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Fourier-transform infrared spectroscopy of ethyl lactate decomposition and thin film coating in a filamentary and a glow dielectric barrier discharge

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ABSTRACT

Glow and filamentary regimes of Atmospheric Pressure Plasma Enhanced Chemical Vapor Deposition (AP-PECVD) in a planar Dielectric Barrier Discharge (DBD) configuration were compared for thin film deposition from ethyl lactate (EL) as a

precursor. Space-resolved Fourier Transform Infrared Spectroscopy (FTIR) was used to study both the EL decomposition in the plasma phase and the composition of the thin film. EL chemical bonds concentration along the gas flow decreases progressively in the GDBD while it drastically oscillates in the FDBD, with values higher than that of the initial mixture. EL decomposition route depends on the discharge regime as the decrease of the concentration of the different investigated bonds are not the same for an identical amount of energy provided to the EL molecules. CO₂ is systematically formed in the plasma reaching a maximum concentration of 25 ppm in the FDBD and 40 ppm in the GDBD mode.

1. Introduction

Thin film deposition by Plasma Enhanced Chemical Vapor Deposition (PECVD) on silicon wafers has first been investigated in the 60s. Later, the PECVD technology was extended to atmospheric plasma (AP PECVD)¹⁻⁶. The main advantage of atmospheric pressure plasma is the ability to lower the costs for treating materials by avoiding pumping systems and enabling large surface treatments by a continuous process. Thanks to its simple scalability from small laboratory reactors to large industrial installations and the homogeneity of deposited layer, DBD⁷⁻⁹ is a good candidate for making a polymer thin film¹⁰⁻¹³. For this reason, non-equilibrium atmospheric pressure plasma in a Dielectric Barrier Discharge (DBD) configuration is an interesting option for treatment and coating of surfaces.

As reported by Massines et al.¹⁴, five different discharge regimes are possible while working with dielectric barrier discharges at atmospheric pressure. These regimes are filamentary DBD (FDBD), glow like DBD (GLDBD), glow DBD (GDBD), Townsend DBD (TDBD) and radiofrequency DBD. This work will focus on two of them, selected for their differences in electron energy levels and electron density. On one hand, FDBD is characterized by a multitude of microdischarges with a high electron density (10^{13} to 10^{14} cm⁻³) for very short duration (100ns). On the other hand, GDBD is characterized by a homogenous discharge with a lower electron density (10^{10} to 10^{11} cm⁻³) but a longer duration (μ s)¹⁴. Previous works have shown that in identical atmospheres, FDBD and GDBD could lead to different surface treatments.^{15, 16} Accordingly, the aim of this work is

to better understand the differences of the chemistry occurring in the two aforementioned DBD modes. These two discharge regimes are easily obtained in Ar-NH₃ Penning gas mixture. GDBD is observed for higher frequencies. The higher repetition rate maintained a higher energy in the gas gap and induces a higher power¹⁴.

Ethyl lactate (EL) was chosen as vaporized liquid precursor. This choice was motivated by two reasons. First, EL displays a wide variety of chemical bonds with various dissociation energies. These different bonds are easily detected by infrared absorption spectroscopy, allowing an in-situ observation of the molecule transformation. Second, the plasma polymerization process of EL is likely to produce a “polylactic acid like” polymer. Polylactic acid presents a great interest related to its biodegradability by water or microorganism^{17, 18} and its non-toxicity. It could be used for controlled drug release for biomedical application¹⁹⁻²¹. For this reason, scientists started to pay close attention to the synthesis of “polylactic acid like” films through plasma-based technologies. Ethyl lactate (EL) plasma polymer (EL PP)^{13, 22, 23} was shown to be biodegradable²⁴, therefore paving the way for its use as a drug delivery system.

The decomposition scheme of ethyl lactate has been studied using several characterization techniques among which mass spectrometry^{12, 25}, x-ray photoelectron spectroscopy¹⁰, and electrical characterizations⁶. In this work, Fourier Transform Infrared (FTIR) absorption spectroscopy was used. This method is convenient to characterize both the plasma and the thin film. Space resolved measurements were used to analyze the decomposition of EL in the plasma and the thin film composition as a function of the gas residence time in the

plasma²⁶. On one hand, the decomposition kinetics of EL in both FDBD and GDBD plasma regimes was ascertained through *in-situ* FTIR measurements. On the other hand, the thin film composition was also characterized by FTIR along its whole length and correlated with the EL decomposition scheme along the plasma.

