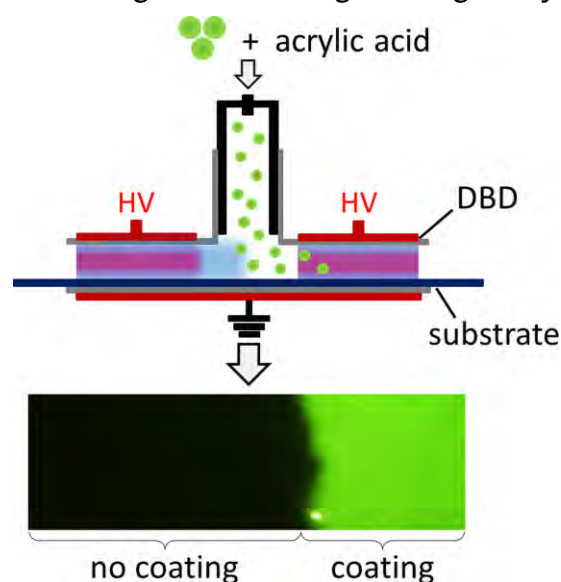


# Incorporation of Fluorescent Dyes in Atmospheric Pressure Plasma Coatings for In-Line Monitoring of Coating Homogeneity

Wesley Somers,\* Marjorie F. Dubreuil, Erik C. Neyts, Dirk Vangeneugden, Annemie Bogaerts

This paper reports on the incorporation of three commercial fluorescent dyes, i.e., rhodamine 6G, fluorescein, and fluorescent brightener 184, in plasma coatings, by utilizing a dielectric barrier discharge (DBD) reactor, and the subsequent monitoring of the coatings homogeneity based on the emitted fluorescent light. The plasma coatings are qualitatively characterized with fluorescence microscopy, UV-vis spectroscopy and profilometry for the determination of the coating thickness. The emitted fluorescent light of the coating correlates to the amount of dye per area, and deviations of these factors can hence be observed by monitoring the intensity of this light. This allows monitoring the homogeneity of the plasma coatings in a fast and simple way, without making major adjustments to the process.



## 1. Introduction

Low-temperature plasma technology offers an interesting alternative to more standardized coating processes, such as dip-coating procedures and plasma sprays.<sup>[1–3]</sup> Besides its unique and efficient way to enhance the surface properties, it is also more environmental friendly than the alternative processes, which involve solvents and/or higher energy consumption. Various functionalized coatings, such as

superhydrophilic and bioactive coatings can be made through plasma processing.<sup>[4–10]</sup>

Furthermore, atmospheric pressure plasma is also suitable for use in continuous coating processes, such as the food packaging industry, in which framework this study has been carried out. One of the major difficulties, however, lies in the characterization of these ultrathin (with a thickness range in the order of 10–250 nm) plasma coatings. In particular, the monitoring of the coating homogeneity in terms of thickness of the coating remains a challenge. Many characterization techniques can be used at a lab-scale level, but in-line characterization of the coating quality and its properties, without interfering with the coating process, is an important issue in industrial environments.

The coating thickness can in principle be measured with the quartz crystal microbalance (QCM) technique, in which the resonance frequency of the quartz crystal is dependent

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on the amount of material on it.<sup>[11,12]</sup> However, small variations in temperature, which are likely to occur in a plasma, also influence the resonance frequency. With broadband optical monitoring (BOM) systems, which involve reflection and transmission of incident light, additional information about the coating properties is obtained.<sup>[13]</sup> With this technique, the reflectance and transmittance are measured as a function of the wavelength, and information about the film thickness and the refractive index is deduced from the spectrum. In order to measure the transmittance, transparent coatings or substrates are required. However, this requirement limits the applicability. Furthermore, this technique is mainly used in vacuum batch processes, but is less favored in continuous processes, such as atmospheric pressure in-line plasma treatments.

