Energetics of reactions in a dielectric barrier discharge with argon carrier gas: VII anhydrides

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1 | INTRODUCTION

Atmospheric-pressure (AP) plasmas have been gaining interest during recent decades, and they are nowadays used in a wide range of applications including surface functionalization and the synthesis of various types of coatings by PECVD (plasma-enhanced chemical vapor deposition). An important advantage is the absence of vacuum systems, thereby rendering AP potentially economically more suitable for industrial uses.¹⁻³ High-voltage (HV) dielectric barrier discharge (DBD) reactors, using one or more electrodes covered by a dielectric layer and separated by a small (~mm) gap, are a preferred approach because they can readily be scaled up.⁴ Of course, if the application is PECVD, properties of AP plasma-polymerized (PP) coatings strongly depend on the nature of the monomer/precursor gas or vapor. Nevertheless, the understanding of fundamental mechanisms involved remains elusive. The so-called Yasuda parameter (W/FM)⁵ from the late 1970s, where W, F, and M, respectively, represent the applied discharge power, precursor flow rate, and mass, was proposed to help predict low-pressure (LP) plasma polymerization/fragmentation
mechanisms. Although useful to some extent, it has major limitations under AP conditions: here, the monomer is generally diluted in an inert carrier gas (He or Ar), which totally changes the energy transfer mechanisms. Indeed, such AP plasmas are not only governed by inelastic electron collisions, like LP plasmas, but mainly by Penning-transfer via excited metastable species of the inert carrier gas. Some of the present authors have developed a method for evaluating this energy transfer, through analyses of $V(t)$ and $I(t)$ measurements, when a monomer flow, $F_d$, is added in $\%$ concentration to the much greater Ar carrier gas flow.\[6\]–\[8\] The resulting parameters, $\Delta E_g$ and $E_m$, respectively, represent energy absorbed from the plasma by $F_d$ per monomer molecule, and per duration time of the applied a.c. voltage period. This has allowed the authors to observe, for example, the effect of slightly modifying the chemical structure of molecules within various families of monomers.\[9\]–\[12\] In this present work, the seventh of a series in this same journal, special attention was given to the importance of the C/O ratio and to the presence of double bonds in a new such monomer family: anhydrides. Potentially hydrolyzable into two carboxylic acids,\[10\] molecules in this family of precursors have already been used to deposit thin films by LP and AP plasmas, coatings that are both sensitive to hydrolysis\[11\] as well as biocompatible.\[12\]–\[14\] The shapes of the $\Delta E_g$ and $E_m$ curves for each different molecule as a function of $F_d$ will be discussed and correlated with deposition rates and chemical compositions of the resulting PP coatings.

2 | EXPERIMENTAL SECTION

A complete description of the DBD reactor and its electrical power supply used in this study can be found in references cited above. Nonetheless, it is useful to repeat certain important technical aspects below. The planar DBD system had a 2 mm-wide gap between the upper (Macor® ceramic, 3.50 ± 0.05 mm thick) and lower (glass, 3.00 ± 0.02 mm$^2$) dielectrics. The plasma was sustained at fixed audio-frequency, $f = 20$ kHz, and peak-to-peak applied voltage, $V_a = 8$ kV (2.8 kV$_{rms}$). The flow rate of argon (Ar) carrier gas (99.99% purity, Air Liquide Canada Ltd., Montréal) was kept constant, $F = 10$ standard L min$^{-1}$ (slm). The five liquid monomers, acetic anhydride (AA), propionic anhydride (PA), butyric anhydride (BA), isobutyric anhydride (IA), and methacrylic anhydride (MA) were used as received. Varying known amounts, $F_d$, of their vapors were admixed with the 10 slm Ar carrier gas flow. This was accomplished by bubbling a smaller fixed flow of Ar through the liquid precursor in a glass bubbler, the liquid and the gas lines being heated to 60 °C for AA, PA, and IA and to 80 °C for BA and MA to prevent condensation. In each case, a calibration curve had first been obtained gravimetrically, as described elsewhere.\[9\]

