ELECTRODE CLEANLINESS IMPACT ON THE SURFACE TREATMENT OF FLUOROPOLYMER FILMS FOR A LONG-LASTING PLASMA PROCESS

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ABSTRACT

A dielectric barrier discharge in a continuous process configuration is used to coat the surface of polymer films. The effect of the growth of a coating layer on top of the uncovered electrode with regards to the physicochemical properties of the film treatment is studied. Plasma electrical parameters such as power density (W.cm^{-2}) and voltage (kV) are monitored during a typical cycle, which is comprised between two electrode cleanings. In addition, the surface energy and chemistry are determined at chosen time-points of the process by contact angle measurements with two liquids and X-ray photoelectron spectroscopy (XPS). Based on these analyses, no major modification of the coated polymer physicochemical properties was attributed to the deposition of an organic layer on top of the bare electrodes after the equivalent of 1 h of continuous treatment.

KEYWORDS

Dielectric barrier discharge
Fluoropolymer
Surface modification
Electrode cleaning

CITATION

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1 INTRODUCTION

Surface modification using a plasma discharge is a clean, safe and eco-friendly way of optimizing a material superficial physicochemical characteristics without altering its bulk properties. This process is used, among others, to increase or decrease the surface energy or wettability of materials [1,2].

Such a plasma modification can be performed at atmospheric pressure, thus preventing the need for expensive pumping systems and enabling continuous process. A simple and inexpensive system of atmospheric pressure plasma process, well suited for industries, consists in using an electrical discharge. Typically, plasma discharges can be initiated in air, nitrogen or argon, then called carrier gas, and can be used to functionalize the surface of different types of flat substrates such as polymers, glasses, fabrics, etc. In practice, the material to be treated is placed between a high voltage and a ground electrode. Most of the time, the substrate lays directly on the ground electrode. In such a configuration, the side of the polymer film in close contact with the ground electrode is not treated, while only the surface of the polymer film exposed to the plasma is modified.

The addition of a chemical precursor diluted in the carrier gas leads to the deposition of a coating instead of limiting the functionalization to the first atomic layer of the substrate [3]. Moreover, coating the surface, as opposed to functionalization, leads to a better durability of the treatment [4]. However, adding a precursor also has its disadvantages. While the surface of the substrate is being coated with the precursor-based layer, the coating also accumulates at the surface of the high voltage electrode that is not covered by the substrate. This means that the uncovered electrode must be regularly cleaned. Having a layer of material buildup on the electrode could lead to: (i) etching of the newly formed coating, (ii) the modification of the dielectric characteristics of the electrodes. The first point implies that, as the layer on the electrode builds up, some fragments may detach from the electrode surface, deposit onto the polymer and change the surface properties of the treated substrate. This phenomenon would be easy to notice since flakes or powders would accumulate on the surface. The second observation could be associated with a modification of the power density in the discharge during the treatment resulting in the modification of the plasma characteristics.

Since changing the discharge properties usually implies a variation in the treated/coated surface characteristics, it is of major importance to validate the stability of the treatment between each electrode cleaning procedure, i.e. over a production cycle.

In this context, this communication aims at measuring the effects of the electrode cleanliness over a production cycle. To do so, a typical industrial plasma reactor was replicated at lab scale and equipped with control and monitoring apparatus [5]. Rolls of fluorinated ethylene polypropylene (FEP) films were treated using this plasma setup while controlling discharge properties such as the power density. Then, the treated film surface was characterized in terms of chemical composition and surface energy to assess the differences between the beginning and the end of a treatment cycle, from one cleaning procedure to the next.

2 MATERIAL AND METHODS

2.1 Lab-scale process

2.1.1 Discharge cell

Fig. 1A shows a diagram of the discharge cell including the roll to roll system. To ignite the plasma, a pulsed sinusoidal waveform of 20 kHz generated by an AFG-2021 (Tekronix) is sent to a PL380 amplifier (QSC) taking the signal power to around 8 kVA giving a maximum voltage output of around 180 Veff. This signal is then going through a transformer (RAF Tabtronics) raising the Veff to 18 kV which is the maximum voltage that can be applied to the electrodes. This gives rise to a filamentary discharge. The resulting Lissajous Q-V plot of the discharge is shown at Fig. 1B.