2. Materials and methods

2.1. Materials

The reactor chamber was filled with nitrogen (Alphagaz 1, 99.999% purity) to avoid arcs formation around the electrodes. Then the vaporized liquid precursor was injected between the electrodes, together with the carrier gases. The organic precursor chosen for the study was (-)-Ethyl L-lactate $C_5H_{10}O_3$ (manufactured by Sigma-Aldrich, USA) with confirmed purity at 97.5%. The carrier gas was argon (Alphagaz 1, 99.999% purity) as the main gas and NH_3 (Alphagaz 1, 99.999% purity) for ensuring discharge stability. The reactor chamber was filled with nitrogen (Alphagaz 1, 99.999% purity) for ensuring discharge stability.

2.2. Methods

2.2.1. Plasma reactor

The plasma reactor is a plane-to-plane Dielectric Barrier Discharge (DBD) already described elsewhere²⁷. Briefly, it was composed of two electrodes (2 cm x 5 cm), one is connected to a high voltage (HV) and the other is connected to the ground. The electrodes were metallized on the rear face of the alumina plates of 69 mm x 69 mm and of 1 mm in thickness. Two transformers (Boige et Vignal) are used for these experiments. The first

one is operated at a frequency range from 1 to 10 kHz whereas the second one enables working between 50 kHz to 100 kHz. Both transformers made it possible to work at amplified voltages (Crest CC4000 audio amplifier) ranging between 1 and 15 kV with waveforms selected using an Agilent 33210 waveform generator. The gap between the alumina plates was kept at 2 mm. EL PP was deposited on top of a 275 μm thick round silicon wafer of 5.08 cm in diameter. The deposition area was the same than that of the electrodes, that was $2 \times 5 \text{ cm}^2$. The characteristics of the two DBDs of this work are given in **Table 1**.

Table 1. Characteristics of the chosen DBD regimes ¹⁴.

Property/Type of DBD	Filamentary FDBD	Glow GDBD
Frequency	15 kHz	50 kHz
Voltage [kV]	3	1.3
Average power [W]	1	4
Average power density [W/cm^2]	0.1	0.4
Homogeneity of the discharge	No	Yes
Maximum electron density [$1/\text{cm}^3$]	$10^{13} - 10^{14}$	10^{10}

The plasma reactor was pumped down to 2.2×10^{-2} Torr, and then filled with nitrogen (to reach a pressure of 760 Torr. Initial filling with nitrogen minimizes arc formation around the electrodes, as nitrogen has 10 times higher breakdown voltage than argon, which has been chosen as the carrier gas due to its lower breakdown voltage, lower cost compared to

helium, and its inability to incorporate itself within the molecular structure of the plasma polymer, as shown by Laurent et al.²²

An aerosol made of 1.1 slm of argon + ethyl lactate by the means of an atomizer (TSI atomizer model 3076 creating droplets in the size range between 0.3 and 3 μm) was diluted in 1.9 slm of argon + 133 ppm of NH_3 , making a total flow of Ar of 3 slm containing 350 ppm of EL and 133 ppm of NH_3 . This gas mixture was injected in the reactor through a 0.1 x 4 cm^2 slit located 4 cm away from the DBD. Two zinc selenide (ZnSe) IR transparent windows (2 x 2 x 70 mm^3) were placed parallel to the gas stream in order to maintain the laminar flow by avoiding any gas flow perturbations. The gas injection was perpendicular to the long axis (5 cm) of the electrode and the spectral acquisition was performed every 2 mm along the 2 cm-wide plasma. Therefore, the position of the measurement along the plasma can be correlated to the residence time and the mean energy sensed by the species^{28, 29}. The voltage amplitude for each regime was chosen to ensure a stable discharge and reproducibility of the results. The power being the integral of the product of the measured voltage and current over a cycle divided by the cycle duration, it is the result of the chosen plasma parameters.

