Atmospheric Pressure Plasma Enhanced Chemical Vapor Deposition of nanocomposite thin films from ethyl lactate and silica nanoparticles

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Abstract

Nanocomposite coatings are made by Atmospheric Pressure PECVD from ethyl lactate (EL) and silica nanoparticles (NPs) in a Dielectric Barrier Discharge (DBD) using Frequency Shift Keying (FSK) to alternate between 1 and 15 kHz voltages. In-situ plasma FTIR and thin film FTIR, SEM, AFM and profilometry show that (i) 1 kHz DBD mainly deposits NPs, 15 kHz only polymerizes EL (ii) the EL polymerization rate is the same in FSK and continuous modes (iii) despite the 50/50 contribution of both frequencies, the NPs deposit is 3 times faster in FSK mode than in 1 kHz DBD and compared to 1 and 15 kHz coatings, in the nanocomposite, NPs Si-O-Si and EL C=O bonds per unit length are equal to 68 and 34% respectively. In-situ FTIR

detects SiO₂ NPs, their functionalization, and the formation of CO₂.

KEYWORDS

gas phase FTIR, plasma phase FTIR, mid-infrared, Frequency Shift Keying, double modulation, dielectric barrier discharge, nanoparticles, Atmospheric Pressure Plasma Enhanced Chemical Vapor Deposition.

1. Introduction

The idea of incorporating nanoparticles (NPs) in other materials has grown exponentially in the past 20 years[1-5]. This is due to their versatile properties and tunable size and shape, which enhance the macroscopic properties of nanocomposites (NC).

NC of small thickness (not greater than 1 mm) are gaining more and more interest in various scientific disciplines, due to their ability to provide materials with tailored properties. They find applications in various domains like photovoltaics, photocatalysis, solar cells[6], depollution[7], modification of the surface of wood[8] or surface modification for biomedical applications[9, 10]. Controlled biodegradability of polymer NC (PMNC) is a key point that can be reached with polymers like polylactic acid or ethyl lactate.

Nanocomposites have been already synthesized using several methods such as sol-gel, interferometric photo-reduction[6], double emulsion solvent evaporation[11, 12], spin coating[13], and dip coating[14] to name a few. An innovative approach based on Atmospheric Pressure Plasma Enhanced Chemical Vapor Deposition (AP PECVD)[15], to create materials with desired properties and controlled ratio of nanoparticles within the plasma deposited film, has recently been considered[3, 8, 16-20]. Essentially, it is a two-step process. The first step is the preparation of a suspension of NPs in a solvent. In the second step, a spray of the dispersion is injected in between the electrodes. In the plasma, the solvent is polymerized to form a thin film and the NPs are included in this thin film to produce the NC. One of the key points is to control the proportion of NPs to the polymer matrix. In a dielectric barrier discharge in a plane-to-plane configuration, useful for in-line treatment, this is achieved through the reactivity of the solvent[9, 21, 22] or through the power and the frequency of the plasma[3]. The Dielectric Barrier Discharge (DBD) power defines the solvent polymerization and thus the growth rate of the matrix, while lower frequencies induce the transport of the NPs onto the substrate. NC were previously synthesized in a DBD using TiO₂ NPs in isopropanol[3]. It was shown that

frequencies higher than 10 kHz are required to polymerize isopropanol while frequencies in the range of 1 kHz or lower are needed for efficient transportation of NPs of diameter close to 100 nm. In addition, the smaller the size of NPs, the higher the frequencies that could be used for their deposition. Given the aforementioned considerations, using a homogenous mixture of isopropyl alcohol and TiO₂ NPs, Brunet et al.[3] made the proof of concept that it was possible to control the composition of plasma deposited nanocomposite by alternating two frequencies through Frequency Shift Keying (FSK)[19, 23] double modulation as presented in Figure 1. These two frequencies are alternated at a given time scale (FSK rate) and duty cycle (DC) defined as $T_{HF} / (T_{FSK})$ (Figure 1). Accordingly, the low frequency regime (typically in the range of 1 kHz) is used for transporting NPs to the surface, while the plasma high frequency (10-15 kHz) is used for building a polymer matrix on the surface. Homogeneous deposition of NPs and plasma polymer was shown to occur when at least two FSK cycles were conducted during the gas residence time in the plasma (T_R).

Figure 1. Example of a FSK double modulation oscillogram with frequencies of 1 and 15 kHz, a 50% duty cycle and $T_{FSK} = 5$ ms. The high frequency, 15 kHz, is applied for 2.5 ms (T_{HF}) and the low frequency, 1 kHz, is applied for 2.5 ms (T_{LF}).

This proof of concept was done with isopropanol, a solvent useful to prepare the dispersion without consideration of its potential to polymerize within the plasma environment. In the present work, ethyl lactate (EL) was chosen as a precursor capable of polymerizing within the plasma to form a nanocomposite matrix[24-28]. The idea of using a polymer precursor instead of isopropanol was to create a layer of polymer film, whereas as it was shown by Brunet et al. isopropanol deposits very poorly in the plasma environment and does not polymerize. Indeed, upon exposure to an argon plasma environment, EL molecule is likely to lead to polylactic acid (PLA)-like polymer [24-26]. PLA has been used and studied thoroughly for many applications, namely in the biomedical field. Its biocompatibility, biodegradability and non-toxic degradation products have been confirmed[29, 30]. Hence, a similar behavior was expected for EL plasma polymer (ELPP)[24, 26, 31]. Its ability to polymerize in a DBD and the possibility to control the degradation rate of the resulting plasma polymer through the appropriate selection of the plasma experimental parameters have already been reported[24]. EL can also be easily observed

in the plasma through mid-infrared spectroscopy[25], therefore enabling to follow this precursor consumption within the discharge.

On the other hand, silica nanoparticles (NPs) were selected based on previous investigations on their potential in various biomedical applications[4, 32-53]. Silica NPs are not toxic, have the capacity to encapsulate drugs and act as vehicles for drug delivery[4, 32, 33, 35-37], and can be observed in the mid-infrared.