An interesting alternative is the incorporation of fluorescent dyes in the plasma coating, as fluorescence can be used to characterize the coating homogeneity. Previously, Gharaibeh et al.<sup>[14]</sup> demonstrated the use of such dyes to detect defects in coated surfaces with fluorescence emission. The non-solvent based coatings consisted of two parts: a primer and a hardener for curing the primer. The coatings were either formed with a drawdown blade, or with an airless spray gun. A cautionary remark is that the fluorescent dye was directly added to the primer part of the coating, which has a small risk of breaking down the fluorophore group of the dye. This is in contrast to the incorporation of the dye by using atmospheric plasma technology, where the high reactivity of the plasma might decompose the fluorescent dye, and thus, eliminate the fluorescence effect. Furthermore, the presence of the dye in the plasma coating should not influence the properties of the coating.

In this work, we demonstrate for the first time the incorporation of fluorescent dyes in acrylic acid-based plasma coatings, utilizing a dielectric barrier discharge (DBD) reactor, as a new tool for monitoring the homogeneity of plasma coatings in a continuous process.

## 2. Experimental Section

### 2.1. Plasma Reactor

The experiments were carried out in a parallel plate DBD reactor, as shown in Figure 1.<sup>[6]</sup> Both top stainless steel electrodes are covered with an insulating glass plate of 3 mm thick. The bottom electrode, also made of stainless steel, is covered with a thin metallized polyethylene terephthalate film. The gap between the electrodes was limited to 2 mm to ensure stable plasma operation.

The discharge was generated using a nitrogen gas flow of 20 standard liter per minute (slm), a voltage of 35–40 kV, a frequency of 1.5 kHz and a dissipated power density of  $0.8 \text{ W cm}^{-2}$ , corresponding to a total power of 490 W. These values for the

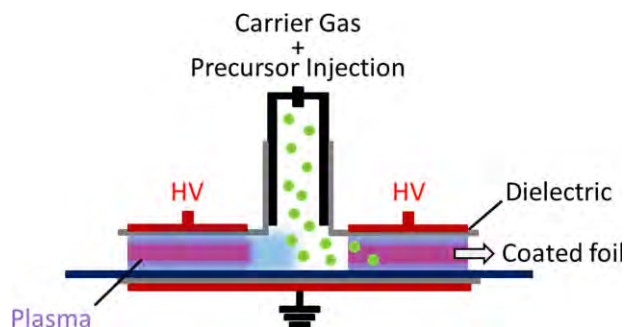


Figure 1. Schematic diagram of the parallel plated DBD reactor.

process parameters resulted in a homogeneous discharge, which is necessary to obtain a homogeneous coating. Liquid chemical precursors were nebulized with an atomizer (TSI model 3076) to produce a fine aerosol, which is added to the plasma. The nitrogen gas flow in this aerosol generator was 3 slm. This type of atomizer is capable of generating submicrometer aerosols. Measurements of the droplet sizes of an (3-aminopropyl)triethoxysilane (APTES) aerosol with a particle size analyzer (TSI model 3080) confirmed the submicrometer range of the atomizer, which has a nozzle diameter of 0.5 mm. The droplet size was distributed between 10 and 200 nm with a maximum concentration around 50 nm. These measurements were performed for a distance range of 20–40 cm from the nebulizer, and no significant differences were found.

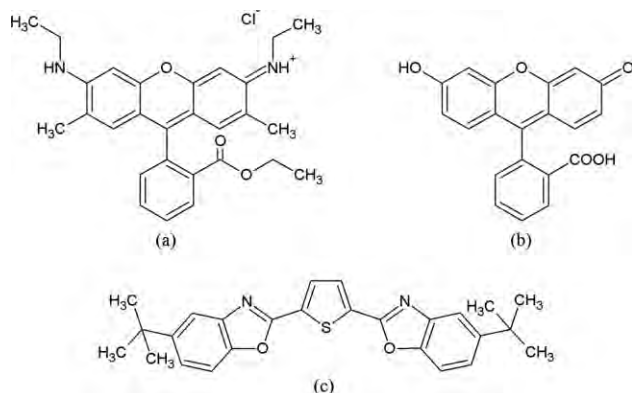
The low particle size generated by the atomizer ensures optimum reaction conditions in the plasma. The plasma treatment time was varied between 5 and 216 s. Prior to coating deposition, an activation step of the substrate was carried out during 4 s under similar conditions, with a nitrogen flow of 20 slm.