2.3. In flight precursor FTIR

The FTIR setup used to record in-flight and in-situ spectra of the precursor, in both gaseous and plasma phases, is described elsewhere.²⁶ The spectrometer was an Agilent Cary 670 equipped with a KBr beam splitter and a narrowband MCT-A detector. The spectra were recorded between 4000 and 400 cm^{-1} by co-adding 256 scans at a resolution

of 4 cm^{-1} . The absorption length across the plasma was 10 cm, corresponding to a back-and-forth passage along the long axis of the electrodes.

The background spectrum was recorded in pure argon without plasma while the plasma spectra were recorded 5 minutes after injecting ethyl lactate at a concentration of 350 ppm in argon in the plasma reactor. This was done to ensure constant and reproducible amount of EL in the gas between the electrodes at the time of lighting up the discharge. The infrared beam path located outside the reactor was always purged with dry CO_2 -free air. The plasma reactor was systematically pumped down between each experiment. Of note, CO_2 absorption was never observed without plasma. After each measurement with EL, the plasma region was flushed with pure argon. Another spectrum was recorded in these conditions and subtracted from that of the EL plasma. This enabled to eliminate the spectral contribution of adsorbed ethyl lactate on the ZnSe windows.

The resulting spectra were then smoothed using Origin FFT filter with 5 points to improve the accuracy of the measured peak absorbances. Five analysis positions were considered for both plasma and thin film analysis at 0 ± 1 , 5 ± 1 , 10 ± 1 , 15 ± 1 , 19 ± 1 mm along the 2 cm wide plasma, the corresponding mean residence time of the gases in the plasma are 1.2 ± 1.2 , 6.0 ± 1.2 , 12.0 ± 1.2 , 18 ± 1.2 and 24 ± 1.2 ms respectively. Calibration curves were built to follow the concentration of each of the EL chemical bonds by measuring their infrared absorbance while injecting EL between the electrodes at concentrations ranging 0 to 700 ppm without igniting the plasma. The quantification limits, defined as being ten times the standard deviation of noise fluctuation³⁰, are reported in **Table 2**. CO_2 being a decomposition product of ethyl lactate¹¹, it was calibrated by measuring the integrated

absorbance of the 2340-2360 cm^{-1} feature of infrared spectra recorded with known amounts concentration of CO_2 introduced in the plasma chamber.

2.4. Thin film FTIR

A Nicolet 6700 (THERMO Scientific) FTIR spectrometer purged with CO_2 -free dry air was used to analyze the thin films. The thin film transmission spectra were the results of the co-addition of 64 scans at a resolution of 4 cm^{-1} . The spectrum of a clean silicon wafer was first recorded and subtracted from the spectrum of the plasma polymerized EL on silicon. Measurements were made with a 2 mm spatial resolution along the direction of the gas flow (i.e. 2 cm), enabling to compare spectra recorded at the corresponding positions in the plasma and on the thin film.

3. Results and discussion

The interest of ethyl lactate for this study came from its efficient absorption in infrared useful for its characterization by FTIR, its biocompatibility and non-toxicity. It also has well defined and distinctive energies for dissociating a given bond within the molecule **Figure 1**, which also makes it an interesting candidate to determine the plasma chemical reactivity.

Figure 1. Structure of EL with energies needed to dissociate its chemical bonds³¹.

3.1. FTIR spectra

Figure 2. Typical normalized FTIR spectra of ethyl lactate in the gas with (solid black line) and without (blue dash-dotted line) plasma, and of the “polylactic acid like” polymer thin film (red dashed line) state.