Fig. 1A is a cross section of the system. Each high voltage electrode is 1 cm wide and 15 cm long for a discharge area of 15 cm^2 per electrode. The gas gap between the ground electrode and the two top electrodes can be adjusted but was maintained at 1 mm during the experiments. Between the two high voltage electrodes, a Super Air Knife air flow laminator (EXAIR) is used to send a laminar flow of the mixture made of the carrier nitrogen gas and the gaseous precursor by the small space located between the two top electrodes. For calculation purposes, the gap between the top electrodes is negligible.

The Super Air Knife takes a compressed air flow input through an inlet into the plenum chamber. The flow is then directed to a precise, slotted orifice. As the primary airflow exits the slotted nozzle, it follows a flat surface that directs the airflow in a straight line.

2.1.2 Lab scale roll-to-roll process

The industrial process replicated here consists of 3 main tasks: installation of a polymer roll, plasma treatment and removal of the polymer roll. These steps are likely to be repeated several times throughout a working day and the electrodes require cleaning every few cycles. This process was adapted to the lab (Fig. 1) in order to save material and time while keeping the same exposition duration between the plasma and the polymer film. The simulated lab procedure is shown in Fig. 2.

Typical industrial cycles are designed to treat multiple rolls of films between each electrode cleaning steps. Moreover, after each treatment the plasma is turned off and a certain amount of time is required to remove and install a new roll of polymer (represented by the straight arrow). This pause can cause the coating to dry over the electrodes. It also leaves enough time for a recombination of the long-life species and charges created during the discharge. It is to be noted that, before the lab scaled procedure was launched, the gas administration system was purged with the nitrogen carrier gas in order to remove residual oxygen and other unwanted elements from the tubing. For the adapted lab scale process, each roll (R1, R2) was separated in 3 sections (S1, S2, S3) in order to minimize material consumption. S1, S2 and S3 (hashed circles) correspond to time periods of one minute during which the roll to roll (R2R) system and the discharge are on. Accordingly, surface characterization was performed on these zones. Between these industrial surface treatment simulation on which the analyses are made, the discharge is still on, but the R2R speed is lowered (chevron arrows). Setting the R2R to low speed produces less material that will be discarded while preventing too much accumulation of the coating over the treated polymer. The discharge exposition time is kept similar to that of the industrial process so that the amount of coating over the electrodes is representative. The lab scale cycle was repeated twice (R1S1, -2, -3 and R2S1, -2, -3, see the bottommost text of Fig. 2) to produce a thick coating over the uncovered electrodes and evaluate if there is any difference in the electrical characteristics of the discharge caused by a modification of the dielectric constant upon building up of the plasma deposited film on the high voltage electrode. Of note, additional repetitions of this cycle were attempted during this study but led to overheating of the lab-scale electrodes. This resulted in elongating the polymer film during treatment. This phenomenon could be avoided by using electrodes with a cooling system. However, for the purpose of having accurate comparison for this study, only data obtained with the first two cycles (without film elongation) will be presented in this manuscript.

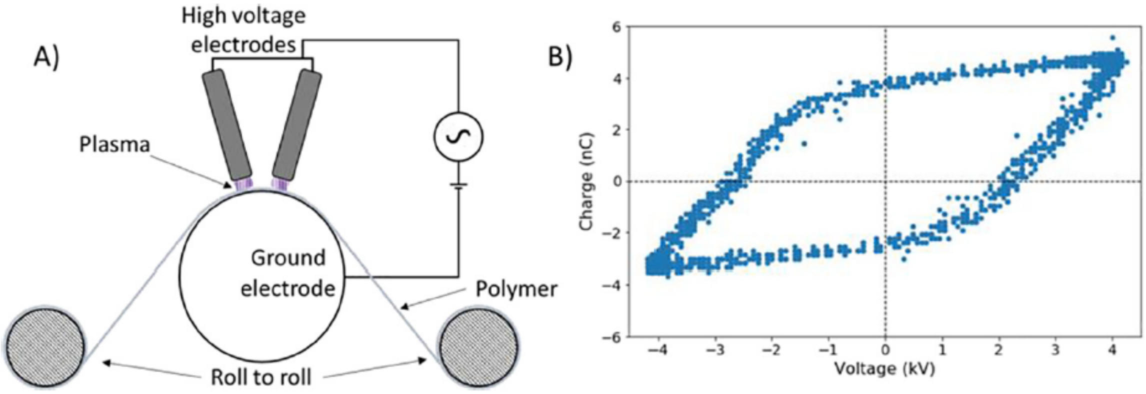

Fig. 1. A) Simplified scheme of the lab scale reactor. It shows the roll to roll system and the plasma discharge apparatus. B) Typical Q-V plot of the discharge.