### 2.2. Materials

Three fluorescent dyes were selected: rhodamine 6G (R6G), fluorescein (FL), and fluorescent brightener 184 (FB184), which exhibit different absorption and emission characteristics (see Table 1). Their chemical structure is given in Figure 2. They were purchased from Acros Organics, Sigma-Aldrich, and ABCR, respectively, and used as received. These dyes are dissolved in acrylic acid and injected into the plasma zone as an aerosol. More information about the concentrations of the precursor solutions is given in the results section. Acrylic acid was purchased from Alfa Aesar and used without any further purification. Two types of substrates were used for this study: glass microscope slides for

Table 1. Absorption and emission wavelengths of the three fluorescent dyes.

Dye	$\lambda_{\text{abs}}$ [nm]	$\lambda_{\text{em}}$ [nm]	Refs.
R6G	530	590	[15,16]
FL	440–480	515	[17]
FB184	374	435	[18]



**Figure 2.** Chemical structure of: a) rhodamine 6G (R6G), b) fluorescein (FL), and c) fluorescent brightener 184 (FB184).

thickness measurements and low-density polyethylene-coated paper obtained from Sappi Netherlands for other characterization measurements.

### 2.3. Characterization

The plasma coatings were qualitatively characterized with fluorescence microscopy, profilometry and UV–vis spectroscopy.

A Leica fluorescence microscope was used to determine the fluorescence intensity of the plasma coatings. Three types of filter blocks (TX, I3, and A) composed of an excitation filter, a dichroic mirror, and emission filter were used to irradiate the coatings with the correct wavelength and to detect the fluorescent light from each specific dye. The fluorescence images were taken with a DeltaPix camera. The exposure time was mostly kept constant to allow for a proper comparison between the samples. Only when the image was too dark, due to a low dye concentration, the exposure time was increased. This equipment did not allow us to measure the fluorescence intensity quantitatively.

The coating thickness was analyzed using a WYKO NT3300 surface profiler in phase-shifting (PSI; resolution: 3 Å) or vertical scanning mode (VSI; resolution: 3 nm) on glass plates. The precision is 0.1 μm in {x,y} directions and 0.01 nm in the z-direction. Due to light absorption, it was not possible to directly measure the coating thickness on the paper substrate. Therefore, during the plasma experiments, a glass plate was coated under the same conditions as the paper sample and used to determine the thickness of the deposited coating. The thickness measurements were performed using the peak-to-peak method, taking into account surface statistics for separated regions.

The UV–vis spectra were taken with a Perkin-Elmer Lambda 900 UV–vis/NIR spectrometer, over a wavelength range of 300–800 nm and with an accuracy of ±0.08 nm. These measurements were performed on the coated glass slides.

## 3. Results and Discussion

It should be kept in mind that the use of a fluorescent dye in a plasma coating is not straightforward. The dye has to be

compatible with the targeted precursor, and to a certain extent be soluble in this precursor. Furthermore, it should not drastically influence the coating properties, nor the precursor reactivity in the plasma. However, the most challenging parameter remains the conservation of the fluorescence properties, i.e., the emission of fluorescent light, after reactions in the plasma. Indeed, very reactive species are present in the plasma (ions, electrons, excited molecules, radicals, ...), which lead to fragmentation reactions of the introduced precursor. As the fluorescence of the dyes is due to their particular structure, too severe plasma conditions could lead to a (at least partial) destruction of the dye structure, and the loss of its fluorescence.