Using the earlier-reported equivalent circuit model and MATLAB® program, we determined $E_g$ (in $\mu$J), the energy dissipated in the AP DBD plasma during each applied a.c. HV cycle. The energy difference, $\Delta E_g$, associated with monomer admixture was evaluated for wide flow ranges, 0.1 $\leq F_d \leq 20$ sccm, which in turn permitted calculation of $E_m$ (in eV). Resulting PP coatings were then characterized using the following techniques:

Attenuated total reflectance Fourier-transform infrared (ATR-FTIR) measurements were performed on a VERTEX 70 instrument between 500 and 4000 cm$^{-1}$ with 4 cm$^{-1}$ resolution, averaging 64 scans and using OPUS software. KBr pellets, used as IR-transparent substrates, were prepared from 99+% IR grade powder (Fisher Scientific). These KBr pellets were then coated with ca. 200 nm thin PP films in order to measure their FTIR spectra. Spectroscopic ellipsometry (SE) measurements were performed on PP-coated silicon wafer fragments using a J.A. Woollam RC2® instrument operating between 193 and 1700 nm. The $\Delta$ and $\Psi$ parameters were determined at 45°, 55°, 65°, and 75° incidence angles; data were interpreted using the CompleteEASE™ software and a B-spline or Cauchy-EMA-based optical model, depending on the average roughness.

3 | RESULTS AND DISCUSSION

The results will be presented separately in two sections, first the influence of C/O ratio and unsaturation in the monomer structure on $\Delta E_g$ and $E_m$, as introduced earlier,\[9,15\] AA, PA, and BA were used to highlight the effect of C/O ratio, while the other two monomers (MA and IA) with identical size, shape, and C/O ratio were used to investigate the influence of double bonds. Chemical structures and molecular masses ($M$, in g mol$^{-1}$) of the five monomers are presented in Scheme 1. In the second section, physico-chemical properties of the deposited PP coatings, based on ATR-FTIR and SE measurements will be discussed.

3.1 | Energy measurements

3.1.1 | Effect of non-polar chain length of the anhydride function

Figure 1(a) shows plots of $\Delta E_g$ versus $F_d$ for the first three monomers, (i)–(iii) in Scheme 1. One notes that the maximum energy absorbed by a monomer molecule (hereafter termed “energy absorbance”) strongly depends on its number of breakable bonds, indeed on the non-polar chain length of the anhydride function: $\Delta E_g = 209.5, 350.1,$ and 453.9 $\mu$J for AA, PA, and BA, respectively. Also, the maximum, $\Delta E_{g(max)}$, that demarcates the so-called “monomer-deficient” and “monomer-rich” regions is seen to shift to lower $F_d$ with
rising molecular weight, $M$, in relation with the sums of breakable bond energies, namely 55.2, 79.5 and 103.7 eV for AA, PA, and BA, respectively. For comparison, $F_d$ values corresponding to $\Delta E_g(\text{max})$ have been normalized with respect to those total bond energies, yielding quite similar values of 13.8, 13.2, and 13.0 eV sccm$^{-1}$. Therefore, for the case of these three saturated monomers, comparable energy absorption mechanisms appear to be taking place. Since none of them can be polymerized by conventional routes, one may presumably relate $\Delta E_g$ values to fragmentation-recombination processes. Similar trends are observed for $E_m$ [Figure 1(b)] where $E_m(\text{max})$ is seen to increase with rising numbers of breakable bonds in the monomer, namely $E_m(\text{max}) = 21.6$, 27.6, and 53.1 eV for AA, PA, and BA, respectively.

Nisol et al.\textsuperscript{[8,9]} associated the “dips” observed in both (a) and (b) to bonded oxygen in the monomer. This feature is enhanced at lower C/O ratio, therefore more evident in the case of anhydrides than for esters or acidic monomers. The “dip intensity” (difference in $E_m$ values just before and at the bottom of the dip) can be correlated with the C/O ratios of the respective monomers. These energy variations are found to be 33, 41, and 62% for BA, PA, and AA, respectively. According to previous work, this dip may possibly be associated with conditions that favor the formation of CO$_2$, a molecule that consumes little energy in the discharge.\textsuperscript{[8]} A lower C/O ratio in the monomer would thus lead to more impact on the $E_m$ curves. The energy minima in the dips of the three monomers could then be attributed to their remaining hydrocarbon backgrounds, increasing with the sizes of the non-polar chains.\textsuperscript{[16]} Compared with esters and acids, the higher “dip intensity” values of this family of anhydrides can tentatively be attributed to opening of the anhydride functions, the formation of two carboxylic acid groups which can then eventually be converted into CO$_2$.

