



Growth rate, morphology, chemical composition and oligomerization state of plasma polymer films made from acrylic and methacrylic acid under dielectric barrier discharge

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ABSTRACT

Plasma polymerization is a powerful coating technology for many technological areas, notably in the coating of biomaterials, particularly when it is applied under atmospheric pressure conditions which allow to avoid expensive pumping systems. In the present investigation, the properties of coatings based on acrylic acid and on methacrylic acid prepared using atmospheric pressure plasma in dielectric barrier discharge conditions and at atmospheric pressure under various operating parameters were compared. The obtained films were characterized using different analytical and spectroscopic techniques with the aim to understand the influence of small changes in the monomer structure as well as in the operational plasma parameters on the film structure. Differences in chemical structure, deposition rate and functional group preservation were determined using FTIR, X-ray photoelectron spectroscopy combined with chemical labeling, and mass spectrometry (MALDI-TOF). As a main result, we show the possibility to quickly design architectures with tunable carboxylic functions by modifying the structure of the used monomer as well as the plasma processing parameters. Our investigation is one of the first in which the molar mass distribution of the plasma polymers, made either from acrylic acid or methacrylic acid, is directly measured from the solid state film without selective solvent extraction.

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1. Introduction

For various industrial applications, there is an urgent need to obtain cost effective coatings having the desired functional groups. The deposition methods which allow to obtain such coatings should be fast and performed in environmental friendly conditions. Among such methods, dielectric barrier discharge (DBD) at atmospheric pressure [1] makes it possible to modify the physical properties and the chemical composition of various substrates [2]. It is possible to control the chemical nature of the resulting plasma polymer by using appropriate plasma parameters (e.g., monomer flow rates, applied power) to provide homogeneous and pinhole free films with good surface coverage and preservation of the functional groups present in the used monomers [3]. In this way different articles show the possibility of using plasma deposition to obtain coatings with different chemically reactive moieties such as primary amine ($-\text{NH}_2$) and carboxyl ($-\text{COOH}$) groups which are widely used for applications in sensor technology and in life science [4–8]. It has been established that through the control of

the plasma parameters it is possible to produce plasma polymers coatings from acrylic acid with a high fraction of carboxylic functionality retained from the monomer [4]. Nevertheless, the properties of the films produced via atmospheric plasma polymerization do not only depend on their composition but also on their morphology and degree of oligomerization. The morphology and surface roughness are important for functional properties like the adhesion of the film with cells or colloids and the oligomerization state of the deposited polymers plays a huge role in the long term stability of the coating. Very few investigation address the full characterization of films produced under atmospheric pressure dielectric barrier discharge (APDBD) and it is mandatory to address this question for improving the applications of those coatings.

The APDBD method constitutes a promising method of preparation [9], compared to low pressure processes. Indeed, it can afford an in-line deposition process because it is compatible with a roll-to-roll process [10]. Moreover, it has been observed that in most case, APDBD allows for a low degree of monomer fragmentation thanks to a pressure sufficient for limiting the kinetic energy of charged species producing then less excited species [11].

Moreover, thanks to this advanced technique which is completely different from the conventional polymerization methods,

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we can tune the chemical surface composition without affecting its bulk properties. The aim of this study is to investigate plasma coatings made from acrylic acid (AA) and methacrylic acid (MAA) in order to determine how the addition of a methyl group on the acrylic acid to yield methacrylic acid from acrylic acid will affect the deposition rate as well as the film morphology and its chemical composition. Such an investigation is mandatory to get a better understanding of structure deposition mechanism and coating properties relationships. Indeed, only very few reports were devoted to a careful and multi-technique characterization of coatings produced from acrylic acid or its derivatives under atmospheric pressure conditions [12].

In addition, this paper will focus on a physical and chemical characterization of the films obtained under three different operational conditions in the plasma phase. The films were deposited by working at three different values of the Yasuda parameter [13,14]. The value of this parameter corresponds to the ratio between the energy applied between the two dielectric plates of the reactor and the precursor's mass flow.

The full characterization of the coatings was performed using a combination of surface and volume sensitive techniques such as Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), Fourier Transform Infrared Spectroscopy (FT-IR), X-ray photoelectron spectroscopy combined with chemical labeling and Matrix-Assisted Laser Desorption/Ionization Time of Flight (MALDI-TOF). This last method will allow to determine the oligomerization state of the obtained polymers which is only rarely investigated. In addition, in a previous attempt by our team, only the mass distribution of the soluble fraction of plasma polymerized hexadimethylsiloxane could be determined [15]. The aim of this work is to investigate the mass distribution from the polymers present in the solid state. A real picture of the mass distribution of the polymer species without possible bias due to selective extraction of oligomers by the solvent will hence be obtained.