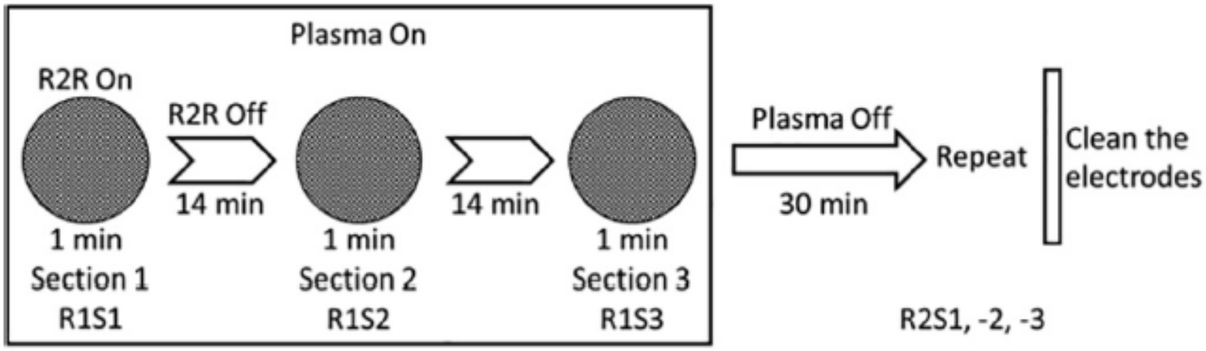

Fig. 2. The adapted lab scale process used in this study. The framed parts are equivalent in term of discharge exposition time.

2.2 Material

The FEP film rolls were provided by Saint-Gobain Research North America. The film thickness was 0.127 mm (5 mil). The datasheet of the polymer is provided by the manufacturer [6].

2.3 Validation of the plasma parameters

Monitoring of the discharge was done by in-situ power density and voltage measurements. The monitoring was made during the 1-minute periods where the film was moving between the electrodes with the plasma discharge on (see Fig. 2 B, Sections 1–3). The charge of the discharge was calculated using the potential difference at the terminals of a capacitor (80 pF), which was measured using a TPP0500B probe (Tektronix). The voltage of the discharge was measured by a P6015A high voltage probe (Tektronix) connected to the output of the transformer. The signal from the probes were displayed on a DPO 2024A oscilloscope (Tektronix) and sent to a LabVIEW program (National Instruments Corp) in order to compute the power density in W.cm^2 using Q-V plots [7].

2.4 Surface characterization

The surface physicochemistry was analyzed using contact angle measurements and X-ray photoelectron spectroscopy (XPS). The analyses were performed on the 1-minute zones where the polymer was passing through the electrodes with the discharge on.

2.4.1 Contact angle

The contact angle was calculated using a VCA optima XE (AST Products Inc.) instrument with 0.5 mL droplets of deionized water and diiodomethane (ReagentPlus®, 99%, contains copper as neutralizer, Sigma-Aldrich). Using the contact angle values of these two liquids at the interface of the treated polymer film enables to obtain the surface energy from the polar and dispersive surface energy components described by the Fowkes theory [8,9] using Eq. (1):

$$\left(\sigma_{\mathbf{L}}^{\mathbf{d}}\right)^{1/2}\left(\sigma_{\mathbf{s}}^{\mathbf{d}}\right)^{1/2}+\left(\sigma_{\mathbf{L}}^{\mathbf{p}}\right)^{1/2}\left(\sigma_{\mathbf{s}}^{\mathbf{p}}\right)^{1/2}=\frac{\sigma_{\mathbf{L}}}{2}(\cos\theta+1) \tag{1}$$

2.4.2 X-ray photoelectron spectroscopy

The surface chemistry of the coated film was investigated by XPS survey analyses using a PHI 5600-ci (Physical Electronics) equipped with a standard aluminum X-ray source (1486.6 eV) operated at 300 W with a charge neutralizer, enabling to record spectra ranging from 0 to 1200 eV. A take-off angle of 45 ° was used for a detection area of 0.5 mm^2. The spectra were then analyzed using the Multipak software provided by the spectrometer manufacturer to determine the relative concentration of carbon, fluorine, nitrogen and oxygen.