When plotting $E_m$ versus $1/F_d$, Figure 2, one notes the “monomer-rich” linear region at low $1/F_d$, immediately followed by the oxygen “dip” just discussed. The linear slopes, 9.2, 8.4, and 4.5 W for BA, PA, and AA, respectively, signal more energy consumed per monomer molecule with rising size.
3.1.2 Influence of unsaturation

We now compare two monomers, IA and MA, of comparable molecular weights and C/O ratios, that only differ in unsaturation (see Scheme 1). Figure 3 presents plots of (a) $\Delta E_g$ and (b) $E_m$, both versus $F_d$. IA is seen to present three sections, similar to those of the other saturated anhydrides (Section 3.1.1), namely a rise, followed by the “dip” and a maximum with a plateau. Note that $\Delta E_{g(max)} = 427 \mu J$ is very close to the value for BA (452 $\mu J$); also, the plateaus in the “monomer-deficient” regions occur near the same $F_d$, combined observations for IA and BA that underline the similar energetic behaviors of these two comparable molecules. On the other hand, the very different behaviors observed between MA and IA may therefore be attributed to MA’s double bonds. For MA, the absence of appreciable dips in both (a) and (b) suggests a significant reduction in CO$_2$ formation. Among others,$^{17-19}$ Loyer and coworkers$^{20}$ reported limited fragmentation of acrylate precursors containing a double bond, which reduces the formation of volatile (oxygenated) species, supporting the results presented here. Higher reactivity of the unsaturations in MA protects the anhydride function, at the origin of CO$_2$ formation. Widely different $\Delta E_{g(max)}$ (427 and 215 $\mu J$ for IA and MA, respectively) and systematically lower $E_m$ for MA can presumably be attributed to easier formation of radicals in MA, because less energy is needed to open the C=C $\Pi$ bond than the C–C $\sigma$ bond.$^{21}$ Values of $E_{m(max)}$ for the saturated (IA) and unsaturated (MA) monomers, respectively, 61.9 and 58.6 eV, are so close as to seem in contradiction with those of other similar molecules. Yet, closer analysis of Figure 3(b) suggests that the “monomer-deficient” region had not been accessed for MA, hence that higher $E_m$ values might have been observed at lower $F_d$. While the transition from “deficient” to “rich” is clear for IA, this is not so for MA. Nevertheless, a slope discontinuity near $F_d = 3$ sccm suggests change in the energy absorption mechanism, possibly due to high polymerization rate and formation of oligomers in the plasma, leading to “dust” formation in the reactor.

In Figure 4, slopes of the quasi-linear “monomer-rich” regime are 3.4 and 9.5 W for MA and IA, respectively; this tends to confirm lower degree of fragmentation of other bond

![FIGURE 2](a) Plots of $E_m$ (eV) versus $1/F_d$; (b) zoom on the linear region, for acetic, propionic, and butyric anhydrides

![FIGURE 3](Plots of (a) $\Delta E_g$ ($\mu J$) and (b) $E_m$ (eV) versus $F_d$ for isobutyric and methacrylic anhydrides)
types when unsaturated ones are present, because the latter have higher reactivity and require lower energy to open. Additionally, very similar slope values for IA and BA (see Section 3.1.1) tend to support the proposed interpretation of data and reliability of the developed method.

