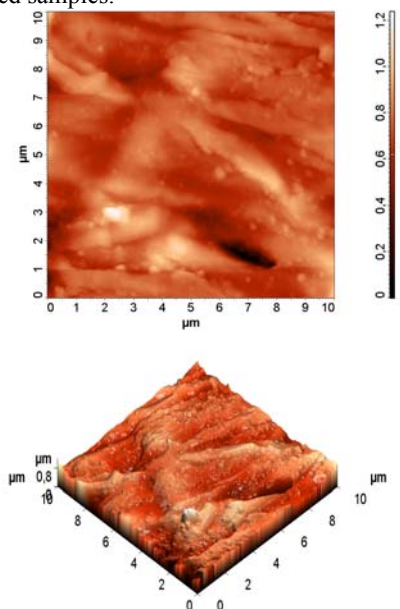

Fig. 3. AFM images (2D, 3D) of reference paper sheet.

The AFM images of the reference sample (Fig. 3) evidence the typical fibrillar morphology of cellulose in paper sheet. A qualitative comparison between topographies of the paper sheets coated with (PP) films evidenced some modifications and differences. Thus, the surface topography imaging of (PP) PMMA coated paper (Fig. 4) reveals how polymer penetrates into the paper substrate and fills the pores, the resulted morphology following the fibrous template cellulose support. It can be remarked an insignificant decrease of RMS value (Table 2) in comparison with reference paper sheet.
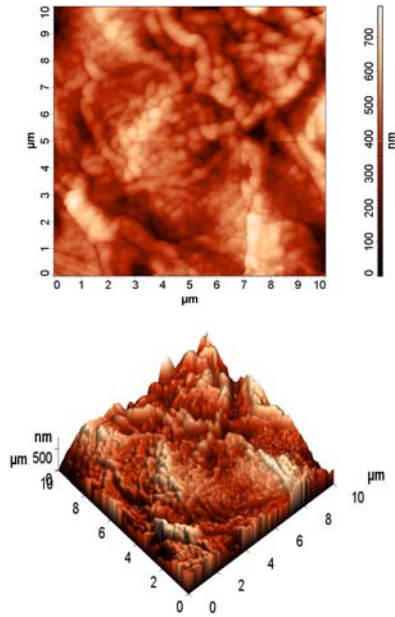
Fig. 4. AFM images (2D, 3D) of (PP) PMMA coated paper sheet.

Fig. 6. AFM images (2D, 3D) of (PP) PEtA coated paper sheet.

In the case of (PP) PMeA coated paper sheet (Fig. 5), it can be noticed that the RMS value slightly increases (Table 2) in comparison with reference sample accompanied by an evolution of the surface morphology. This case, plasma polymerization with thin film deposition doesn't take place in some aleatory manner. Practically, under the specified plasma conditions, polymerized anisotropic oriented structures are obtained.
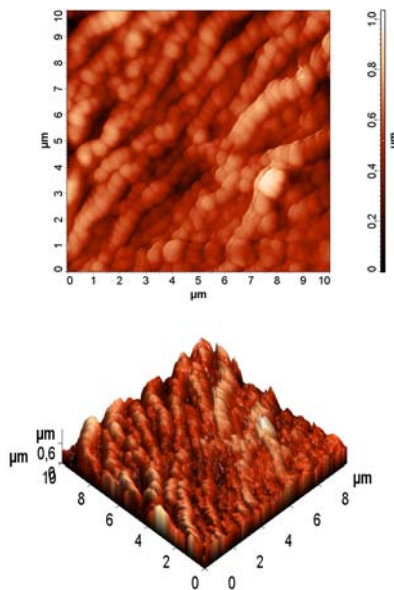
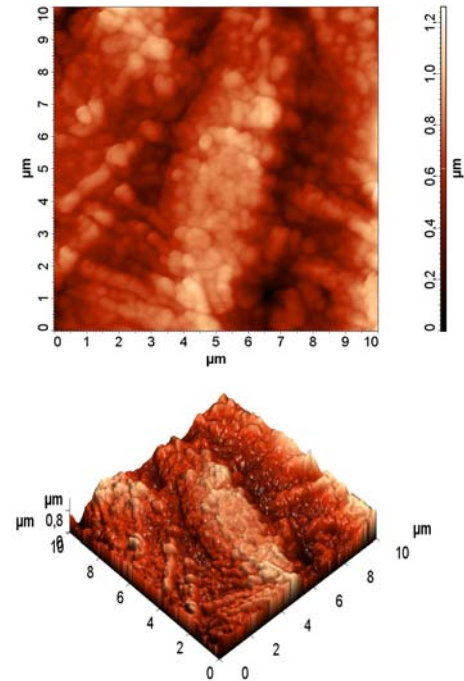AFM image of (PP) PEtA coated paper sheet (Fig. 6) shows a surface morphology that follows the cellulose template support, too. It can be remarked a more significant increase of the RMS value (Table 2) in comparison with the reference paper sheet.
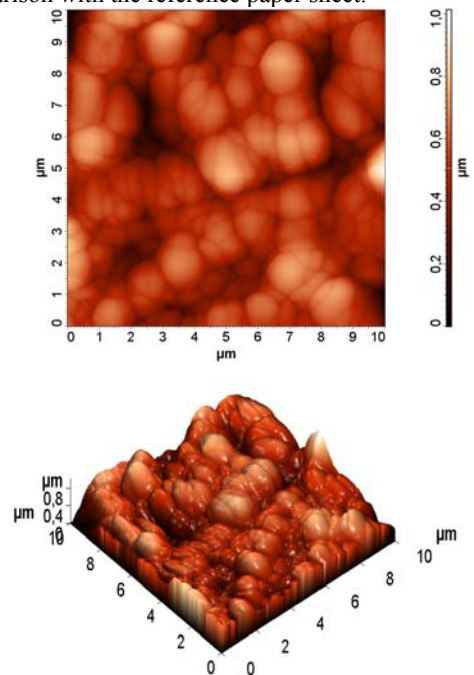