In this context, the aim of this publication is to extrapolate the proof of concept of Brunet et al.[3], made with isopropanol and TiO₂ NPs, which implies extending the FSK process to different precursors. Nanocomposites were synthesized using ethyl lactate and SiO₂ NPs in continuous frequency plasma regimes (1 and 15 kHz) and in FSK conditions by sequentially alternating frequencies of 1 and 15 kHz. These plasma deposited nanocomposites were characterized by scanning electron microscopy (SEM) and profilometry. In addition, mid-infrared spectroscopy was used to characterize and correlate the compositions of both the plasma phases and the nanocomposites.

2. Materials and methods

2.1. Materials

Fumed silicon dioxide nanopowders (Sigma Aldrich S5505) were used for these experiments. The size of the nanoparticles ranged from 200-300 nm with surface area $(20 \pm 3) \times 10^1 \text{ m}^2/\text{g}$ and bulk density 0.037 g/cm^3 at 25 °C. (-)-Ethyl L-lactate (manufactured by Sigma-Aldrich, USA) with confirmed purity at 97.5% was chosen as a liquid precursor. The carrier gas was argon (argon Alphagaz 1, AirLiquide, purity 99.999%) mixed with 133 ppm of NH₃ (ammonia Alphagaz 1, AirLiquide, purity 99.999%) to decrease the breakdown voltage and enhance the discharge homogeneity. The reactor chamber was filled with nitrogen (nitrogen Alphagaz 1, Airliquide, purity 99.999%) in order to avoid arc creation outside of the electrodes, as nitrogen has a greater breakdown voltage than argon[15].

2.2.Methods

2.2.1. *Synthesis of the plasma deposited nanocomposite coatings*

The dispersion was prepared in heavy duty 100 mL borosilicate glass media bottles (Thermo Fisher) by mixing the NPs with EL at a concentration 1% in weight. The ultrasonicator used in this study was a SONIC Vibracell with maximum power of 130 Watts and frequency of 20 kHz. The titanium alloy (Ti-6Al-4V) probe had a diameter of 6 mm and a length of 113 mm. Due to high power level (130 Watts), the amplitude of the frequency was reduced to 50%. The ultrasonication time has been set to 5 min per dispersion.

Dynamic Light Scattering (DLS) measurements demonstrated that the size of NPs in this dispersion was not altered by placing them in the liquid and that their polydispersity index was lower than 0.7 and that the mean particle diameter was around 200 nm with standard deviation not higher than 50 nm.

A 1% in weight silica NPs dispersion was co-injected in the atmospheric pressure discharge with a total gas flow of 5 L/min. First, the dispersion was atomized with a flow of 1.1 L/min of argon by means of an atomizer (TSI atomizer model 3076). Then, it was diluted by the carrier gas made of 3.9 L/min of argon containing 133 ppm of NH_3 before to be injected in the plasma through a $0.1 \times 4 \text{ cm}^2$ slit located 4 cm away from the discharge. To minimize any gas flow perturbations, two zinc selenide (ZnSe) windows were placed parallel to the gas stream along the discharge. ZnSe has been chosen due to its transparency in the mid-infrared spectral region. The concentration of EL and silica NPs were in the range of 350 ppm.

The plasma reactor that was used to synthesize the nanocomposites has already been described elsewhere[3]. Briefly, a plane-to-plane Dielectric Barrier Discharge (DBD) was sustained between two alumina plates with dimensions $69 \times 69 \times 1.016 \text{ mm}^3$. The gap between the electrodes was kept at 2 mm. The mean gas residence time in the plasma was 24 ms. This time is calculated using the equation: $T_R = p_p / (F_g / A)$, where p_p is the position in the plasma (20 mm),

F_g is the total flow rate (5L/min) and A is the cross section (50 mm length of the electrode x 2 mm of the gap = 100 mm²) is 100 m². The nanocomposite layers were deposited on 5.08 cm diameter and 275 μ m thick silicon wafers. Deposition time was 20 min.

Metalization (Electronic Science Laboratories ESL 9916 - silver based conducting material) was performed on a 20x50 mm² area on the plates. The upper electrode was connected to a high voltage (HV) generator, and the bottom electrode was grounded. The HV was issued from a low frequency waveform generator (Agilent 33210) connected to an audio amplifier (Crest CC4000) linked to a voltage transformer (Boige et Vignal). The optimal frequency range for this transformer was between 1 and 10 kHz and with a voltage from 1 to 15 kV. According to Brunet et al. the DC was set at 50% to simultaneously deposit NPs and polymer matrix. The FSK rate set at 200 Hz (5 ms), which corresponds to 1/5 of the mean gas residence time in the plasma enables a deposition of a homogeneous coating.

Three different frequency parameters have been used and compared. On the one hand, 1 kHz continuous plasma excitation frequency was used, which is likely to mainly lead to NP deposition. On the other hand, 15 kHz continuous plasma excitation frequency was utilized to synthesize the EL plasma polymer matrix of the nanocomposite. Finally, to synthesize a nanocomposite made of both plasma polymerized EL and NPs, FSK modulation was performed using both 1 and 15 kHz frequencies.

2.2.2. Characterization of thin films

Imaging of the layers

Scanning electron microscope (SEM) SEM HITACHI SEM-FEG S-4500 (model I) was used in order to record high resolution images (with magnification up to 180 000 X). All plasma

deposited layers were metalized with a thin layer of gold (10 nm) to enhance the sample conductivity and enable efficient sample imaging.

Atomic Force Microscopy (AFM) AFM NT-MDT model Smena was also used in non-contact mode and the images shown are the height images, which were correlated with the phase images to confirm a proper image collection.

Both SEM and AFM images were analyzed using ImageJ in order to count the NPs in each deposition condition, as well as estimate the roughness of the samples.

Profilometry

Profilometry measurements were made in order to assess the thickness of the thin films and to estimate their roughness. A DektaXT Profilometer was used, which enabled measuring thin or thick samples (up to 50 mm) with a vertical resolution of several Å according to the z axis.

Fourier-Transform Infrared Spectroscopy (FTIR)

Fourier-Transform Infrared spectra of the nanocomposite layers were recorded using a Nicolet 6700 instrument (THERMO Scientific). Sixty-four scans were routinely acquired at a spectral resolution of 4 cm⁻¹. The transmission spectra of the thin film presented therein resulted from the subtraction of the silicon wafer spectrum from that of the plasma deposited layers on top silicon wafers by nulling the substrate spectral contribution between 1000 and 700 cm⁻¹.

