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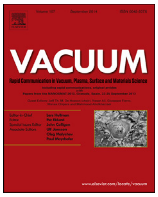

Acetylene plasma polymer treated by atmospheric dielectric barrier discharge

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ABSTRACT

Plasma polymer films are very attractive for industrial applications in several sectors such as in the electronic, mechanic, biomedic, coating and others, due to its good adhesion, being insoluble in mild acids and bases and having a high crosslinking structure. This work reports the physical, structural, and surface properties of the polymer obtained from an acetylene plasma polymerization technique and treated by dielectric barrier discharge (DBD). The film was deposited in a reactor supplied by a radio-frequency power source at low pressure. After deposition, the nanofilms were treated in a DBD plasma reactor operating in air. The treatment times varied from 1 to 5 min. The analysis of molecular structure of the samples was investigated by FTIR spectroscopy, showing absorption bands in 3480, 2930, 1720, 1450 and 1380 cm^{-1}. The water contact-angle was investigated by goniometric technique and presented values from 5 to 65°. The aging effect of these films was also studied. The alteration in the films surface morphology was assessed by an atomic force microscopy (AFM) which indicated that the roughness increased from 60 nm to 160 nm as a result of the DBD treatment. The refractive index of the samples presented values near 1.7, measured by UV–Visible spectroscopy.

1. Introduction

Plasma processing of materials using low pressure RF excited glow discharge presents great importance in many scientific and technological issues encompassing microelectronics, biomaterials, and aeronautical industries. The great versatility of the process is due the fact that, within such kind of discharge, a thermal non-equilibrium situation is attained where electrons are thermally decoupled from neutrals and ions resulting in a highly reactive chemistry in a reactive cold environment. This situation allows one to synthesize materials with remarkable properties that could not be synthesized in a thermal equilibrium situation [1–4]. Among such materials, plasma polymer acetylene (C_2H_2) (pp-acetylene herein) is the one that has been keeping the scientific community's attention for years due to its pinhole-free structure, good adhesion to different kind of substrates and because it is inert to mild acids and bases making it appropriate for several kind of applications as protective coatings [5–8]. In the field of biomaterials technology, the hydrophilicity of a surface has great importance for an optimized coupling between the material and the human tissue, since the mean water content in a cell is approximately 80% [9–14]. Therefore, a customized plasma polymerization process for biomaterial applications must take this figure into account [15,16]. The paper hereby presented deals with a pp-acetylene post-treatment by an atmospheric pressure dielectric barrier discharge (DBD herein) [17–19] in order to attain this goal. Polymers obtained by conventional chemical techniques were treated by DBD. However, the plasma polymers exhibit little discussion in literature. This provides a fertile field of research for these materials class due to their promising applications, as the pp-acetylene ones.

2. Experimental

Acetylene plasmas were generated by RF (13.56 MHz at 15 W) (Tokyo HY-Power model RF-300™) coupled to a parallel plane electrode plasma reactor with a 210 mm internal diameter and 225 mm high cylindrical stainless steel chamber. The RF power was coupled to the plasma reactor through an appropriate matching network (Tokyo HY-Power model MB-300™) that allows one to minimize the reflected RF power. The vacuum inside the plasma chamber was monitored by Pirani™ (thermocouple) and Penning™ (inverse magnetron) gauges. The turbo-molecular pump was

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coupled to the chamber through a gate-valve, and was used for cleanliness purposes. The pressure was pumped down to 10^{-4} Pa, and the chamber was purged with argon several times before each run of the experiment. The inner side of the plasma chamber was polished up to an optical quality (roughness of 0.5 μm or less) in order to minimize the retention of impurities and facilitate the cleaning process. Acetylene was placed into the plasma chamber through a flowmeter and using a needle valve. Films of pp-acetylene were deposited at a fixed pressure of 4 Pa during 15 min. All pp-acetylene samples were post-treated at atmospheric pressure by DBD, generated by a sinusoidal wave-form (peak voltage of 35 kV at 60 Hz). The treatment time varied from 1 to 5 min. The molecular structure of the polymeric films was studied by FTIR spectroscopy in the spectra ranges of 4000 cm^{-1} to 1200 cm^{-1} using a PerkinElmer FTIR Spectrometer Spectrum 100™. The film morphology was analyzed by atomic force microscopy (AFM) using a Shimatsu Microscope. The wettability of pp-acetylene was analyzed using a Ramé-Hart goniometer 300-F1™. The optical properties of the samples were investigated by UV–Visible spectroscopy using a PerkinElmer UV–VIS Lambda 25 spectrometer.