Figure 2 presents normalized spectra (to the peak at 1750 cm^{-1}) of EL in-gas phase with and without plasma and of the “polylactic acid like” polymer coating. All three spectra show the usual IR absorption of EL, as listed in **Table 2**. However, differences are observed. The peaks in EL in the gas phase are easily distinguishable, compared to the

solid phase, where overlapping between absorption bands can be observed. This is due to the lesser number of interactions between molecules in the gas phase as compared to the thin film. In addition, the plasma spectrum shows significantly higher noise-to-signal ratio compared to the gas phase without plasma, due to the electromagnetic noise. The first striking observation is the almost complete disappearance of the OH stretching mode feature (P₁) in both the gas and plasma made with EL due to the absence of intramolecular interactions in these phases. In addition, the absorbance of P₁₂ (free OH stretching) decreases from the gas phase to the plasma, with a concomitant appearance of P₁ in the deposited thin film spectrum. Another observation that is worth mentioning is the creation of CO₂, manifested through the feature at 2340-2360cm⁻¹ (P₁₁), without any gaseous H₂O production, only observed in the plasma.

Table 2. Infrared assignments of the observed absorptions: ethyl lactate and carbon dioxide^{11, 32-34} and their quantification limits in the experimental conditions of this work.

	Wavenumber (cm ⁻¹)	Vibrational mode	Quantification limit (ppm)
P₁	3570–3200 (broad)	OH stretching (intermolecular)	150
P₂	2990	CH ₃ asymmetric stretching	90
P₃	2940	CH ₂ asymmetric stretching	186
P₄	1750	Ester group, C-(C=O)-R Ketone, R ₁ -(C=O)-R ₂ asymmetric stretching	38
P₅	1620	Carboxylate group, R-(C=O)-O	
P₆	1455	CH _x bending	
P₇	1380	Primary or secondary, OCO-H (intramolecular) in-plane OH bend	158
P₈	1266	CH(OH)CH ₃ bending	158
P₉	1222	C-OC(=O) stretch	

P₁₀	1140	C-OH asymmetric stretching	44
P₁₁	2360-2340	C=O in CO ₂	5
P₁₂	3575	Free OH	

3.2. *In-situ* plasma FTIR analysis

3.2.1. *Glow DBD*

Figure 3 presents the plasma IR absorptions at 5 different positions in a GDBD along the gas flow e.g. for 5 different gas residence times in the plasma. Peak identification reported in the graphs corresponds to those of **Table 2**. The overall tendency is that the EL absorption bands decrease when this precursor residence time in the gas increases, showing a continuous fragmentation of the molecule along the plasma. At the same time, the concentration of CO₂ (P₁₁) increases along the plasma. As no H₂O absorption is observed, the CO₂ formation cannot be explained by combustion reactions, meaning that the discharge does not entirely decompose the molecule (as in combustion process for instance) but mostly fragments EL.

Figure 3. EL bands by position in GDBD regime from the plasma phase spectra. Higher is the position, the longer is the EL residence time in the plasma.

From **Figure 3**, it can be seen that the so-called decrease of the P₁₂ absorbance begins between positions 5 and 10 mm in the plasma, therefore showing that dissociation of this chemical group from the overall EL molecule starts somewhere from these positions.

It is also interesting to observe the behavior of the CH₂ and CH₃ groups of the EL molecule in the plasma, which can be followed through either their stretching (P₂ and P₃) or bending (P₆) modes. As may be seen in **Figure 3**, CH_x stretching mode features (P₂ and P₃) remain present for all plasma positions, whereas CH₂ and CH₃ bending (P₆) is much less intense. This is a clear indication that some of the CH₂ and CH₃ groups of EL lose some of their

hydrogen atoms to form CH containing moieties, which still can give rise to C-H stretching mode spectral contributions but, of course, cannot provide bending vibrations, as at least two hydrogen atoms need to be bound to a single carbon for such as spectral contributions to be observed. Finally, the absorbance of the C=O (P₄), C-OC (P₉), and C-OH (P₁₀) stretching mode features also tends to decrease along the plasma, while their wavenumbers remain in the range typical of esters (P₉) and/or aldehyde (P₁₀) showing that these bonds are still present in the plasma phase.