2. Materials and methods

2.1. Chemicals and plasma polymerization

Methacrylic acid (MAA) and acrylic acid (AA) were purchased from sigma Aldrich and used without any further purification. Silicon wafers and glass were purchased from Siltronix (Archamps, France) and Carl Roth, respectively. In this investigation, the deposits produced from MAA and AA monomers will be called ppMAA and ppAA respectively where pp means "plasma polymer". Silicon substrates were cleaned in a freshly prepared piranha solution (3:1 v/v in concentrated sulfuric acid and 30% hydrogen peroxide solution) during 15 min, rinsed in H₂O and ethanol prior to the deposition process (extreme care should be taken during the manipulation of piranha solution which may turn to be explosive in the presence of organic compounds). KBr pellets were prepared before the deposition experiments for the film characterization by means of infrared spectroscopy in the transmission mode.

The poly (acrylic acid) (MW 450,000) was supplied from sigma Aldrich and the poly (methacrylic acid) (MW 100,000) by Poly-science. The polymers were dissolved in methanol (20 µl per sample of 5% solution) and spun cast at 4000 rpm for 60 s onto 2 cm² silicon wafer substrates.

The different films were deposited using a semi dynamic atmospheric pressure dielectric barrier discharge (DBD) open air plasma reactor from VITO. This reactor has already been described in a previous paper [16]. During plasma polymerization, a gas mixture consisting of the carrier gas, helium, and small precursor particles (~100 nm) is allowed to flow between two aluminum plate electrodes in which a 3.25 mm thick glass plate prevents from direct

arcing. The precursor is nebulized via a glass bubbler carried by a secondary flow of helium adjustable in the range of (1–2 bars) at room temperature. Then the mixture is introduced in the plasma area by the main flow of helium at 10 slm (standard liters per minute). The flow of carried gas is controlled using a mass flow controller (MKS instruments). The sample is placed between the electrodes and thus in the plasma area which is at atmospheric pressure and ambient temperature in an open air reactor.

To avoid a variation in film thickness which can occur during the process, the upper electrode is able to move at a constant speed (4 m min⁻¹) above lower electrode. The power and atomization pressure are controlled to check the influence of the operating parameters on the final coating. These two latter parameters are linked to the Yasuda parameter ($Y = W/FM$). In the definition of this parameter, W is the electrical power absorbed by the plasma, F the flow of monomer, and M its molar mass. The average value of the monomer mass flow can be directly obtained by weighing the tube containing the monomer before and after plasma polymerization taking time for a duration of Δt . The electrical power is directly obtained from the voltage difference and the current circulating. The value of the Yasuda parameter describes the ratio between the energy applied and the precursor's mass flow and constitutes an important parameter allowing to produce reactive species able to undergo polymerization. The plasma polymers have been deposited under 3 different conditions corresponding to 3 different values of the Yasuda parameter: $Y_{low} < Y_{intermediate} < Y_{high}$. The corresponding Y values are given in Table 1. Note that in the configuration of an atmospheric plasma chamber, the value of the Yasuda parameter can only be approximate because there exist a probability that non ionized molecules may diffuse out of the plasma zone to the open air without being ionized, meaning that the same plasma power is distributed over a smaller number of monomers. This would mean that the given value of Y is an overestimation of the accurate value. The probability of molecules to escape from the plasma zone without undergoing energetic collisions is however small when the flow of monomer droplets is close to the power supply, which is the case in the configuration of the plasma reactor used in this investigation [16].

The thickness of the plasma coatings was investigated as a function of the number of passes of the upper electrode above the substrate to be coated. One pass correspond to a polymerization time of about 6 s.

2.2. Characterization of the plasma polymer films

The chemical structure of the coating was investigated by an FTIR Bruker Optics Tensor 27 spectrophotometer which allows for the characterization of the functional groups which have been generated during the plasma polymerization. Plasma polymer films were directly deposited on KBr pellets and their infrared spectra were recorded in the transmission mode by accumulating 50 scans with a resolution of 4 cm⁻¹ between 4000 and 400 cm⁻¹. The spectral region corresponding to the carbonyl groups (1600–1800 cm⁻¹) was decomposed in order to determine the fraction of carboxylic acid and ester moieties using the Casa XPS software. To determine the number of spectral components, the secondary derivative of the spectrum was calculated. Each

Table 1

Values of the Yasuda parameters applied in this investigation. Note that for a given pressure and plasma power, the values of Y are not the same for MAA and AA.

Samples	Yasuda (kJ/g) MAA	Yasuda (kJ/g) AA
Y_{low}	16.8 ± 2	11 ± 2
$Y_{intermediate}$	40.8 ± 2	22 ± 2
Y_{high}	73.3 ± 8	42 ± 3

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