3. Results and discussions

Fig. 1 shows infrared spectra of films deposited from C_2H_2. The absorption bands in spectrum *a* are typical of a plasma polymer derived from hydrocarbon discharges with the hydroxyl and carbonyl modes, respectively centered at 3480 cm^{-1} and 1720 cm^{-1} [15,20,21]. The absorptions around 2930 cm^{-1} are characteristic of C–H stretching in groups CH_3 and CH_2 and those close to 1450 cm^{-1} and 1380 cm^{-1} are due to C–H bending modes in CH_3 and CH_2 groups. It can be observed that oxygen is not present in the monomer acetylene molecular structure, responsible for the films deposition. The presence of hydroxyl and carboxyl groups in the films may originate from two probable sources. The first may be desorption of residual oxygen from the reactor walls during the thin film growth; the second one may arise from the reactions of the dangling bonds in the deposit with the atmospheric oxygen and moisture after the film exposure to the ambient environments. This is a commonly observed effect in plasma polymers that contain a high concentration of free radicals [12].

Spectra of the films after treatment with dielectric barrier discharge (*b*, *c*, *d*) weakly differ from spectrum *a*. The same vibrational modes corresponding to the same wavenumber are present in all thin polymer films treated by DBD. Thus, the untreated polymer and those films treated by DBD exhibit similar molecular structure, but they are not equal. The thicknesses of the films were slightly decreased by DBD exposure times. Although the treatment was realized at atmospheric pressure, the intensity of the hydroxyl group near 3480 cm^{-1} decreased in treated polymers. This result can be attributed to collisional energetic ions created by DBD, which interact with the surface of plasma polymers, specially breaking the hydroxyl group and the carbonyl one in 1720 cm^{-1}. It is important to note that the band intensities at 2930 cm^{-1} and 1720 cm^{-1} were also changed in comparison of the treated and untreated samples, which shows modifications in the molecular structure performed by DBD.

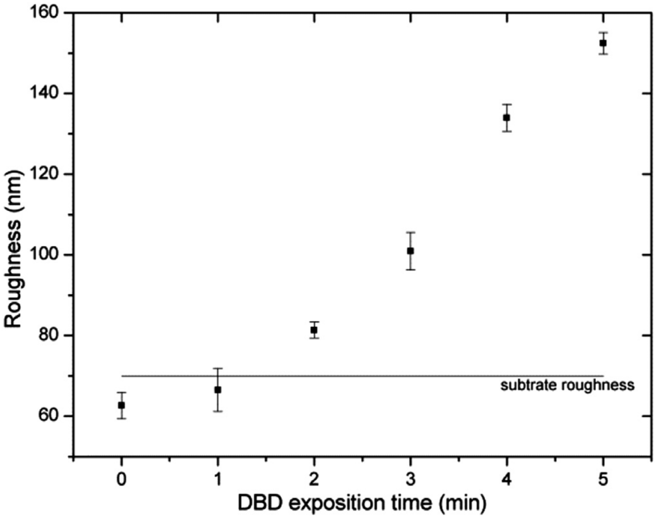

Fig. 2. Roughness of pp-acetylene films as a function of DBD exposure time.

In Fig. 2, the average roughness of untreated pp-acetylene (i.e. 0 min) and pp-acetylene films treated by DBD are shown as a function of the DBD exposure time. It was observed by atomic force microscopy that the treated or untreated films re-cover the substrate completely, e.g. as can be seen in the images of Fig. 3(a) and (b) which show samples treated for 1 and 5 min respectively. Smooth surfaces were not observed at different DBD exposition times. However, the films were not perforated. The thickness of the samples before treatment was 230 nm and 165 nm when exposed to DBD for 5 min. Thus, the DBD has probably promoted ablation in the plasma polymer films by erosion and an etching effect, increasing their roughness. Fig. 4 shows the contact-angle as a function of aging time for different DBD exposure times. As can be seen, the as-deposited pp-acetylene films are hydrophilic since their contact-angles are lower than 90°. The first measurements of contact-angle for the treated samples present low values, and these increased for subsequent measurements. After a few days, the contact-angle remains constant. This type of behavior is approximately the same for thin pp-acetylene films treated between 1 and 5 min of DBD. However, the samples wettability increased to longer times of exposure by DBD. Some considerations must be taken into account to explain this behavior: parameterizing the absorption

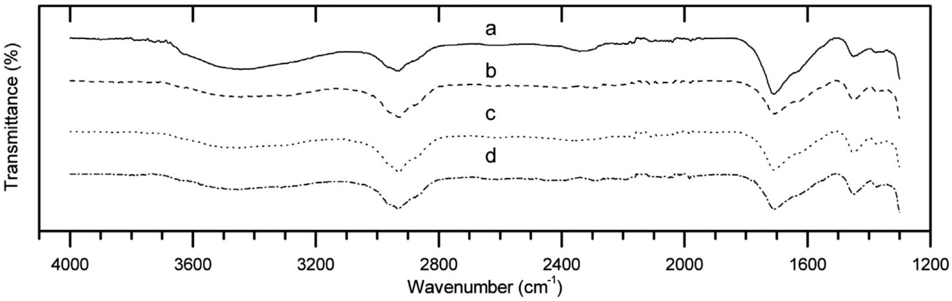

Fig. 1. Infrared spectra of pp-acetylene films deposited at 15 W of radio-frequency power and pressure of 4 Pa. *a* corresponds to untreated pp-acetylene; *b*, *c* and *d* respectively to 1, 3 and 5 min of DBD treatment.