3.2.2. Comparison of glow and filamentary DBD

Figure 4 shows the comparison of the concentration evolution with the energy provided per EL molecule injected in the plasma of some selected chemical groups for both GDBD and FDBD as a function of the energy provided per EL molecule injected in the plasma. Energy is the product of the gas residence time and the DBD power. This energy could potentially be transferred to the EL molecule and to the plasma-dissociated EL molecule fragments. As the GDBD power is four time larger than that of the FDBD (**Table 1**) with identical EL concentration, the energy per EL molecule is also four times larger in the GDBD. The conversion from absorbance to concentration was made based on the aforementioned calibration curves (see Materials and Methods). The selected chemical groups are related to C-O, C-H, and O-H bonds of EL and CO₂ molecules. The error bars are obtained by calculating the error propagation from intensity to concentration, from the standard deviation of the intensity measurements and the uncertainty of the calibration curves.

Generally speaking, the various chemical species concentration evolution with the energy provided per EL molecule follows a similar trend for both GDBD and FDBD. However, GDBD leads to a more gradual decomposition of EL whereas FDBD shows rather large oscillations. These concentration oscillations in FDBD are likely due to variation in the plasma homogeneity. Indeed, FTIR measurements last about a minute while the repetition rate of the FDBD is 15 kHz (0.067 ms). Accordingly, FTIR measurements should lead to concentration values that would be averaged in time. In addition, the IR absorption path length is much longer (10 cm) than the microdischarge radius (typically 200 μ m)¹⁴ with a mean distance between two microdischarges in the range of mm. These two observations point toward the fact that the various chemical group observed concentration oscillations are real. Interestingly, the CH₃ and CH₂ (P₂ and P₃) concentrations sometimes reach higher values than what would have been expected from the single injection of EL, indicating that another source is responsible for these moieties production. Because a very high concentration of energetic species is reached locally and for a short time in a FDBD as compared to GDBD, in which energetic species concentrations are lower and more uniformly distributed, it is theorized that surface etching occurs in FDBD, therefore leading to this increase of hydrocarbon moieties in the plasma discharge.

Figure 4. Evolution of concentration of different IR absorption bands in both GDBD (red) and FDBD (black) as a function of energy per EL molecule in the plasma phase. The values at 0 eV were taken from vaporized EL without plasma.

For FDBD the C=O (P₄) chemical bond behavior shows that the concentration in the plasma oscillates in the first two positions and then stabilizes at around 225 ppm at 10 eV/molecule and does not change significantly as more energy per molecule is provided. In this plasma regime, both C-OH (P₁₀) and C-OC (P₉) follow this similar oscillating trend between positions, but in general shows a decrease from the beginning to the end of the plasma zone and reaches a minimum of around 125 ppm. When 3 eV/molecule are provided, both CH₃ (P₂) and CH₂ (P₃) show a greater concentration than due to the initially injected EL, probably due to the fact that the FDBD could induce etching of the surface and reintroduction of fragments into the plasma region. With the increasing of the energy provided to each EL molecule, the concentrations of these hydrocarbon moieties decrease to reach 450 and 250 ppm, respectively. On the other hand, the concentration of free OH (P₁₂) in the FDBD decreases by position to reach 200 ppm for 15 eV/molecule. Interestingly, the amount of OCO-H_{intra} (P₇) decreases significantly as EL enters the plasma and then reaches a plateau of around 100 ppm at 6 eV/molecule which does not change with more energy being provided to each molecule.

As mentioned previously, the concentration changes in GDBD are distinctive of those in FDBD.

In GDBD C=O (P₄), C-OH (P₁₀) and CH₃ (P₂) show a similar behavior with the increasing energy, where a slight decrease is observed until 40 eV/molecule is reached and then plateaus at 200, 150 and 300 ppm, respectively. The concentration of C-OC (P₉) bonds decreases steadily with the increasing energy and reaches a concentration very close to 0 ppm, coherent with the fact that this is the bond with the lower dissociation energy in the EL molecule. A decrease is observed at 4 eV/molecule for CH₂ (P₃) concentration, which plateaus at 175 ppm between 2.5 and 40 eV/molecule, and then decreases to 100 ppm at 52 eV/molecule. The free OH group concentration (P₁₂) shows a rather continuous decrease up to 40 eV/molecule where it reaches a concentration close to 0 ppm. A slight increase is observed at the very exit of the plasma discharge area, suggesting creation of free OH likely due to the important fragmentation of the whole molecule at these energy levels. Similarly to what was observed with FDBD, the concentration of OCO-H_{intra} (P₇) in the GDBD decreases from 350 to 210 ppm at 4 eV/molecule, then plateaus up to 40 eV/molecule to finally slightly increase to reach final concentration of 300 ppm.