2.2.3. Infrared absorption spectroscopy of the plasma

The plasma phase was investigated using a mid-infrared Agilent Cary 670 FTIR spectrometer with an experimental setup previously described by Laroche et al. [54]. Briefly, an infrared beam originating from the spectrometer is directed toward the 5-cm wide plasma. A retroreflector collects back and redirects the 2 mm x 2 mm infrared beam across the plasma

exactly at the same place to allow a spatial resolution. Therefore, the overall optical path of the infrared beam across the plasma is 10 cm-long. The infrared beam is then directed to a liquid nitrogen-cooled MCT-A detector located within the spectrometer. Two hundred and fifty-six scans were co-added at a resolution of 4 cm^{-1} . Of note, the whole infrared beam path, external to the plasma reactor, was purged with dry-air free of CO_2 . Accordingly, the CO_2 infrared features observed in the plasma spectra arise from the decomposition of ethyl lactate.

3. Results and discussion

3.1. FSK influence on morphology and chemical characteristics of the thin films

The effect of the plasma frequencies on the morphology of the composite thin films is characterized by SEM, profilometry and AFM measurements. The effect on the chemical composition is determined from infrared absorption.

3.1.1. SEM images

Figure 2. SEM images of depositions depending on the plasma parameter; **A, B, C** – 1 kHz continuous deposition; **D, E** – 15 kHz continuous deposition; **F, G, H** – FSK protocol: 1 kHz and 15 kHz in 50/50 ratio and FSK rate at 200 Hz (A, D, F - 200 μm scale; B, G - 4 μm scale; E - 700 nm; C, H - 1 μm).

Figure 2 shows the SEM images of nanocomposites deposited using the 3 plasma excitation frequency conditions. As expected, random nanoparticle spatial deposition was only observed for plasma conditions where a 1 kHz excitation frequency was used during the plasma process, either in a continuous manner or during the FSK protocol. A single excitation frequency of 15 kHz leads to the formation of a dense polymeric layer without NP deposition. This result confirms that in the configuration used, the low diffusion at atmospheric pressure, as well as limited amplitude of NPs oscillation traps NPs in the discharge bulk, therefore inhibiting their incorporation in the nanocomposite. Both 1 kHz and FSK modulation lead to coatings entirely covered by NPs. However, major differences were observed between the continuous 1 kHz

condition and the deposition made using the FSK modulation. Indeed, in addition to nanoparticle deposition, the 15 kHz excitation frequency component applied during the FSK modulation also leads to the formation of a PLA-like plasma-deposited matrix which coats the nanoparticles. Of note, in FSK conditions, the plasma-deposited matrix increases the amount of NPs at the surface, as seen during the manipulation of the samples. Interestingly, a closer look to Figure 2H shows that some of the nanoparticles are coated by the plasma polymer, while others are clearly uncovered. This suggests that the nanoparticle coverage occurs at least partially on the substrates surface.

Also seen in Figures 2A and 2F is the fact that some of the nanoparticles agglomerated, leading to aggregates on the surface of the plasma-deposited layers. As already demonstrated by Boissière et al[55] and Iskadar et al[56], at least part of these aggregates are formed from NPs contained in the same droplet of the vaporized dispersion when the liquid evaporates.

Figure 3. Histograms and exponential fits with their decay constants of the diameter of NPs aggregates (in semi-log scale) observed on SEM images of the surface presented in Figure 2A for 1 kHz and 2F for FSK mode: A – Histogram and the two exponential fits for the layer deposited by continuous 1 kHz discharge (first decay constant – solid line, second decay constant – dotted line); B - Histogram and the two exponential fits for the layer deposited by FSK double modulation (first decay constant – solid line, second decay constant – dotted line).

The size distributions of these NP agglomerates were calculated using image analysis. For 1 kHz and FSK DBD, the distribution is well fitted using a two-phase exponential decay function, Figure 3. The larger exponential amplitude indicates a larger amount of the smaller NPs in the FSK mode. When FSK mode is used, a greater number of NPs with size lower than 500 nm is deposited, whereas aggregates with diameters larger than 500 nm are observed for the 1 kHz thin film. These mathematical calculations revealed that one of the decay constants (solid lines) of the exponential equations were rather similar for both plasma conditions, while the second decay (dotted lines) constants significantly differ. It is therefore likely that the first decay constant is related to a process that is identical in both cases and it could be due to both: the atomization[19, 22] and the plasma environment, as in both cases 1 kHz frequency is used at least for 50% of the time. The second decay constant is likely linked with the NPs agglomeration mechanisms in the plasma or at the surface, which probably vary in the two regimes. In FSK mode the NPs are trapped in the plasma during the time when 15 kHz frequency is applied, hence they stay in the discharge longer. This can lead to creation of an EL coating around the NPs, which then are deposited on the surface and do not agglomerate further. This does not occur for the thin film which is created solely in 1 kHz discharge and as the NPs are not functionalized, they might agglomerate without the EL coating. In FSK mode (Figure 2F) they do not aggregate as much as with continuous 1 kHz plasma frequency (Figure 2A). Figure 2A shows that agglomerates in the size of several μm are observed with continuous 1 kHz plasma. These distances between the large agglomerates are around 200 μm , which is in the range of a microdischarge diameter[15]. This suggests that the agglomerates transport to the surface is related

to the microdischarge development[15, 22, 57-59], as in the condition used the discharge was filamentary as shown in the current-voltage curve in Figure 1.

3.1.2. Profilometry measurements

Table I. Sample thickness, deposition rate and mean roughness results from measurements.