3 RESULTS AND DISCUSSION

3.1 Cleanliness of the electrodes

Fig. 3B displays the layer formed on the electrode after 1 hour of treatment (Sections 1–3 of Fig. 2 repeated twice) versus the clean electrodes before the process (Fig. 3A). The yellow colored layer forming on the electrode shown on Fig. 3B results from the thick layer of organic coating deposited after 1 h, as a further cleaning of the assembly brings back the stainless steel metallic aspect.

3.1.1 Electrical measurements

As aforementioned, the plasma reactor used allows plasma monitoring via electrical measurements such as the in-situ power density to which the polymer film is submitted. In all the following figures, RxSy means Roll x, Section y of the process (see Fig. 2).

3.2 Effect of shear stress on HSVECs on patterned surfaces

As aforementioned, the plasma reactor used allows plasma monitoring via electrical measurements such as the in-situ power density to which the polymer film is submitted. In all the following figures, RxSy means Roll x, Section y of the process (see Fig. 2).

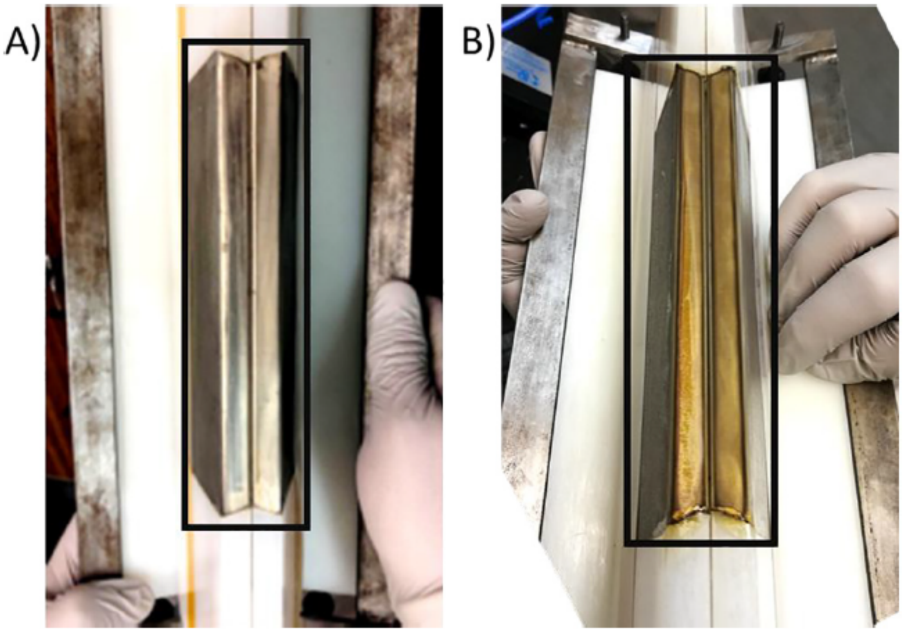

Fig. 3. Pictures showing the parts of the electrodes (frames) directly exposed to the plasma. A) shows the electrodes before the treatment while B) demonstrates the deposited layer that forms on the electrodes.

3.2.1 Electrical measurements

Fig. 4 A shows the evolution of the power and voltage of the discharge, acquired in real-time. During the experiments, the voltage was slightly adjusted to keep the power density at a constant value of 1.5 W.cm_2. A difference can be observed between R1S1 and the rest of the first roll R1. Indeed, a plasma discharge requires more energy to be initiated than to be sustained. That is why a higher voltage is observed for R1S1, which corresponds to the discharge initiation step. After a while, the charges accumulated on the electrodes and in the gas gap from previous discharges facilitate the discharge sustainability, which is why the voltage had to be decreased to keep the power constant for R1S2 and R1S3.

After the 30 min without discharge between R1 and R2, the breakdown voltage needed to initiate the new discharge for R2S1 was similar to the one needed for R1S1. However, maintaining the discharge power for R2S2 and R2S3 required a slight voltage increase overtime, contrarily to what was observed for R1S2 and R1S3. This increase could be explained by the accumulation of a dielectric layer of coating on the electrodes. Indeed, adding a dielectric layer on the electrodes means that among the total voltage applied to the system, a part will be lost within the dielectric layer. This implies that to maintain a constant discharge power, a higher total voltage should be applied. This could also involve a change in the discharge homogeneity and hence a different coating, which will be evaluated in the next section.

