Properties of the acrylic acid polymers obtained by atmospheric pressure plasma polymerization

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A B S T R A C T
Plasma polymers of acrylic acid were obtained using an atmospheric pressure discharge system. The plasma polymerization reactor uses a dielectric barrier discharge, with the polyethylene terephthalate dielectric acting as substrate for deposition. The plasma was characterized by specific electrical measurements, monitoring the applied voltage and the discharge current. Based on the spatially resolved optical emission spectroscopy, we analyzed the distribution of the excited species in the discharge gap, specific plasma temperatures (vibrational and gas temperatures) being calculated with the Boltzmann plot method. The properties of the plasma polymer films were investigated by contact angle measurements, infrared and UV–Vis spectroscopy, scanning electron microscopy. The films produced by plasma polymerization at atmospheric pressure showed a hydrophilic character, in correlation with the strong absorbance of OH groups in the FTIR spectrum. Moreover, the surface of the plasma polymers at micrometric scale is smooth and free of defects without particular features.

1. Introduction

Interactions between electrons, ions and UV photons from gas discharge plasmas and monomeric gases lead to bond breaking and appearance of polymerizable compounds. In this way, on substrates arranged in different regions of the discharge or even out of the discharge region, deposition of plasma polymers occurs in form of a three dimensional network of molecules and oligomer chains. The physico-chemical properties of these polymers are different from the ones of the same polymers obtained by conventional polymerization reactions [1]. Moreover, different properties can be adjusted to desired levels using appropriate plasma parameters.

Nowadays, plasma polymerization is a useful tool to obtain thin polymer films on various substrates. These plasma polymers give new surface properties for the materials used as substrates, such as adhesion, corrosion resistance, friction, optical characteristics, biocompatibility, as interfacial layers in different deposition processes or as beads for active biological compounds immobilization [2]. Promising results have been obtained lately by plasma polymerization in discharges at atmospheric pressure, such as dielectric barrier discharges [3–5]. Specific advantages of the atmospheric pressure polymerization systems are the elimination of vacuum systems and the rapid kinetics of chemical reactions.

In this work we present results concerning the plasma polymerization of acrylic acid in an atmospheric pressure reactor. Acrylic acid thin films were reported in the literature as materials with different applications in the biomedical field, such as cell culture substrate [6,7], support for biological molecules immobilization [8,9], biosensors [10] and barrier against corrosion of implants [9].

2. Experimental

The plasma polymer films were obtained in a polymerization reactor based on an atmospheric pressure discharge (APD) in helium. The plasma is generated in a dielectric barrier discharge with plan–plan geometry. The dielectric barrier, foils of polyethylene terephthalate – PET, Goodfellow Co, 125 μm thick, acts as substrate for polymer deposition. The discharge is driven by high voltage monopolar pulses, with 3 kV amplitude and 2 kHz frequency.

The monomer is introduced in the discharge region by a gas handling system at room temperature (Fig. 1). Two helium pathways are used in the experimental arrangement to feed the plasma polymerization reactor: the working pathway (150 mL/min) used to sustain the discharge and the carrier pathway (25 mL/min), used to transport the monomer vapors (acrylic acid – AAc, purity >99%, Merck) into the plasma region. The deposition duration was fixed at 2 min.

Discharge diagnosis was performed by electrical measurements of current and voltage, using probes connected to a digital scope, LeCroy 434 and by spatially resolved optical emission spectroscopy. The optical signal is collected with optical fibers through a two slit system and analyzed by a Triax 550 monochromator.

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Acrylic acid plasma polymers were investigated by contact angle measurements, based on sessile drop method with two liquids (distilled water and formamide). Attenuated total reflectance infra-red absorption spectroscopy ATR-FTIR (Nicolet Impact 4000 with Golden Gate Single Reflection Diamond ATR accessory) and UV–Vis absorption spectroscopy (Jasco V-570 spectrophotometer with integrating sphere) were used to study the chemical structure of the plasma polymers. The surface morphology was investigated by scanning electron microscopy SEM (S-4500 Hitachi microscope, 100K magnification).

3. Results

3.1. Discharge characterization

The working regime of APD was the glow mode at atmospheric pressure [11,12], confirmed by the discharge current shape and the specific discharge regions (i.e. the negative glow and positive column) evidenced by optical diagnosis.

In the absence of the working gas a displacement current is introduced in the system (the dot line in the Fig. 2). When the working gas is introduced in the gap two sharp current peaks appear corresponding to the conduction current trough the system. The positive current peak corresponds to the primary discharge, while the negative one is due to the internal field inversion under the effect of the charge deposited on the dielectric surface during the primary discharge. The presence of monomer vapors reduces the discharge current (from 120 mA to 80 mA) and delays the discharge ignition (Fig. 2). Minimal thermal effect on the polymerization process is assured by the relative low values of the current.

Our previous optical investigations showed that the spatial distribution of the total light emission intensity in the gap corresponds to the well-known regions of the glow discharge [13]. In front of the cathode a maximum of the emitted light intensity was found, followed by a relative constant region, for both primary and secondary discharge.