Plasma parameters	Thickness [nm]	Deposition rate [nm/s]	Roughness R_a [nm]
1 kHz	$(128 \pm 3) \times 10^1$	1.06	152 ± 3
15 kHz	$(94 \pm 2) \times 10^1$	0.78	4 ± 2
FSK	$(202 \pm 3) \times 10^1$	1.68	307 ± 6

Table I presents the profilometry measurement made perpendicularly to a scratch line on the deposition. The height of the step made this way corresponds to the coating thickness. Layers deposited at a frequency of 1 kHz for 20 min have a thickness of approx. 940 nm while those synthesized at a HV frequency of 15 kHz are 1280 nm-thick. The average roughness, R_a , is in agreement with a coating mainly made of NPs for 1 kHz and with a dense thin film for 15 kHz. The deposited layer reaches a thickness of approx. 2020 nm when FSK is used, as a result of the quasi-simultaneous deposition of both NPs and EL plasma polymer. This large growth rate – 1.68 nm/s compared with half the sum of 1 kHz and 15 kHz which is equal to 0.9nm/s, is explained by a significant increase in the adhesion of the NPs to the surface due to the reactivity of the polylactic acid (PLA)-like polymer thin film growing. The roughness of the NC thin film is close to 300 nm, which is twice that of the layers deposited at 1 kHz. These values are in the range of the silica NPs diameter. In FSK mode, we can assume that the surface reactivity is high due to the PLA thin film, thus NPs stick to the surface as soon as they are in contact with it. While the surface reactivity is smaller in the case of 1 kHz DBD and the NPs slip on the

surface until it encounters a surface defect. This hypothesis is in agreement with the low growth rate with the 1 kHz DBD, the formation of large aggregates and the smaller roughness.

3.1.3. AFM imaging of the surface of the nanocomposites

Figure 4. AFM representations of the depositions surfaces; **A,B** – 1 kHz continuous deposition; **C, D** – FSK protocol: 1 kHz and 15 kHz in 50/50 ratio and FSK rate at 200 Hz.

AFM images were made to better analyze the roughness of FSK thin films. These data show a smoother surface in FSK conditions in agreement with the fact that EL covers the nanoparticles, filling the empty spaces between them with a polymer matrix making the surface smoother. Calculation of the kurtosis parameter (which provides an indication of the profile sharpness associated to the Poisson distribution of the AFM method of parameter evaluation) is indicative of a less spiky surface when the layer contains the EL plasma polymer. The ratio between the roughness of the two thin films in both AFM and profilometry measurements is the same $1 \text{ kHz}/\text{FSK} = 0.5$. However, the discrepancy between the profilometry and AFM results in terms

of amplitude is likely due to the very different scales that were used to perform both measurements (close to 1 mm for profilometry and 10 μm for AFM). In addition, the profilometry data were recorded in a single dimension, while AFM images were acquired in 2D. As it was shown in the profilometry measurements, AFM did not enable to calculate any significant surface roughness parameter for the coatings deposited at 15 kHz.

Table II. Roughness characteristics based on AFM images.

Plasma parameters	R_a [nm]	R_{ku}
1 kHz	78 $\pm$ 2	5
FSK	154 $\pm$ 5	3

3.1.4. Thin film FTIR

The study of the morphology of the thin films was completed by the analysis of their chemical composition based on FTIR absorption made in transmission mode. To simplify the comparison, the IR absorbance is divided by the thin film thicknesses, as measured by profilometry.

Figure 5 presents the absorbance per unit length of thin films proceed with the 3 plasma modes measured in transmission, of SiO₂ NPs also measured in transmission mode FTIR and of liquid EL measured in the attenuated total reflection mode. The assignment of the different peaks is given in Table III.

Figure 5. FTIR spectra of the thin films made by AP-PECVD with different plasma parameters, **A** – FSK modulation: 1 kHz and 15 kHz in 50/50 ratio and FSK rate at 200 Hz; **B** – 15 kHz continuous plasma deposition; **C** – 1 kHz continuous plasma deposition and **D** – a spectrum of silica NPs, **E** – an ATR spectrum of liquid ethyl lactate.

Table III. Assignments of the infrared features observed in the spectra of EL and silica NPs.

	Wavenumber (cm ⁻¹)	Vibrational mode[31, 60, 61]
P₁	3570	OH stretching (intermolecular)
P₂	2990	CH ₃ asymmetric stretching
P₃	2940	CH ₂ asymmetric stretching
P₄	1750	C=O asymmetric stretching
P₅	1455	C-CH ₃ bending
P₆	1380	CH(OH)CH ₃ umbrella (intramolecular)
P₇	1266	CH(OH)CH ₃ bending
P₈	1222	COC asymmetric stretching
P₉	1140	H-C-OH asymmetric stretching
P₁₀	1100	OCC stretching
P₁₁	1050	CH-CH ₃ stretching
P₁₂	1080	Si-O-Si asymmetric stretching

The main alterations arising from the spectra of liquid EL Figure 5E and in the deposited layer Figure 5B, come from the difference in the state of matter of liquid (E) and plasma polymerized solid (B). Indeed, the bands are narrower and better defined when observing a liquid solution spectrum, while broader features are observed when a solid is analyzed due to more interactions between molecules. The part of the spectra related to EL polymerization is very similar for FSK and continuous 15 kHz DBD.

Significant differences in the spectra are observed depending on plasma mode used to synthesize the coatings as presented in Figures 5A, 5B and 5C. The comparison of these figures to Figure 5D which is the spectrum of NPs alone and Figure 5E which is the EL spectra shown

an excellent agreement with the aforementioned results. The infrared spectrum of the layer deposited at 1 kHz (5C) mostly exhibits the infrared bands characteristic of the silica nanoparticles (P_{12}) similar to Figure 5D, with few spectral contributions arising from the ethyl lactate plasma polymerized molecule. Despite the overlap of P_{12} with some of the EL absorption bands, the shape of the SiO_2 NPs is very different and specific and cannot be mistaken for EL. An inverted situation is observed at 15 kHz (5B) where the main infrared spectral contribution arises from ethyl lactate (from P_1 to P_{11}), with no absorbance arising from the presence of silica nanoparticles. Finally, the layers deposited under FSK (Figure 5A) conditions present a mixture of both infrared spectra of ethyl lactate and silica nanoparticles. That being said, the ethyl lactate infrared features somewhat change depending on whether this molecule is plasma polymerized or not. Indeed, more polymer matrix in the deposit leads to a greater absorption associated with the chemical bonds of ethyl lactate and is observed through an increased amplitude and a broadening of the bands. In other words, the peak amplitude is causally related to the amount of plasma polymerized EL, while peak broadening probes the intermolecular interactions with broader peaks corresponding to greater interactions such as cross-linking.