3.3. Surface characterization

Once treated, the polymer films were analyzed using contact angle measurements to compute the surface energy and their surface chemical composition were determined by XPS analyses.

3.3.1. Contact angle and surface energy

Fig. 4 B shows the evolution of the surface energy throughout the process. Comparison between the untreated FEP surface energy values (dashed line of Fig. 4B) and those of the treated polymer films shows that a treatment indeed happens on the polymer surface. Overall, both the polar and dispersive components of the polymer surface energy show no significant change during the process. Greater uncertainties are observed on the measurement made between R1S1 and R1S2. Similarly to the voltage drop observed between R1S1 and R1S2, such larger errors observed soon after the beginning of the treatment are expected because the plasma discharge requires some time to stabilize. However, once the discharge is stable, all measurements demonstrate that the treatment remains fairly identical over time. This indicates that, despite the formation of a thin dielectric layer on top of the electrode, adjusting the voltage to maintain a constant discharge power enables to prevent treatment variations in terms of surface energy. For production purposes, one should consider (i) maintaining the discharge power of the process constant (ii) discarding the first few minutes of deposition to enable the plasma process to reach a steady state.

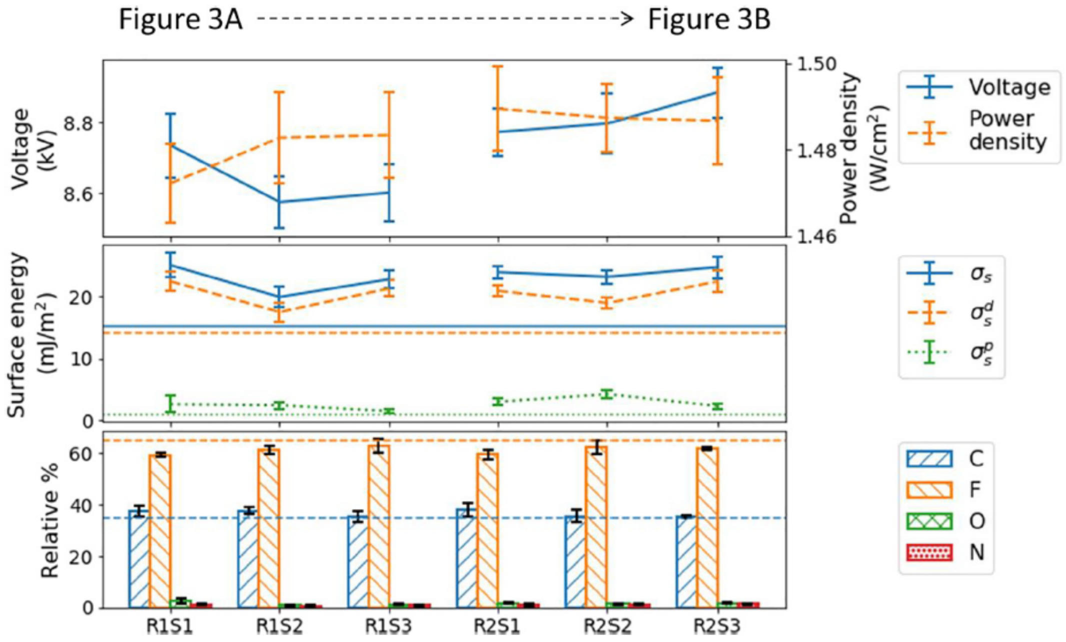

Fig. 4. A) Electrical characteristics of the discharge measured in-situ. B) Surface energy obtained using Fowkes theory with water and diiodomethane. σ_s^d = dispersive component, σ_s^p = polar component and $\sigma_s = \sigma_s^d + \sigma_s^p$ (total surface energy) for the treated and untreated (straight lines) FEP. C) Evolution of the Carbon, Fluorine, Oxygen and Nitrogen concentration at the surface of the treated film. The left hand side of the figure is related to Fig. 3A, where the electrodes are still clean, while the Fig. 3B represents the end of the one hour treatment, on the right hand side of Fig. 4.