In the first two parts of this section, we investigate the conservation of the fluorescence properties of the dyes in the plasma coatings, as a function of the precursor solution concentration and of the treatment time. Furthermore, suitable characterization techniques for proper monitoring of the coatings are determined. In the third part of this section, the effect of dye addition to the precursor solution on the coating growth rate is investigated. In the final part, the use of the fluorescent dyes for monitoring the homogeneity of the plasma coating is discussed.

### 3.1. Influence of Precursor Solution Concentration on Fluorescence Properties of the Plasma Coating

The effect of precursor solution concentration on the fluorescence properties of the plasma coatings was investigated for the R6G dye, since it has the highest solubility in acrylic acid (see the next section), allowing to vary the concentration over a wider range. Three precursor solutions of R6G in acrylic acid were prepared, with concentrations of 0.44, 1.68, and 3.00 g L<sup>-1</sup>.

After treatment times of 54 and 108 s, a pink/red colored plasma coating is formed for each case, which is an indication of the successful incorporation of the fluorescent dye. Table 2 summarizes the obtained coating thickness for four measurements, i.e., for the three different precursor solution concentrations with a treatment time of 108 s, as well as for a treatment time of 54 s, in the case of the middle precursor solution concentration. This last measurement was performed in order to determine whether the concentration was high enough to detect the dye in thinner coatings. The UV–vis spectra of the different coatings are given in Figure 3. The plasma coatings formed with the two highest precursor solution concentrations (PC1–PC3) have a small absorbance peak at a wavelength of 533 nm, corresponding to the presence of R6G. Furthermore, a very weak signal of the dye is observed in the spectrum of PC4, corresponding to the lowest precursor solution concentration. Considering that the

**Table 2.** Coating thickness of four R6G containing plasma coatings, as a function of the precursor solution concentration and the treatment time.

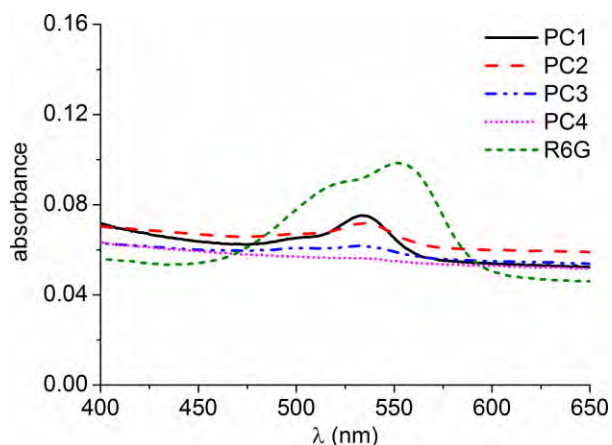
Plasma coating nr.	Precursor solution concentration [g L <sup>-1</sup> ]	Treatment time [s]	Coating thickness [nm]
PC1	3.00	108	172
PC2	1.68	108	164
PC3	1.68	54	87
PC4	0.44	108	158

coating thickness of PC4 is only 14 and 6 nm lower than that of PC1 and PC2, respectively (see Table 2), the weak signal in PC4 can be attributed to the low concentration of the dye in the plasma coating. The R6G concentration in the plasma coatings can be estimated by using Equation (1), in which  $A$  is the absorbance,  $l$  is the coating thickness (in cm), and  $\epsilon$  is the extinction coefficient (here  $\epsilon = 116\,000\text{ M}^{-1}\text{ cm}^{-1}$ )

$$c = \frac{A}{l\epsilon} \quad (1)$$

Multiplying the obtained molar concentration with the molar mass of R6G, i.e.,  $479\text{ g mol}^{-1}$ , gives concentrations of 3.84, 2.27, 1.90, and  $0.52\text{ g L}^{-1}$  for PC1, PC2, PC3, and PC4, respectively. These values show that the dye concentration in the coating is higher than in the precursor solution. This indicates that the dye has a higher probability of surviving the deposition process than acrylic acid, possible due to evaporation of the latter.

