Characterization of the Atmospheric DC Glow Discharge

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Abstract
The atmospheric pressure DC glow discharge is a new approach for the surface treatment of polymer films. The active species (mainly O, O₃, N₂⁺, OH) formed in the plasma have been characterized by optical emission spectroscopy and wet-chemical reactions downstream with different solutions. In the paper we will report how the discharge power and the water concentration effect the formation of these species. The influence of water vapor is of particular interest because water was found to suppress the formation of ozone without reducing the treatment efficiency.

1. Introduction
The general setup of the atmospheric pressure DC glow discharge [i] (APGD) is shown in Figure 1. The plasma is generated by applying a high voltage between an anode and a multi-pin cathode which are passed by a high flux of air. First of all the air flow removes charge carriers from the plasma zone to prevent the formation of sparks. Secondly, it transports the chemically active species (mainly O, O₃, N₂⁺, OH) to the surface of the polymer film. The formed plasma is almost as homogeneous as a low pressure glow discharge. Its high power density up to 30 W/cm² allows the generation of a comparably high concentration of active species. We have presented the main parameters (i.e. electric power, gas velocity, gas temperature, treatment time) of this discharge and their effect on the surface oxidation of PE films in a recent paper [ii]. The greatest benefit of the APGD is its high power density. Therefore it produces a much higher concentration of active species which should lead to an efficient activation of polymer foils and textiles at high web speed. Recent experiments have shown that this does not happen. So the necessity arises to understand the complex process in more detail. A first step is the characterization of the active species which are produced within the plasma.
2. Methods

Optical emission spectroscopy (OES) and wet-chemical reactions of different solutions with the downstream air have been used for the characterization of the active species.

**OES**
The OES measurements have been carried out for the determination of atomic oxygen and hydroxyl radicals within the plasma zone.

**Wet-chemical reactions**
This method uses the fact that the active species can be bound by a wet-chemical reaction. Therefore, the downstream of the plasma is led by a hose into a gas washing bottle with a special solution.

One solution is prepared from potassium iodide and starch in water. The iodide ions can be oxidized to iodine which forms a blue complex with the starch molecules. This reaction is known for its capability to detect very small concentrations of iodine up to $10^{-5}$ N [iii]. Therefore, the potassium iodide starch solution is a sensitive indicator for oxidizing particles. The color change of the solution can be measured by UV-Vis spectroscopy. For the quantitative analysis of the concentration a calibration curve can be recorded by titration with a sodium thiosulphate solution. The reaction of iodide ions with ozone molecules runs as follows:

$$O_3 + 2I^- + H_2O \rightarrow O_2 + I_2 + 2OH^-.$$ 

The potassium iodide starch solution has been used for the detection of oxidizing particles namely atomic oxygen, hydroxyl radicals, and ozone. In a two-stage process it is possible to measure separately the concentrations of the radicals and ozone molecules. Therefore, the first stage is formed by a solution of galvinoxyl, a free radical with comparably long lifetime. It is used as a radical scavenger because it reacts very fast with alkyl, alkoxy, and alkylperoxy radicals [iv]. Thus, it can be used for the detection of atomic oxygen and hydroxyl radicals. A possible reaction is shown in Figure 2. Because of the yellow color of the galvinoxyl solution, which is due to its unpaired electron, its consumption can be measured by UV-Vis spectroscopy. The second stage consists of the potassium iodide starch solution for binding the remaining ozone molecules.

3. Experimental

**OES**
The OES measurements have been carried out with a 0.2 meter monochromator/ detector by Verity Instruments. The fiber optic has been placed in front of the electrodes at a distance of about 0.1 m. The spectra have been taken in a range from 250 nm to 900 nm.
**Wet-chemical reactions**

For the preparation of the potassium iodide starch solution a 0.1 N potassium iodide solution was used. 50 ml of it were given into a gas washing bottle and 5 ml of a water based starch solution (1 vol%) were added. The stoichiometry of the reaction between ozone and iodide depends on the pH value [v]. Experiments have shown that this dependency is negligible for the absorbance measurements but not for the titration (Figure 3). For a quantitative titration the solution has to be neutral or slightly acidic [3]. So we usually adjusted the pH of this solution to about 6. The absorbance of the solution is stable for at least 6 hours.