To better analyze the composition of the nanocomposite layer, the amplitude of different peaks respectively attributed to EL and NPs were compared for the 3 investigated plasma frequency conditions. Figure 6 shows the amplitude of the most intense infrared features related to EL and NPs which are C=O stretching (1750 cm^{-1}), and Si-O-Si asymmetric stretching (1080 cm^{-1}). In agreement with the SEM images, the layers deposited at 15 kHz exclusively show the presence of the plasma polymer. Also concurring with the SEM data, the FTIR results showed that the layers deposited at 1 kHz mostly contained silica nanoparticles, with a very low content in the plasma deposited EL polymer. Nanocomposites deposited under FSK conditions clearly shows the presence of both components in the layer.

Figure 6A shows the absorbance of the C=O (ethyl lactate) and Si-O-Si (NPs) without normalization for the film thickness. The purpose is to probe the amount of polymerized EL and silica NPs deposited in the coating during the 20 minutes-long deposition. This amount should be proportional to the growth rate of each component of the composite thin film. The horizontal lines that were added in 1 and 15 kHz column bars indicate half the height of the column to help in taking into account the fact that each frequency is only applied during half the coating duration in FSK mode, as compared to continuous frequency conditions. According to Figure 6A, in FSK mode, the height of SiO-Si is 3 times the half height of 1 kHz. Assuming that NPs are mainly deposited when the DBD frequency is 1 kHz, one can conclude from figure 6A that the NPs deposition rate is three times larger in the FSK conditions than with a continuous 1 kHz DBD. This is in agreement with a higher growth rate in FSK mode (Table I) explained by a higher amount of NPs deposited due to prior EL polymerization. Figure 6A also shows that the amount of EL PP deposited during the 20 minutes FSK process is equal to the sum of PLA deposited for 10 minutes at 1 kHz and 15 kHz (half the height of the column). This result shows that the growth rate of EL matrix in FSK mode is well determined by EL growth rate at 1 and 15 kHz.

A

B

Figure 6. FTIR features of characteristic components of EL (C=O) and NPs (Si-O-Si) for continuous 1 and 15 kHz and FSK mode; **A** - absorbance of the considered band in the whole coating thickness; **B** - absorbance normalized to the film thickness.

The absorbances of the C=O and Si-O-Si presented in Figure 6B are normalized to the coating thickness and accordingly are proportional to the polymerized EL molecules or NPs deposited per thickness unit of the coating. According to this figure, the Si-O absorbance of NPs per unit length of the coating in the FSK-deposited layer is 68% of that measured for the NP-rich layer deposited at 1 kHz. The C=O absorbance arising from the plasma polymerized EL under FSK

conditions is 34% of that of the layer deposited at 15 kHz, where no NP are deposited. It therefore seems that these FTIR data, once corrected for the sample thickness, may be used as a probe to evaluate the relative amount of the plasma polymer and NPs proportion in the nanocomposite.

3.2. Plasma FTIR

3.2.1. In-situ spectra of EL and silica NPs

First, infrared spectra of ethyl lactate and ethyl lactate + 200 nm NPs (1%) were recorded in the gas gap without turning the plasma on to obtain a gas phase spectrum of the two precursors. The spectra were normalized with respect to the absorbance of the peak of $\nu_{\text{as}}\text{CH}_3$ at 2990 cm^{-1} of EL, because the observation was mostly focused on observing the NPs in the gas phase.

Figure 7. Gas phase IR spectra of vaporized liquid precursors; **A** – ethyl lactate; **B** –dispersion of ethyl lactate and silica nanoparticles.

These infrared spectra exhibit a typical gas phase peak features with narrow and well-resolved bands, characteristic of the fact that gaseous molecules have few interactions with each other.

The spectrum of EL alone shows all the characteristic peaks of EL (Figure 5E), whereas the addition of NPs enable to observe changes in the shape of the spectrum in regions where Si-O-Si spectral mode vibrations are observed (1080cm^{-1}), therefore showing that silica NPs can be observed through FTIR at 1% concentration in weight in EL at 350 ppm in Ar. For the best of our knowledge, it is the first time that silica nanoparticles were detected by in flight FTIR.

3.2.2. In-situ FTIR of EL+1% of silica NPs plasmas at 1 and 15 kHz

. Plasma spectra of ethyl lactate and 1% of 200 nm silica NPs were recorded during AP-PECVD. As aforementioned, plasmas were made at continuous frequencies of 1 kHz and 15 kHz, to observe the consequence of the NPs transport to the surface on the gas chemistry.

Figure 8. FTIR spectra of EL with 1% of NPs in Ar/NH₃ plasma at **A** – 15 kHz; **B** – 1 kHz and **C** – infrared spectra in the 1100-700 cm⁻¹ range of plasmas of ethyl lactate and nanoparticles at 1 kHz (black), 15 kHz (red) and of a plasma made with ethyl lactate alone at 15 kHz (blue).

These two spectra recorded in the middle of the plasma region with the plasma lighted on, were compared with those recorded without plasma (Figure 7) to put in evidence the consequences of the plasma at both 1 kHz and 15 kHz (Figure 8). Of note, the 1266 cm^{-1} feature observed at plasma at 1 kHz is overlapped with an artifact occurring at 1263 cm^{-1} . The origin of this artifact was previously explained by Milaniak et al.⁵³.

Spectrum recorded at 15 kHz (Figure 8A) exhibits features related to EL and silica NPs (P_{12}). The infrared spectrum measured at 1 kHz (Figure 8B) display features very similar to those observed in the infrared spectra of pure ethyl lactate without plasma (Figure 7A), without any absorption related to SiO_2 . The main difference between 15 kHz (Figure 8A) and 1 kHz (Figure 8B) plasmas are the amplitude of P_{12} (Silica NPs) and the occurrence of P_{13} due to SiO-H stretching vibrations absorption in the 15 kHz spectra. Figure 8C zooms on these absorptions and presents a comparison with the spectrum of a plasma made only with EL at 15 kHz. It confirms that the spectra of 1 kHz DBD with EL+NPs is very similar to that of pure EL, while the spectra of 15 kHz with EL+NPs clearly contains silica contribution. These infrared data, recorded from the plasma phase, correlate extremely well with those measured from the plasma deposited layers. Indeed, nanoparticles are observed in plasmas generated at 15 kHz, e.g. in frequency conditions for which they are trapped in the plasma with few possibilities to move to the substrate surface. In these circumstances, they are almost not seen in the deposited layer. On the contrary, NP infrared features are not seen in plasmas at 1 kHz because such a plasma frequency enables these nanoparticles to move to the substrate surface and be incorporated within the deposited layer. This comparison clearly highlights that infrared spectroscopy made in the plasma enable to follow the presence of silica nanoparticles.