The importance of the concentration of the precursor solution is further illustrated by the fact that R6G is



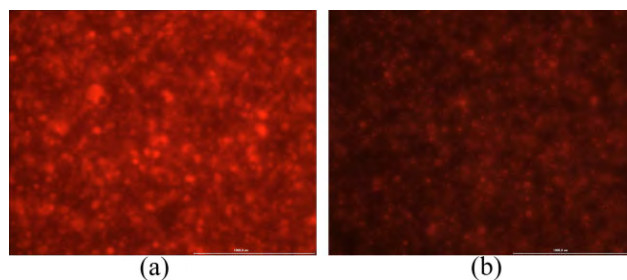
**Figure 3.** UV-vis spectra of four plasma coatings with incorporated R6G (PC1–PC4), and of R6G dissolved in acrylic acid. The meaning of PC1–4 is explained in Table 2.

detected in PC3. This coating is much thinner than the other coatings, since the treatment time is reduced by a factor of 2, but the concentration of the dye is sufficiently high to observe an absorbance signal. We conclude that the concentration of the precursor solution mainly influences the concentration of the dye in the coating, and not the coating thickness, which is mainly determined by the treatment time, as shown in Table 2 and further discussed in the following section.

The UV-vis spectrum of PC4 shows only a very weak signal of R6G, as discussed above. However, under a fluorescence microscope, the dye still emits enough fluorescent light for proper detection. Furthermore, comparison between PC1 and PC2 shows a clear difference in concentration between both coatings (see Figure 4), as the emitted fluorescent light of PC1 is more intense. This observation is verified by the UV-vis spectra, since the estimated concentration of PC1 is higher than that of PC2. Likewise, for the other plasma coatings containing R6G that were investigated, the dye is observed with fluorescence microscopy, and the intensity of the emitted fluorescent light is proportional to the dye concentration in the plasma coating and the coating thickness, i.e., the amount of dye per area. This method is thus very suitable for monitoring the plasma coatings, since even low dye concentrations can be detected and a proper comparison between the dye concentrations in different plasma coatings, with a similar coating thickness (see Figure 4) is possible.

### 3.2. Influence of Treatment Time on Fluorescence Properties of the Plasma Coating

When comparing the three different dyes, it was found that they have a different solubility in the precursor solution. Indeed, the maximum concentration of FL was only  $0.75\text{ g L}^{-1}$ , while FB184 dissolves better, up to  $1.30\text{ g L}^{-1}$  and the highest solubility was obtained for R6G, with a maximum concentration of  $3.00\text{ g L}^{-1}$  (see above). As the results for R6G were discussed in detail in the previous section, we here focus on the two other dyes to discuss the

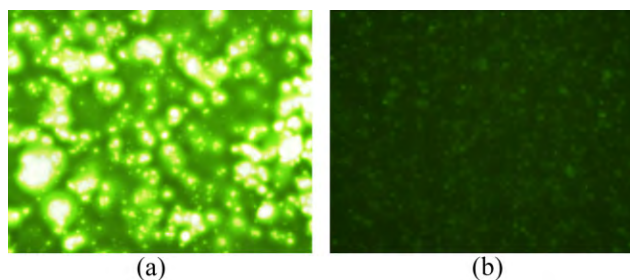


**Figure 4.** Fluorescence images of (a) PC1 and (b) PC2, obtained with R6G concentrations in the precursor solution of 3.00 and  $1.68\text{ g L}^{-1}$ , respectively.

influence of the treatment time on the fluorescence properties of the plasma coating.