3.2.3. Carbon dioxide creation from ethyl lactate dissociation in the plasma phase

One of the important byproducts of plasma dissociation of EL is CO₂, which necessarily comes from the dissociation of either CO-C, CO-H or C=O moieties. Thus, the concentration of CO₂ was plotted as a function of the consumption of these oxygen-containing functionalities. Among the plotted curves, only the consumption behaviors of C-OC (P₉) in GDBD regime and C=O (P₄) in FDBD discharges were shown to follow

trends that could be reasonably defined by mathematical equations. The results are presented in **Figure 5.**

Figure 5. CO₂ concentration as a function of the decomposition of A: C-OC (P₉) for GDBD and B: C=O (P₄) bands for FDBD.

As it is seen in **Figure 5**, the formation of CO₂ as a function of the C=O group decomposition in the filamentary discharge follows a simple linear regression, typical of a first order reaction and reaches a maximum of 25 ppm. This suggests a reaction $CO + \frac{1}{2}O_2 \leftrightarrow CO_2$. Conversely, the creation of CO₂ in GDBD regime rather follows a quadratic relationship, characteristic of a second order reaction, and reaches a maximum of 40 ppm. The reaction that could be occurring in this case would be that of two CO-C fragments.

Interestingly, some data points show production of CO₂ concomitant with the increase (seen as a “negative” consumption on the curve) of C-OC, which suggests that the CO₂

may arise from the etching of the already deposited plasma coating. In FDBD, the CO₂ concentration never exceeds 25 ppm. Even though the origin of these differences between GDBD and FDBD regimes has not been elucidated yet, it clearly highlights different EL decomposition kinetics and reaction efficiencies. In GDBD, the production of CO₂ is clearly related to the consumption of C-OC (P₉) chemical bonds, whereas in FDBD a linear dependency between C=O dissociation and CO₂ creation was observed.

3.2. Thin film spectra

3.2.1. Comparison between plasma and solid phase spectra

Figure 6. Comparison of EL band evolution in both plasma phase (black) and plasma polymer (red) at 10 mm for GDBD regime.

Figure 6 compares the plasma and thin film FTIR spectra at the same position in the plasma discharge. At first sight, it has to be emphasized that all of the features observed in the infrared spectrum of the plasma phase are seen in that of the solid film, which means that all of the chemical functionalities of the ethyl lactate molecule are, at least, partly transferred in the chemical structure of the plasma polymerized film. For those infrared bands occurring in both the plasma and the solid phases, the general trend is that infrared peaks of the film are shifted to lower wavenumbers, in agreement with a higher level of order with respect to the plasma phase ^{32, 35}. In addition, the infrared features of the thin film spectrum are also broader, in agreement with the fact that more molecular interactions occur in the solid as opposed to the plasma phase³².

Some spectral regions are of particular interest while comparing the chemical composition of both plasma and solid phases. First, the OH stretching mode vibration (P_{12}) does not appear in the spectrum of the plasma, but a rather narrow band with a low absorbance appears at 3575cm^{-1} and is assigned to free OH stretching vibrations (P_{11}), as few molecular interactions are likely to occur in the plasma phase. However, in the plasma polymer spectrum, the presence of the OH groups is rather observed through a much wider feature centered around 3400 cm^{-1} (P_1), which reflects the fact that these chemical moieties are involved in several interactions such as hydrogen bonds.

Major differences are also observed while comparing the C=O (P_4) stretching mode vibration region of both the plasma and solid phases. As seen in **Figure 6**, the infrared

spectrum of the plasma phase exhibits an absorption at 1750 cm^{-1} , assigned to the ester function of ethyl lactate. In the spectrum of the polymer film, this band is shifted to 1725 cm^{-1} . In addition to the aforementioned ordering effect observed when EL is converted from the plasma to the solid phase, the specific wavenumber value of this infrared component may also be due to the fact that the ester group of the EL molecule is converted into a ketone. This presence of a ketone in the thin film could mean that the preferential group to be dissociated is the C-OC (P_9) group, which is the lowest energy bound of EL.