Fig.5. AFM images (2D, 3D) of (PP) PMeA the coated paper sheet.

Fig.7. AFM images (2D, 3D) of (PP) PBuA coated paper sheet.

For the sample (PP) PBuA coated paper sheet (Fig. 7), it is observed a slightly increase of the RMS value (Table 2) in comparison with reference sample, as well as an evolution of the surface morphology. Unlike the other studied samples of (PP) coated paper, the morphological structure formed in this latter case is branched.

The investigation by means of atomic force microscopy of cellulose paper supports coated with (PP) films of vinyl type concludes that, generally, the surface roughness increases. It can be remarked an evolution of the morphology of the deposited films: either an impregnation of the support, by filling the pores and coating the cellulose fibres (methyl methacrylate and ethyl acrylate) or particular surface morphologies are obtained (anisotropic or branched structures) resulted after plasma polymerization (methyl acrylate and butyl acrylate). These results can be explained in terms of plasma polymerization kinetics.

The contact angle of water droplets onto the (PP) films deposited on paper sheets was used to estimate the film protective properties against water and water vapours, and it is presented in Table 2. This concept is important not only because it can offer information on the plasma treated surface energies but on the wettability, too.

Table 2. RMS surface roughness and contact angle for the investigated samples

Sample	RMS, nm [x]	Average contact angle, degree
Reference paper sheet	113.783	Instantaneous absorption
(PP) PMMA coated paper	112.853	92
(PP) PMeA coated paper	125.821	95
(PP) PEtA coated paper	171.452	96
(PP) PBuA coated paper	125.884	97

x RMS - Root Mean Square surface roughness evaluated on scanned area (10 μm x10 μm)

For the reference paper sheet it is relevant the hydrophilicity, the droplet being instantaneously absorbed by the support, without the capability for optical recording of the contact angle. In the case of (PP) films PMMA, PMeA, PEtA and PBuA deposited on paper sheets that present topographic modifications (as RMS evidenced in Table 2) relative to the reference paper, the average contact angle has increased values, in the range of 92 – 97 °.

Although the theoretical literature [19, 20] consents that the surface roughness of a non-planar substrate may enhance wetting, but a quantitative description is still lacking. A theoretical study of Chow [21] mathematically analyses and explains how roughness results in local changes in the contact angle. Finally, the author gets at the conclusion that roughening of the surface reduces the contact angle and increases the critical surface tension.

In our study, by analyzing the change in the contact angle by (PP) film deposition on paper sheets, it is clearly that such a correlation with microstructure disorder cannot be made, because the chemical structure of these films has the main influence on the contact angle. Its average values are slightly higher as the alkyl group in the side chain is more voluminous. The found out ordering is: (PP)PBuA > (PP)PEtA > (PP)PMeA > (PP)PMMA

4. Conclusions

1. The intend of this work is to bring more understanding of the plasma polymerization process with film deposition, in correlation with its applicability for protective coatings for degraded supports of different nature (i.e. paper) that may constitute items of historical heritage.

2. The resulting plasma polymers harmonized well spectroscopically with those from classical polymerization, indicating that stoichiometric polymers with no evident crosslinking can be achieved in the plasma environment.

3. The data obtained through AFM and contact angle are also discussed, relative to the (PP) film deposited on the paper. Thus, the surface cellulose pattern coated and "followed" by the (PP) film through plasma polymerization has irregularity and the average contact angle is placed in the range of 92 – 97 °.

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