In both cases, the precursor solutions were injected in the plasma zone for treatment times ranging from 27 to 216 s. After a treatment time of 27 s, the plasma coating deposited from the FL precursor solution has no characteristic yellow color. For longer treatment times, on the other hand, this color is clearly observed. Even though the presence of the dye is obvious, the UV-vis spectra of these coatings have no absorbance peaks that can be attributed to FL. Apparently, the concentration is too low for UV-vis detection of the dye. For FB184, a treatment time of at least 81 s is required to have a plasma coating with a characteristic shiny white color. Additionally, UV-vis spectroscopy is, again, not capable for detecting the dye in the plasma coating. Hence, we can conclude that this technique is only of limited value for the monitoring of plasma coatings with incorporated dyes. Indeed, the applicability of UV-vis spectroscopy is dye specific, since it was only possible to detect one of the three dyes, namely R6G, in the plasma coating.

It turns out that an accurate comparison between the plasma coatings with incorporated FL or FB184 is only possible with fluorescence microscopy, since the intensity of the emitted fluorescent light is proportional to the amount of dye per area. Even at treatment times of 27 s, fluorescence activity is observed while the coating is visually completely transparent. A comparison between two FL containing plasma coatings, after treatment times of 81 and 216 s, is made in Figure 5. For both images, the same exposure time was used to allow a proper comparison. The plasma coating formed after 81 s emits little fluorescent light, while the fluorescent signal of the other plasma coating is very intense. This indicates that the plasma coating formed after 216 s is thicker, and thus contains more dye. The FL detection in coatings, formed after shorter treatment times, is also possible, but requires a higher exposure time for a clear fluorescent signal. The same observations are made for the plasma coatings with incorporated FB184. Again, a higher exposure time is



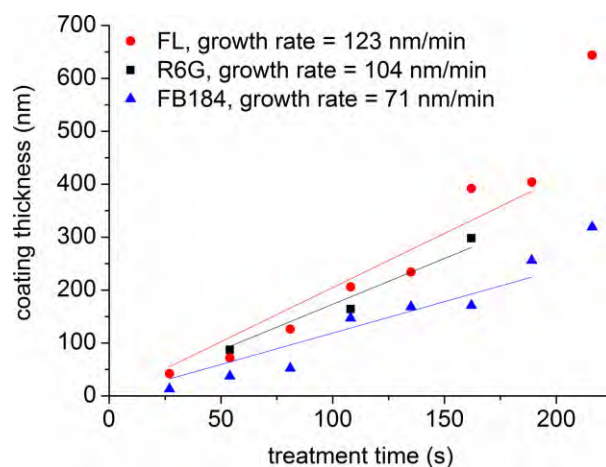
**Figure 5.** Fluorescence images of plasma coatings with incorporated fluorescein (with precursor solution concentration of  $0.75 \text{ g L}^{-1}$ ), after treatment times of (a) 216 s and (b) 81 s.

needed to analyze the plasma coatings formed after shorter treatment times (i.e., 27–81 s).

### 3.3. Influence of the Dye on the Plasma Coating Growth Rate

As discussed above, the fluorescence properties, i.e., the emission of fluorescent light, of the dye are maintained during the coating procedure, which illustrates that this method of including dyes in the precursor solution is promising for coating homogeneity monitoring. In this section, we investigate the effect of the dye in the precursor solution on the coating growth rate. Figure 6 shows the measured coating thickness as a function of treatment time for the three different dyes. The average growth rates of the plasma coatings are 123, 104, and  $71 \text{ nm min}^{-1}$  for the precursor solutions of FL, R6G, and FB184, respectively. This is lower than the growth rate of a pure acrylic acid solution, which was found to be  $139 \text{ nm min}^{-1}$ . This clearly indicates that the dye affects the coating thickness, especially for FB184, for which this effect is quite significant (reduction by a factor of 2). Note that for longer treatment times, the linear character of the growth rate for the FL coatings tends to become exponential. However, this only occurs for treatment times above 200 s, which is quite long, certainly for continuous industrial processes. Therefore, the average growth rates are calculated over the first 200 s, to make a valid comparison between the three dyes.