By optical emission spectroscopy, we analyzed the excited species in the discharge ignited in "pure" helium. Besides helium lines (388.8 nm, 501.5 nm, 587.5 nm, 667.8 nm, 706.5 nm, 728.1 nm), which presents the maximum intensity in the spectrum, other species (impurities) are identified in the discharge volume, such as atomic oxygen (O), molecular nitrogen (N₂), nitrogen molecular ion (N₂⁺) and hydroxyl free radical (OH) [13].

The spatial distribution of excited helium (the line at 706.5 nm), corresponding to the 3S–2P transition with a threshold of the excitation energy of 22.72 eV (Fig. 3), suggest that energetic electrons are generated in the cathode region.

Information about the electron energy distribution in the discharge gap can be obtained also from the vibrational temperature distribution of the molecular nitrogen. This temperature was calculated using the Boltzmann plot of molecular nitrogen bands intensities from the second positive system (C^2Π_u–B^2Π_g). Fig. 4 shows that the vibrational temperature has maximum values (around 3000 K) in front of the cathode and smaller values in the anode region, around 2000 K. Since the vibrational levels are separated with energies in the range of 0.1 eV and the neutral molecular have no sufficient energy, in average, to excite these states (e.g. the energy of neutrals molecules at 1000 K is 0.086 eV) [14], we can consider that the primary mechanism for vibrational levels excitation is assured by electron impact processes.

Thermal effects in the discharge were appreciated from the gas temperature. These values were calculated using the Boltzmann plot of nitrogen molecular ion rotational lines intensities from the (0–0) band of the first negative system (B^2Σ_u^+–X^2Σ_g^−) at 391.4 nm. In case of dielectric barrier discharge the similarity between the gas temperature and the rotational temperature was studied and proved [15]. The values of the gas temperature in case of our atmospheric pressure discharge are around 340 K in the cathode region and 380 K in the anode region, thus thermal...
polymerization reactions are less probable. Spatial distribution of gas temperature in the gap was presented elsewhere [13].

3.2. Plasma polymers properties

The hydrophilic character of the acrylic acid plasma polymers was proved by the water contact angle that was around 20°. Regarding the surface energy ($\gamma$), the acrylic acid plasma polymers show high values of the polar component ($\gamma^p = 51$ mN/m), and low values of the dispersive component ($\gamma^d = 17$ mN/m). The polarity of the films (i.e. the ratio between the values of the polar component and the total surface energy) is 0.75.

The ATR-FTIR spectrum of the plasma polymers of acrylic acid shows strong absorbance in the OH region (3600–3000 cm$^{-1}$), with a broad band centered at 3300 cm$^{-1}$ (Fig. 5). It should be noted that acrylic acid monomer presents no absorption band in that region, and only the plasma polymerization processes, trough fragmentation and rearrangement phenomena, induces a completely new chemical structure, with supplementary vibrations frequencies. In the 3000–2750 cm$^{-1}$ region signatures of $\text{CH}_3$, $\text{CH}_2$ and CH groups are found for all presented spectra (substrate, plasma polymer and monomer).

The plasma polymers of acrylic acid preserve the transparency of the PET substrate in the visible range. The films show no significant absorbance up to 325 nm, while in UV strong absorption bands are present (Fig. 6). The broad band around 300 nm corresponds to $n \rightarrow \pi^*$ transition of oxygen atoms form C=O groups.

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**Fig. 4.** Spatial distribution in the discharge gap of the vibrational temperature of the molecular nitrogen (K – cathode, A – anode).

**Fig. 5.** ATR-FTIR spectra of the substrate (PET) and plasma polymers of acrylic acid (ppAAc). For comparison a spectrum of acrylic acid solution is shown (NIST database [16]).

**Fig. 6.** UV–Vis spectra of the substrate (PET) and plasma polymers of acrylic acid (ppAAc).

**Fig. 7.** SEM images of the substrate (PET) (a) and plasma polymers of acrylic acid (ppAAc) (b).
while the bands at 270 nm and 215 nm are assigned to $\pi \rightarrow \pi^*$ transitions in orbitals of C=C bond.

The surface morphology of the plasma polymers of acrylic acid were investigated by scanning electron microscopy.

The morphology of the PET substrate presents characteristic surface features for polymers, with worm like structures, homogenously distributed and without a specific orientation (Fig. 7(a)). After deposition of acrylic acid plasma polymers on the PET, the surface morphology is changed (Fig. 7(b)). The surface features of PET are filled with the plasma polymer and, as a result we obtained a smooth surface at micrometric scale, free of defects or inhomogeneities. No particular structures, like grains, cracks or pores were observed.

4. Conclusions

Plasma polymerization in atmospheric pressure reactors is a good solution for obtaining polymers of acrylic acid on the dielectric substrates. The energetic character of the discharge was demonstrated by specific distribution of excited species and temperatures in the gap. No thermal effect can be considered in our plasma polymerization reactor.

The acrylic acid plasma polymers have hydrophilic character with high value of the surface energy. Strong absorbance of the OH groups in the polymers structure is found by the FTIR analysis. The films show smooth surface at micrometric scale, free of defects or inhomogeneities. These properties make the acrylic acid plasma polymers suitable candidates for applications in the immobilization of biological active species or as cell culture substrates.

References