3.4. X-ray photoelectron spectroscopy

The bar graph of Fig. 4C shows the difference in term of surface chemistry of all polymer film sections investigated during the plasma treatment process. Because the polymer used is FEP (initial values of carbon and fluorine showed as dashed lines), and the organic precursor is composed of carbon and oxygen carried by a N_2 flow, the elemental composition of the surface reveals the presence of carbon, fluorine, oxygen and nitrogen. Again, it can be noticed that R1S1, and R2S1 to some extent, present more oxygen and nitrogen at their surface than the other films, due to the aforementioned lower stability of the discharge at the beginning of the treatment cycle. Moreover, oxygen remaining species are more likely to be present in the gas feed at the beginning of the treatment cycle. However, once stabilization is achieved, a constant atomic concentration throughout the cycle is observed. These observations support the fact that it should be considered to discard the polymer film that was treated during the first few minutes of the process. This initial treatment could also be done in static or at a much slower line speed to save material.

4 CONCLUSION

Experiments were performed to assess if any difference was observed in terms of the surface chemistry of a FEP film at the beginning versus the end of a 1-hour surface plasma treatment, due to the deposition of a layer on the high-voltage electrode, that was not covered by the material to be treated. This was ascertained by monitoring both the plasma electrical characteristics and the surface chemistry of a treated polymer film.

The plasma electrical characteristics, such as the power density and the voltage used were measured during the process. To keep the power constant, the voltage had to be adjusted all along the plasma treatment process, which means that the continuous layer building-up on the electrode started modifying the dielectric characteristics of the DBD assembly. A stronger variation should be observed when using longer treatment time and/or higher deposition rate of the coating.

The polymer surface energy was then calculated using the Fowkes theory with data from contact angle measurements with drops of water and diiodomethane. Measurements made throughout the process showed no significant difference in terms of surface energy. Finally, XPS results showed that the surface chemistry of the film also stayed constant during all the process, in agreement with the surface energy calculations.

To conclude, no significant change was observed in terms of surface chemistry of the treated film after a treatment duration of 1 h, even if the continuous layer deposition occurring at the surface of the high-voltage electrodes was evidenced by a modification of the electrical properties. Additional studies would require semi-industrial electrodes equipped with a cooling system to avoid overheating of the treated film while evaluating longer process duration. Indeed, determining at which point the coating accumulation becomes problematic in terms of film quality and evaluating if more batches could be produced before electrode cleaning would be highly relevant to the plasma industry, since it could potentially save process time while maintaining the quality of their treatment. For instance, in the case of the present study, the coating becomes thick enough after one hour and causes drips that create either contact between the polymer film and the electrode creating a short circuit or burning the film. The time at which such phenomenon appears would depend on each reactor size and configuration.

DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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REFERENCES

[1] Tendero C, Tixier C, Tristant P, Desmaison J, Leprince P. Atmospheric pressure plasmas: a review. Spectrochim Acta Part B 2006;61(1):2–30.

[2] Yasuda H. Plasma for Modification of Polymers. J Macromol Sci Part A Chem 1976;10(3):383-420.

[3] Massines F, Sarra-Bournet C, Fanelli F, Naudé N, Gherardi N. Atmospheric pressure low temperature direct plasma technology: status and challenges for thin film deposition. Plasma Processes Polym 2012;9:1041–73.

[4] Nisol B, Ghesquière J, Reniers F. Easy synthesis of ageing-resistant coatings with tunable wettability by atmospheric pressure plasma. Plasma Chem Plasma Process 2016;36:1239–52.

[5] Vallade J, Turgeon S, Laroche G. Partial least-squares regression as a tool to predict fluoropolymer surface modification by dielectric barrier discharge in a corona process configuration in a nitrogen–organic gaseous precursor environment. Ind Eng Chem Res 2018;57:7476–85.

[6] Saint-Gobain Performance Plastics. FEP-FG general purpose; 2020. https://www.films.saint-gobain.com/products/chemfilm/fep-films/fep-fg [accessed February 2020].

[7] Pipa AV, Koskulics J, Brandenburg R, Hoder T. The simplest equivalent circuit of a pulsed dielectric barrier discharge and the determination of the gas gap charge transfer. Rev Sci Instrum 2012;83(11):115112.

[8] Fowkes FM. Attractive forces at interfaces. Ind Eng Chem 1964;56:40–52.

[9] Rulison C. So you want to measure surface energy? Technical note TN306e; 1996.