For the galvinoxyl solution 1 mg galvinoxyl were dissolved in 100 ml xylene (~ 0.001 %). 30 ml of this solution were put into a gas washing bottle. Experiments have shown that the solution is stable for at least 3 hours. Due to the low vapor pressure of Xylene the loss of solvent during the experiment was negligible. Furthermore it can act as radical transmitter between the radicals and galvinoxyl.

The inlet of the gas washing bottle were connected to a hose of 0.4 m length which had been placed in front of the electrodes at a distance of less than 1 cm. In case of the two-stage process the second gas washing bottle was connected to the outlet of the first. All experiments lasted 30 s. The transit time of the active species was 20 ms for the single-stage process. For the two-stage process it was 30 ms (galvinoxyl solution) respectively 36 ms (potassium iodide starch solution). The transit time is defined as that time a particle takes from its formation to the place of the detection.

The water vapor was produced by an evaporator (Stritzel GmbH, Germany). Its amount of water vapor in the downstream has been calculated from the flow rate of the fan and the outlet of the evaporator on the basis of its maximum power.

For the spectroscopic measurements we used a Perkin Elmer Lambda 19 UV-Vis spectrometer using quartz cuvettes with a width of 10 mm.

For the calibration curve the potassium iodide starch solution was titrated with a 0.001 N sodium thiosulphate solution until the solution became colorless. This marks the end point of the titration, i.e. all iodine molecules are reduced to iodide ions.

4. Results

**OES**
A wide range spectrum of the air plasma (250 nm to 900 nm) shows the first and the second order of the second positive system of the nitrogen molecule (Figure 4). Measurements carried out with a set of filters eliminate the second order which is a disturbing effect of the monochromator diffraction. Unfortunately, a filter clearly reduces the intensity and the transmittance differs within the set. Besides the second positive system of nitrogen no other species have been found.

Figure 11: Optical emission spectrum of an air plasma at atmospheric pressure. The bands are due to the 1st and the 2nd order of the second positive system of N₂.

Figure 12: The optical emission spectrum shows no transitions due to atomic oxygen (arrows). All peaks are part of the 2nd order of the second positive system of N₂.

Atomic oxygen shows several transitions between 600 nm to 900 nm [vi] but none of them has been detected (Figure 5). Thus, an actinometric determination of atomic oxygen is not possible.

Wet-chemical reactions
The concentration of the oxidizing particles (single-stage experiment) as well as the concentration of ozone and the radicals (two-stage experiment) show an almost linear increase with rising discharge power (Figure 6). This is the result of the rising electrical field which yields a higher mean electron energy and thus more ionization and dissociation events. The concentration of the radicals is about one tenth of the ozone concentration. Since the half-life of the radicals at atmospheric pressure accounts to few μs, most of the atoms are converted into ozone. Thus, for a transit time of 30 ms the decay has progressed far.

The summation of the concentration values of the two-stage experiment (ozone + radicals, Figure 6) results in an approximately 50% smaller value than in the case of the single-stage experiment. This decline in concentration may be caused by the different transit times for the two setups. The concentration decreases with the time due to spontaneous decay, recombination, and reactions with other particles in the downstream. So this decrease is higher for the two-stage setup with transit times
of 30 ms respectively 36 ms than for the single-stage setup with a transit time of 20 ms. The
effect is probably caused by the radicals and not by ozone because its half-life time is about 3 d
at 20°C [5].
For a first approximation the dependency of the ozone concentration on the amount of water
vapor has been characterized by a single-stage experiment. This can be done without major
deviations because the active species in the downstream mainly consist of ozone (about 90
%). Figure 7 shows that the concentration of ozone is clearly reduced by an increasing
amount of water vapor.

5. Conclusions

OES
The small concentrations of atomic oxygen and hydroxyl radicals are not visible on the OES-
spectrum. Only the extremely strong emissions of the second positive system of N₂ were
detected.

Wet-chemical reaction
The concentrations of radicals and ozone molecules can be estimated by wet-chemical reactions.
An absolute quantification, however, is rather difficult. First, the half-life of radicals at
atmospheric pressure is short (few µs). The transit time of the gas in the wet-chemical setup is at
least 10 ms. At that time most of the radical decayed. Moreover, it is still unknown whether the
radical concentration in the downstream is affected by the generation within the plasma only. It is
quite possible that atomic oxygen is formed by dissociation of exited oxygen molecules during its
downstream travel [vii].

References

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