The difference between the growth rates of the plasma coatings is related to the reactivity of the precursor solutions. Acrylic acid has oxygen-containing end-groups, which are more reactive than the alkyl end-groups that are present in the structure of the dyes. Furthermore,



**Figure 6.** Coating thickness of the plasma coatings with the three different dyes, as a function of treatment time. The concentration of the dye in the precursor solution is  $0.75 \text{ g L}^{-1}$  for FL,  $1.68 \text{ g L}^{-1}$  for R6G and  $1.30 \text{ g L}^{-1}$  for FB184. The slope of the full lines is used to calculate the average growth rate, as mentioned in the legend.

the conjugated systems in the dye structures increase the number of pathways for dissipating the energy of the plasma compared to the pure acrylic acid precursor solution. This will influence the efficiency of the discharge on the coating growth rate. From the three selected dyes, FL has most oxygen-containing groups, whereas FB184 has most methyl end-groups (see Figure 2), and is thus less reactive, as follows indeed from the average growth rates illustrated in Figure 6.

The fact that the dyes affect the coating growth rate might have consequences for practical applications. Indeed, this means that longer growth times are needed for the same coating thickness, if dyes are incorporated. However, this is the only process parameter that needs to be changed due to the incorporation of the dyes, and the required treatment time for each specific coating thickness can be derived from the coating growth rate. It should be mentioned that the incorporation of fluorescent dyes in the plasma coating possibly might also influence other coating properties, such as the hardness and hydrophilicity, although these properties are not determined here, as other characterization techniques would be required for this purpose. A more practical aspect that should also be taken into account is the coloring effect of the dye on the equipment. This requires cleaning of certain parts of the equipment if different precursor solutions are used. For instance, the nebulizer needed to be rinsed before a new precursor solution was used, to prevent contamination by the previous one.

We draw the same conclusions for coatings based on a hydrolyzed glycidoxypopyl trimethoxysilane (GLYMO) solution, synthesized through a sol-gel process and received from Fraunhofer ISC. Again, addition of the fluorescent dyes to the precursor solution decreases the growth rate of the plasma coating, so longer treatment times are required. Furthermore, preliminary experiments with UV-active components, namely anthracene, naphthalene, and 1,3-butadiene, showed similar results as for the fluorescent dyes, indicating that a variety of molecules can be incorporated in the plasma coatings.

### 3.4. Incorporation of Fluorescent Dyes as Plasma Coating Monitoring Tool

Usually, quality controls of plasma-based coatings have to be carried out off-line, which implies a delayed intervention in case of problems. The successful incorporation of fluorescent dyes in plasma coatings opens new perspectives for monitoring of the coating homogeneity. This monitoring tool can be used in processes with homogeneous discharges, since (quasi) equal local plasma conditions over the entire discharge are required to maintain the same dye concentration all over the coating. If there is a deviation in one of the process parameters (e.g., frequency,

power, ...) during a coating procedure, this will affect the discharge, and hence the dye concentration in the coating and/or the coating thickness. This deviation is then evaluated by monitoring the intensity of the emitted fluorescent light. In case of an inhomogeneous coating, as illustrated in Figure 7, the absence of the dye (and plasma coating) leads to a dark region, while the bright fluorescent region represents the presence of the coating.

For processes with a homogeneous plasma that use a fixed treatment time and thus have coatings with similar thicknesses (see PC1–PC3), deviations in the precursor solution concentration and/or dye concentration in the plasma coating change the fluorescence intensity, as previously discussed and shown in Figure 4. The higher intensity for PC1 is due to the higher dye concentration in the coating, while the coating thickness is almost the same as that of PC2. Deviations in the treatment time will lead to an altered coating thickness and dye concentration, which is also detected under the fluorescence microscope, as shown in Figure 5.