In the case of 15 kHz discharge the new absorption peak P_{13} corresponding to SiO-H indicates that the NPs in the plasma phase are interacting with the molecule of the precursor as, the H in

the hydroxyl group is a decomposition product of EL. NPs are functionalized, which certainly participates in their higher sticking coefficient onto the surface.

Another interesting observation is the broadening of the OH_{intermolecular} (P₁) band for the 15 kHz plasma excitation frequency, which is not observable in 1 kHz plasma, as it is likely due to higher dissociation of EL into lactic acid and ethanol [62, 63].

Of note, the presence of CO₂ (P₁₄) is also observed in the plasma through the features centered at 2349 cm⁻¹. The presence of these bands indicates that the ethyl lactate plasma polymerization mechanism implies the dissociation of the precursor with CO₂ release. The higher absorbance of the CO₂ infrared features at a plasma excitation frequency of 15 kHz is an indication of a more important precursor dissociation in this condition and hence, a more efficient polymerization, as demonstrated by all analyses performed on the plasma-deposited layers.

4. Conclusions

In agreement with the previously published proof of concept, this work confirms the interest of the utilization of AP-PECVD with FSK modulation to make a nanocomposite. It shows that this method allows the deposition of a nanocomposite of silica NPs in plasma polymerized EL. While 1 kHz plasma excitation mainly leads to the deposition of NPs and 15 kHz creates almost exclusively the polymer matrix, the amount of deposited organic matrix in the FSK mode can be predicted by summing the matrix amount deposited at each individual frequency. Another important conclusion is that the FSK mode induces the coating of the NPs with EL plasma polymer, which limits their aggregation and increases the amount of NPs on the surface. Thus, even if NPs are only deposited onto the surface when the plasma frequency is of 1 kHz, e.g. half of the time in the conditions of this work, the amount of deposited NPs is three times higher when plasma frequencies of 1 and 15 kHz are used alternatively compared to a continuous 1 kHz plasma.

For the first time, NPs were observed through in flight FTIR in a DBD. Thanks to this first in-flight observation of SiO₂ NPs, it was possible to correlate the plasma and nanocomposite compositions, as the NPs remain in the 15 kHz plasma, whereas they are almost absent at 1 kHz. FTIR also shows the functionalization of NPs and the formation of CO₂ related to the decomposition of EL.

Moreover, it has been shown that the relative amount of plasma polymerized EL and NPs can be determined by combining profilometry and FTIR spectroscopy. The Si-O absorbance of NPs per unit length of the coating in the FSK-deposited layer is 68% of that measured for the NP-rich layer deposited at 1 kHz. The C=O absorbance arising from the plasma polymerized EL under FSK conditions is 34% of that of the layer deposited at 15 kHz, where no NPs are deposited. In this particular condition, a plasma frequency of 1 kHz seems to be more efficient to deposit NPs, while a frequency of 15 kHz mainly leads to the polymerization of EL, therefore leading to a higher relative number of NPs in the nanocomposite. In addition, the deposition rate of the nanocomposite in FSK condition is much higher than those of the individual plasma polymer and NPs layers, due to the interaction between the organic precursor and the silica nanoparticles. As it was shown, there is a symbiotic relationship between these depositions, that are not as efficient when continuously using only one of the frequencies. Deposition of EL improves the amount of NPs deposited, whereas NPs create a greater surface for EL to promote polymerization.

5. References

- [1] E. Adbelhamid, *Colloidal Nanoparticles in Biotechnology*, John Wiley & Sons, Inc, New Jersey, 2008.
- [2] S. Basa, T. Muniyappan, P. Karatgi, R. Prabhu, R. Pillai, Production and in vitro characterization of solid dosage form incorporating drug nanoparticles, *Drug Dev Ind Pharm*, 34 2008 1209-1218.
- [3] P. Brunet, R. Rincón, J.-M. Martinez, Z. Matouk, F. Fanelli, M. Chaker, F. Massines, Control of composite thin film made in an Ar/isopropanol/TiO₂ nanoparticles dielectric barrier discharge by the excitation frequency, *Plasma Process Polym*, 14 2017 1700049 (1700041-1700013).
- [4] J.-F. Chen, H.-M. Ding, J.-X. Wang, L. Shao, Preparation and characterization of porous hollow silica nanoparticles for drug delivery application, *Biomaterials*, 25 2004 723-727.
- [5] C. Choi, H.S. Yoo, J.M. Oh, Preparation and heat transfer properties of nanoparticle-in-transformer oil dispersions as advanced energy-efficient coolants, *Current Applied Physics*, 8 2008 710-712.
- [6] E. Nadal, N. Barros, H. Glénat, J. Laverdant, D.S. Schmool, H. Kachkachi, Plasmon-enhanced diffraction in nanoparticle gratings fabricated by in situ photo-reduction of gold chloride doped polymer thin films by laser interference patterning, *J. Mater. Chem. C*, 5 2017 3553-3560.
- [7] P. Mehndiratta, A. Jain, S. Srivastava, N. Gupta, *Environmental Pollution and Nanotechnology*, Environment and Pollution, 2 2013 49-58.
- [8] J. Profili, O. Levasseur, A. Koronai, L. Stafford, N. Gherardi, Deposition of nanocomposite coatings on wood using cold discharges at atmospheric pressure, *Surf. Coat. Technol.*, 309 2017 729-737.
- [9] G. Da Ponte, E. Sardella, F. Fanelli, A. Van Hoeck, R. d'Agostino, S. Paulussen, P. Favia, Atmospheric pressure plasma deposition of organic films of biomedical interest, *Surface and Coatings Technology*, 205 2011 S525-S528.
- [10] C. Hoffmann, C. Berganza, J. Zhang, Cold Atmospheric Plasma: methods of production and application in dentistry and oncology, *Med Gas Res*, 3 2013 21.
- [11] P.H.C. Camargo, K.G. Satyanarayana, F. Wypych, Nanocomposites: Synthesis, Structure, Properties and New Application Opportunities, *Materials Research*, 12 2009 1-39.
- [12] M. Iqbal, N. Zafar, H. Fessi, A. Elaissari, Double emulsion solvent evaporation techniques used for drug encapsulation, *Int J Pharm*, 496 2015 173-190.
- [13] C.I. Yeo, J.H. Choi, J.B. Kim, J.C. Lee, Y.T. Lee, Spin-coated Ag nanoparticles for enhancing light absorption of thin film a-Si:H solar cells, *Optical Materials Express*, 4 2014 346 341 - 346.
- [14] N. Shukla, J. Ahner, D. Weller, Dip-coating of FePt nanoparticle films: surfactant effects, *Journal of Magnetism and Magnetic Materials*, 272-276 2004 E1349-E1351.
- [15] F. Massines, C. Sarra-Bournet, F. Fanelli, N. Naudé, N. Gherardi, Atmospheric Pressure Low Temperature Direct Plasma Technology: Status and Challenges for Thin Film Deposition, *Plasma Process. Polym.*, 9 2012 1041-1073.
- [16] J. Profili, S. Dap, O. Levasseur, N. Naude, A. Belinger, L. Stafford, N. Gherardi, Interaction of atomized colloid with an ac electric field in a dielectric barrier discharge reactor used for deposition of nanocomposite coatings, *Journal of Physics D: Applied Physics*, 50 2017 075201 075201-075213.
- [17] J. Profili, O. Levasseur, J.-B. Blaisot, A. Koronai, L. Stafford, N. Gherardi, Nebulization of Nanocolloidal Suspensions for the Growth of Nanocomposite Coatings in Dielectric Barrier Discharges, *Plasma Process Polym* 13 2016 981-989.