Of note, another C=O (P_5) stretching mode feature appears near 1600 cm^{-1} in the infrared spectrum of the plasma polymer film, which is generally assigned to the presence of carboxylate groups. All in all, this means that the EL ester groups are, at least partly, converted into ketones and carboxylic acid functionalities. The OH components of these latter chemical groups are also likely to contribute to the so-called C-OH stretching mode (P_{10}) feature observed in the infrared spectrum of the plasma deposited film.

Finally, comparison between the C-OC (P_9) and C-OH (P_{10}) stretching mode features (P_9 and P_{10}) for both the plasma and solid phases clearly put in evidence the aforesaid ordering effect along with the increase of the number/intensity of the molecular interactions, as seen through these peaks broadening and shift to lower wavenumbers.

3.2.2. Thin film polymerization level

In order to try to probe the level of EL polymerization along the plasma, the infrared CH_2/CH_3 ratio (P_3/P_2) was measured for each investigated position across the plasma

deposited film. The idea of using this ratio to monitor the EL polymerization level is based on the fact that methyl groups (CH_3 , P_2) are likely to be mostly found at the end of polymeric chains. Accordingly, it is expected that long EL polymeric chains would be characterized by a high CH_2/CH_3 infrared ratio with, of course, no polymerization occurring when this spectroscopic parameter is equal to that of pure EL^{36, 37}.

Figure 7. CH_2/CH_3 infrared ratio measured from the spectra of plasma polymerized films at positions corresponding to each investigated location in the plasma for FDBD (black) and GDBD (red). The horizontal line indicates the CH_2/CH_3 ratio for pure gaseous EL (no polymerization).

According to the defined criteria, Figure 7 shows that the plasma polymerized film deposited under the FDBD regime is more polymerized than the GDBD for all investigated

positions and GDBD shows a greater uniformity in the polymerization throughout all the positions of the coating.

3.2. *Thin film coating and the DBD chemistry*

In order to try to follow the incorporation of the various EL chemical groups within the plasma deposited films, the absorbance of some of the infrared features of these coatings were ratioed to the absorbance of the C=O stretching mode peak (P₄). The absorbance of this latter feature was fairly constant throughout the length of the plasma deposited film (results not shown). These ratios were, in turn, divided by their corresponding counterparts measured from the infrared spectrum of liquid EL. In other words, these calculations (A_N) enable comparing the thin film and liquid EL composition, in terms of their respective relative amount of a given chemical group and the carbonyl functionality, and are described by the following mathematical equation:

$$A_N = \frac{A_{B\ TF} / A_{C=O\ TF}}{A_{B\ L} / A_{C=O\ L}}$$

where $A_{B\ TF}$ is the absorbance of the infrared features of interest in the plasma deposited thin films, $A_{C=O\ TF}$ is the absorbance of the C=O stretching mode band in the thin film, $A_{B\ L}$ is the absorbance of the so-called peaks of interest in liquid EL, and $A_{C=O\ L}$ is the absorption of C=O in the liquid EL. Accordingly, a A_N value lower than 1 means that the relative amount of a given chemical group, as compared with the carbonyl functionalities,

is lower in the film than in the EL molecule, whereas a A_N value higher than one signifies that the plasma polymerized film contains relatively more of the chemical functionality of interest with respect to what is observed in the EL molecule.

Figure 8. Normalized thin film absorbance of different bonds as a function of the FDBD and GDBD plasmas concentration by the same bond.

Figure 8 shows the results of these calculations made by correlating the information originating from infrared spectra recorded at identical positions in the plasma phase and deposited thin films for both FDBD and GDBD regimes.