It should, however, be mentioned that on a microscopic scale, some regions might have a higher intensity than others, as was illustrated in Figure 4 and 5. This suggests that the dyes seem to agglomerate in clusters. This effect could be due to the evaporation of the volatile acrylic acid and precipitation of the nonvolatile dye. This might influence the fluorescence yield in an unpredictable way because the clusters are expected to have a fluorescence yield different from that of molecularly dissolved dyes. However, despite the small fluctuations in intensity under the microscope, no deviations in the visible color of the coatings are observed. Possibly, the use of a spectrometer to quantify the emitted fluorescent light can determine the extent of these deviations, and clarify whether they induce large measurement errors or not. Nevertheless, Figure 7

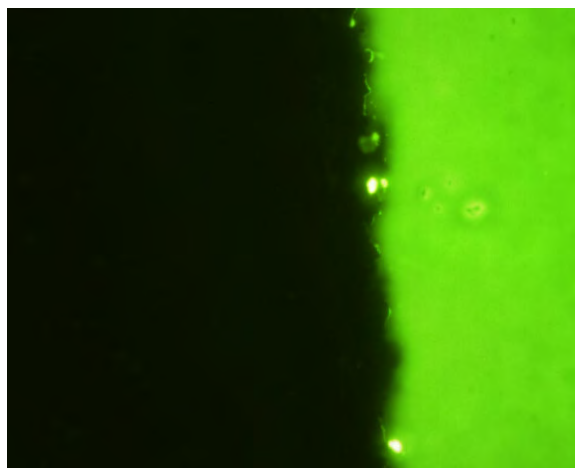


Figure 7. Fluorescence image of a plasma coating with incorporated fluorescein (with precursor solution concentration of  $0.75 \text{ g L}^{-1}$ ). The dark region does not contain a coating.

illustrates the potential use of incorporated fluorescent dyes in plasma coatings, in order to evaluate the coating homogeneity.

#### 4. Summary and Conclusions

We have illustrated the successful incorporation of fluorescent dyes in plasma coatings, utilizing a DBD reactor. Indeed, the fluorescent properties of the dyes are maintained throughout the coating procedure. The presence of the three fluorescent dyes, i.e., R6G, FL, and FB184, in the plasma coatings is clearly observed with fluorescence microscopy, which is demonstrated to be a suitable technique for homogeneity monitoring. Indeed, the fluorescence intensity is proportional to the amount of dye per area. Even for low plasma treatment times (below 10 s), a clear fluorescent image is obtained. In this work, the intensity of the emitted fluorescent light could not be quantified with a spectrometer, because our equipment was not suitable for such measurements. This would be an important added value to the applicability of this process. Characterization with UV–vis spectroscopy, on the other hand, is shown to be dye specific, since only R6G could be detected with this technique.

We have varied the precursor solution concentration and treatment time to investigate their influence on the coating characterization capability. When increasing the precursor solution concentration, while keeping the treatment time constant, the coating thickness hardly changes. However, a higher dye concentration in the plasma coating is obtained, and thus the detectability of the dye is improved. The solubility of the different dyes in the precursor solution, however, appeared to be very different. If the intensity of the emitted fluorescent light of a plasma coating formed with a highly concentrated precursor solution is not high enough, longer treatment times are required. This increases the coating thickness, and as a consequence, the total number of dye molecules in the plasma coating.

We can conclude that the incorporation of fluorescent dyes in plasma coatings allows evaluating the homogeneity of the coating by monitoring the intensity of the emitted fluorescent light. This is a fast and easy

qualitative characterization method, which moreover does not require major adjustments to the process.

**Acknowledgments:** The authors wish to thank the support of the European Commission through the FP7 program PlasmaNice (FP7/2007-2011, grant agreement n°211473) in which framework this study has been carried out. The authors acknowledge also Dr. Klaus Rose and Dr. Katrin Bokelmann from Fraunhofer ISC for providing the hydrolyzed solutions, and Ronald van de Laar from Sappi for providing the substrate.

Received: November 18, 2013; Revised: March 27, 2014; Accepted: March 28, 2014; DOI: 10.1002/ppap.201300178

**Keywords:** acrylic acid; dielectric barrier discharges (DBD); fluorescent dyes; homogeneity monitoring; plasma coating

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