3.2 | Physico-chemical analysis of the deposited PP coatings

We start with ATR-FTIR investigation of PP-coatings prepared using particular monomer flow rates \( F_d = 10 \text{ sccm} \) for AA, PA, BA, IA and \( F_d = 5 \text{ sccm} \) for MA; Figure 5 presents the corresponding FTIR spectra numerically normalized by the total intensity of the signal. Specific attention is given to the ratio of signal areas between the CH\( x \) stretching (2800–3000 cm\(^{-1}\)) and the CO bending (1600–1800 cm\(^{-1}\)) vibrations. These represent a good indicator for the conservation of the monomer’s initial structure. One notes that the chemical structures of PP films prepared from the saturated monomers followed a trend that appears to correlate with their initial C/O ratio: longer non-polar chains led to a stronger CH\( x \) signal because more C–H bonds were initially present in the structure. This readily explains why the COOR/CH\( x \) ratio decreased from 2.34 to 1.74 to 1.14 for acetic (AA), propionic (PA), and butyric (BA) anhydrides, respectively. On the other hand, the replacement of two C–C bonds by C=C bonds (in MA) resulted in much stronger conservation of the carbonyl function near 1700 cm\(^{-1}\) (0.93 for IA, 3.12 for MA). This critical difference in the COOR/CH\( x \) ratio between IA and MA can be related to totally different plasma-polymerization mechanisms in the presence of sp\(^2\) carbons.[22] Without double bonds, the fragmentation and recombination processes dominate the polymerization mechanism, where the presence of unsaturation favors radical propagation within the double bonds into the plasma phase, as recently reported in the literature.[23] The energy needed for polymerization via opening \( \Pi \) bonds in the unsaturated monomer is lower than that required to form radicals in C–C, C–H, or C–O \( \sigma \) bonds. This observation again confirms the higher reactivity of the double bonds.

PP coating thicknesses were determined from SE measurements, and these could then readily yield deposition rates, \( r \) (in \( \text{nm s}^{-1} \)). Values of \( r \) for PP coatings from the various monomers presented in Figure 6 were seen to be strongly influenced by the chemical structures, hence the polymerization mechanisms. In Figure 6(b) \( r \) data of the saturated monomers are shown on greatly expanded ordinate scale. The dual polymerization pathway of the unsaturated monomer (MA, via radical propagation through open double bonds and limited fragmentation/recombination) is seen to have led to much higher \( r \) values than for the saturated monomers. Higher deposition rates of the unsaturated monomers led to visibly rougher surfaces, possibly because formation of dust particles was observed for \( F_d > 5 \text{ sccm} \); however, no \( r \) measurements were performed under “dusty” conditions. The polymerization mechanism of the saturated monomers was strictly governed by fragmentation/radical recombination, relative efficiencies for saturated and unsaturated monomers already having been reported by Hegemann et al.[24,25] For comparison, the \( (F_d = 10 \text{ sccm}) \) \( r \) of IA (\( r = 34.8 \text{ nm min}^{-1} \)) was almost 10 times lower than the corresponding value for MA (\( r = 333 \text{ nm min}^{-1} \), \( F_d = 5 \text{ sccm} \)). Within the group of saturated monomers, \( r = 6.1, 28.8, 34.8 \text{ nm min}^{-1} \) for AA, PA, and BA, respectively, can presumably be simply explained in terms of rising molecular size. This is also compatible with the very similar \( r \) values observed for IA and BA, where their respective
molecular structures do not seem to have influenced corresponding \( r \) values. The latter \( r \) values were measured at various locations on the substrates in order to assess coating homogeneity; corresponding error bars, consistently less than 2%, indicate highly homogeneous deposition. However, as \( r \) rose with increasing size of the monomer molecules, this trend was found to be less pronounced.

4 | CONCLUSION

In this research, we have tried to demonstrate and confirm the high degrees of reliability, transferability, and reproducibility of the previously developed methods for energy measurements in DBD plasmas, here for the specific case of anhydrides. The observed increase in \( \Delta E_g \) with rising molecular size (numbers of breakable bonds, i.e., “energy absorbance”) has been correlated with previous analyses of other families of molecules by members of this group. The intensity and position of the energy drop (“dip”) in the \( E_m \) and \( \Delta E_g \) curves could be correlated with the monomers’ C/O ratios. Significantly different energy absorption mechanisms could be distinguished between the unsaturated MA (methacrylic anhydride) and saturated anhydride monomers. For MA this led to better conservation of the monomer structure and to higher deposition rate, \( r \), on account of the high reactivity of MA’s double bonds.

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REFERENCES


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