- [18] M. Tatoulian, F. Arefi-Khonsari, J.-P. Borra, Deposition of Organic Coatings at Atmospheric Pressure from Liquid Precursors, *Plasma Processes and Polymers*, 4 2007 360-369.
- [19] N. Jidenko, C. Jimenez, F. Massines, J.P. Borra, Nano-particle size-dependent charging and electro-deposition in dielectric barrier discharges at atmospheric pressure for thin SiO_x film deposition, *Journal of Physics D: Applied Physics*, 40 2007 4155-4163.
- [20] J.-P. Borra, Nucleation and aerosol processing in atmospheric pressure electrical discharges: powders production, coatings and filtration, *Journal of Physics D: Applied Physics*, 39 2006 R19-R54.
- [21] G. Da Ponte, E. Sardella, F. Fanelli, R. d'Agostino, R. Gristina, P. Favia, Plasma Deposition of PEO-Like Coatings with Aerosol-Assisted Dielectric Barrier Discharges, *Plasma Processes and Polymers*, 9 2012 1176-1183.
- [22] J.P. Borra, N. Jidenko, C. Dutouquet, O. Aguerre, J. Hou, A. Weber, Nano-droplet ejection and nucleation of materials submitted to non-thermal plasma filaments, *The European Physical Journal Applied Physics*, 56 2011.
- [23] M. Alonso, F.J. Alguacil, J.P. Santos, N. Jidenko, J.P. Borra, Deposition of ultrafine aerosol particles on wire screens by simultaneous diffusion and image force, *Journal of Aerosol Science*, 38 2007 1230-1239.
- [24] M. Laurent, J. Koehler, G. Sabbatier, C.A. Hoesli, N. Gherardi, G. Laroche, Atmospheric Pressure Plasma Polymer of Ethyl Lactate: In Vitro Degradation and Cell Viability Studies, *Plasma Processes and Polymers*, 13 2016 711-721.
- [25] M. Laurent, E. Desjardins, M. Meichelboeck, N. Naudé, L. Stafford, N. Gherardi, G. Laroche, Characterization of argon dielectric barrier discharges applied to ethyl lactate plasma polymerization, *Journal of Physics D: Applied Physics*, 50 2017 475205 475201-475211.
- [26] B. Nisol, S. Watson, S. Lerouge, M.R. Wertheimer, Energetics of reactions in a dielectric barrier discharge with argon carrier gas: IV ethyl lactate, *Plasma Processes and Polymers*, 13 2016 965-969.
- [27] S. Watson, B. Nisol, S. Lerouge, M.R. Wertheimer, Energetics of Molecular Excitation, Fragmentation, and Polymerization in a Dielectric Barrier Discharge with Argon Carrier Gas, *Langmuir*, 31 2015 10125-10129.
- [28] M.R. Wertheimer, Plasma Processing and Polymers: A Personal Perspective, *Plasma Chemistry and Plasma Processing*, 34 2013 363-376.
- [29] W.G. Sanders, P.C. Hogrebe, D.W. Grainger, A.K. Cheung, C.M. Terry, A biodegradable perivascular wrap for controlled, local and directed drug delivery, *J Control Release*, 161 2012 81-89.
- [30] X. Qi, Y. Ren, X. Wang, New advances in the biodegradation of Poly(lactic) acid, *International Biodeterioration & Biodegradation*, 117 2017 215-223.
- [31] S. Ligot, M. Guillaume, P. Raynaud, D. Thiry, V. Lemaire, T. Silva, N. Britun, J. Cornil, P. Dubois, R. Snyders, Experimental and Theoretical Study of the Plasma Chemistry of Ethyl Lactate Plasma Polymerization Discharges, *Plasma Processes and Polymers*, 12 2015 405-415.
- [32] M.W. Ambrogio, M. Frascioni, M.D. Yilmaz, X. Chen, New methods for improved characterization of silica nanoparticle-based drug delivery systems, *Langmuir*, 29 2013 15386-15393.
- [33] M. Colilla, B. González, M. Vallet-Regí, Mesoporous silicananoparticles for the design of smart delivery nanodevices, *Biomater. Sci.*, 1 2013 114-134.
- [34] C. Dai, S. Wang, Y. Li, M. Gao, Y. Liu, Y. Sun, M. Zhao, The first study of surface modified silica nanoparticles in pressure-decreasing application, *RSC Advances*, 5 2015 61838-61845.