Very interesting observations can be drawn from this figure. From a general standpoint, and regardless of the plasma regime, the amount of a given chemical species in the plasma polymerized film does not depend on this chemical functionality concentration within the plasma, as all relationships between A_N and the in-plasma species concentrations can be fairly well described by a horizontal line. For example, A_N measured from the C-OC spectral contribution (P_9) only slightly varies around a value of 0.5 with, however, a rather large variation of the concentration of this chemical functionality in the plasma, that spans from approximately 100 to 350 ppm. Of note, the in-plasma concentration of the OCO- H_{intra} group (P_7) is almost identical (approx. 100 ppm) for both plasma regimes and positions. Second, and also regardless of the plasma regime, the relative amount of oxygen-containing species is clearly lower in the plasma polymerized film than in the EL precursor molecule. This is in agreement with the data presented in Figure 5 which show that some of the EL oxygen-containing species are converted in CO_2 , therefore not being available anymore to be incorporated in the plasma polymer film. Third, the hydrocarbon moieties are the only ones that are observed in greater relative amount in the plasma coating as compared to the EL molecule. For these latter moieties, the plasma regime clearly has an influence as relatively more CH_2 and CH_3 groups are incorporated in the plasma coating with respect to the EL molecule in the FDBD regime while an opposite behavior is observed in the GDBD mode. In the FDBD regime, the A_N values calculated for CH_2 groups are all higher than the corresponding data for CH_3 functionalities, in agreement with the results presented in Figure 7, which shows more precursor polymerization in the

filamentary mode. It is also interesting to highlight the fact that the preservation of a given chemical functionality from the precursor to the plasma coating is not necessarily related to the bonding energy. For instance, the C-OC (2.9 eV) chemical groups are more “preserved” in the plasma polymer structure than the CO-H (3.9 eV) functionalities. This emphasizes the fact that the inherent reactivity of chemical groups should also be taken into account to explain the decomposition mechanisms of organic precursors within plasma.

4. Conclusions

This research has compared ethyl lactate decomposition in the plasma and thin film deposition using atmospheric pressure Ar DBD in both filamentary and glow regimes. The power of the GDBD is 4 times that of the FBDB. Measurements were made as a function of the position along the gas flow e.g., EL residence time in the plasma, which is directly correlated to the energy provided per EL molecule.

The analysis consisted of a thorough space resolved study and comparison of the FTIR spectra in the plasma phase and of the thin films. Given the plethora of absorption bands present in the ethyl lactate infrared spectrum, the most characteristic features with known assignments have been selected for analysis of the two phases.

In the FBDB regime, the analyses suggest that etching could be occurring from the already deposited layer, which results in oscillations of the concentration of the chosen absorption bands in the IR spectra of the plasma phase. Moreover, in certain cases the amount of the observed fragment is greater in the plasma phase than that of the injected precursor, reaffirming the etching hypothesis. For the GDBD regime, the decomposition of EL is much more gradual throughout the plasma width and generally results in a greater decomposition than that of FBDB when the same time of residence is taken into account.

As a result of bond dissociation, CO₂ creation is observed in both regimes. In GDBD, there is an quadratic relationship between the production of CO₂ and the consumption of C-OC groups. In FBDB, CO₂ formation requires less energy than in GDBD, perhaps related to the high electron density of the microdischarges, resulting in CO₂ saturation early

in the plasma zone. On the other hand, the FDBD regime shows a linear correlation between decomposition of C=O and CO₂ creation. The larger GDBD power allows to reach 40 ppm of CO₂ compared to 25 ppm in FDBD.

Moreover, the CH₂/CH₃ peak height intensity ratio measured from the infrared spectra of plasma deposited films demonstrates that the polymerization level is higher when using the FDBD regime as opposed to the GDBD mode, but the polymerization in the coating created with GDBD is more homogenous throughout the coating.

The analysis of the deposited layer as a function of the decomposition of the molecule in the plasma phase showed that there is a dependency of the bond dissociation energy and the preservation of a fragment in the plasma polymer, as the bonds with highest energies are deposited in a greater amount in the coating, and the opposite is seen for the low energy bonds. Another noteworthy observation was that not only the bond dissociation energy, but also the fragments reactivity plays a role in the decomposition mechanisms and the amounts of that fragment being deposited on the substrate, as seen for C-OH, which despite the higher dissociation energy than C-OC is less preserved on the coating.

5. Conflict of interest

The authors claim no conflict of interest.

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