- [35] Q. He, J. Shi, Mesoporous silica nanoparticle based nano drug delivery systems: synthesis, controlled drug release and delivery, pharmacokinetics and biocompatibility, *Journal of Materials Chemistry*, 21 2011.
- [36] Q. He, J. Shi, MSN anti-cancer nanomedicines: chemotherapy enhancement, overcoming of drug resistance, and metastasis inhibition, *Adv Mater*, 26 2014 391-411.
- [37] X. Huang, N.P. Young, H.E. Townley, Characterization and Comparison of Mesoporous Silica Particles for Optimized Drug Delivery, *Nanomaterials and Nanotechnology*, 4 2014.
- [38] S.A. Jadhav, Incredible pace of research on mesoporous silica nanoparticles, *Inorg. Chem. Front.*, 1 2014 735-739.
- [39] Y. Li, N. Li, W. Pan, Z. Yu, L. Yang, B. Tang, Hollow Mesoporous Silica Nanoparticles with Tunable Structures for Controlled Drug Delivery, *ACS Appl Mater Interfaces*, 9 2017 2123-2129.
- [40] A. Liberman, N. Mendez, W.C. Trogler, A.C. Kummel, Synthesis and surface functionalization of silica nanoparticles for nanomedicine, *Surf Sci Rep*, 69 2014 132-158.
- [41] J. Lu, M. Liong, Z. Li, J.I. Zink, F. Tamanoi, Biocompatibility, biodistribution, and drug-delivery efficiency of mesoporous silica nanoparticles for cancer therapy in animals, *Small*, 6 2010 1794-1805.
- [42] V. Mamaeva, J.M. Rosenholm, L.T. Bate-Eya, L. Bergman, E. Peuhu, A. Duchanoy, L.E. Fortelius, S. Landor, D.M. Toivola, M. Linden, C. Sahlgren, Mesoporous silica nanoparticles as drug delivery systems for targeted inhibition of Notch signaling in cancer, *Mol Ther*, 19 2011 1538-1546.
- [43] Z.U. Rahman, T. Zhang, Y. Feng, W. Ye, D. Wang, Preparation of Gold Shells on Hollow Mesoporous Silica Nanospheres and Application to Photothermal-Chemotherapy, *ChemistrySelect*, 2 2017 3969-3975.
- [44] R. Roggers, S. Kanvinde, S. Boonsith, D. Oupicky, The practicality of mesoporous silica nanoparticles as drug delivery devices and progress toward this goal, *AAPS PharmSciTech*, 15 2014 1163-1171.
- [45] J.M. Rosenholm, M. Linden, Towards establishing structure-activity relationships for mesoporous silica in drug delivery applications, *J Control Release*, 128 2008 157-164.
- [46] F. Tang, L. Li, D. Chen, Mesoporous silica nanoparticles: synthesis, biocompatibility and drug delivery, *Adv Mater*, 24 2012 1504-1534.
- [47] Y. Wang, Q. Zhao, N. Han, L. Bai, J. Li, J. Liu, E. Che, L. Hu, Q. Zhang, T. Jiang, S. Wang, Mesoporous silica nanoparticles in drug delivery and biomedical applications, *Nanomedicine : nanotechnology, biology, and medicine*, 11 2015 313-327.
- [48] A. Watermann, J. Brieger, Mesoporous Silica Nanoparticles as Drug Delivery Vehicles in Cancer, *Nanomaterials-Basel*, 7 2017.
- [49] S.H. Wu, Y. Hung, C.Y. Mou, Mesoporous silica nanoparticles as nanocarriers, *Chem Commun (Camb)*, 47 2011 9972-9985.
- [50] S.H. Wu, C.Y. Mou, H.P. Lin, Synthesis of mesoporous silica nanoparticles, *Chem Soc Rev*, 42 2013 3862-3875.
- [51] L. Yuan, L. Chen, X. Chen, R. Liu, G. Ge, In Situ Measurement of Surface Functional Groups on Silica Nanoparticles Using Solvent Relaxation Nuclear Magnetic Resonance, *Langmuir*, 33 2017 8724-8729.
- [52] Y. Zhang, Z. Zhi, T. Jiang, J. Zhang, Z. Wang, S. Wang, Spherical mesoporous silica nanoparticles for loading and release of the poorly water-soluble drug telmisartan, *J Control Release*, 145 2010 257-263.
- [53] Y. Zhu, J. Shi, W. Shen, H. Chen, X. Dong, M. Ruan, Preparation of novel hollow mesoporous silica spheres and their sustained-release property, *Nanotechnology*, 16 2005 2633-2638.

- [54] G. Laroche, J. Vallade, R. Bazinette, P. van Nijnatten, E. Hernandez, G. Hernandez, F. Massines, Fourier transform infrared absorption spectroscopy characterization of gaseous atmospheric pressure plasmas with 2 mm spatial resolution, *The Review of scientific instruments*, 83 2012 103508.
- [55] C. Boissiere, D. Grosso, A. Chaumonnot, L. Nicole, C. Sanchez, Aerosol route to functional nanostructured inorganic and hybrid porous materials, *Adv Mater*, 23 2011 599-623.
- [56] F. Iskandar, H. Chang, K. Okuyama, Preparation of microencapsulated powders by an aerosol spray method and their optical properties, *Advanced Powder Technol.*, 14 2003.
- [57] E. Marode, C. Deniset, Some of the Role of Excited Species in the Chemical Yield of the Streamer-Filament Discharge in Air at Atmospheric Pressure, *IEEE Transactions on Plasma Science*, 39 2011 2272-2273.
- [58] F. Massines, R. Messaoudi, C. Mayoux, Comparison of polypropylene surface treatment between air filamentary and helium glow dielectric barrier discharges, *Plasmas and Polymers*, 3 1998 43-59.
- [59] R. Brandenburg, Dielectric barrier discharges: progress on plasma sources and on the understanding of regimes and single filaments, *Plasma Sources Science and Technology*, 26 2017.
- [60] Y.-C. NING, *Interpretation of Organic Spectra*, Jon Wiley and Sons, Singapore.
- [61] A.S. Khan, H. Khalid, Z. Sarfraz, M. Khan, J. Iqbal, N. Muhammad, M.A. Fareed, I.U. Rehman, Vibrational spectroscopy of selective dental restorative materials, *Applied Spectroscopy Reviews*, 52 2016 507-540.
- [62] J. Coates, *Interpretation of Infrared Spectra, A Practical Approach*, in: R.A. Meyers (Ed.) *Encyclopedia of Analytical Chemistry: Applications, Theory and Instrumentation*, John Wiley & Sons, Toronto, 2006.
- [63] A. Bacher, in, *Chem UCLA, University of California*.