# Decontamination of polymer foils with a combined UV-plasma source at atmospheric pressure

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**Abstract**

Currently, polymer packaging is sterilised by chemical means like hydrogen peroxide or by hot steam. Thermally sensitive foils with thickness of few tens of µm may require efficient and environmentally friendly sterilisation processes which work with web speeds up to several meters per second. UV-emitting plasmas at atmospheric pressure generated in dielectric barrier discharges (DBD) show low working temperature of the plasma gas and can therefore be used for treatment of polymeric materials. By combination of a flat excimer UV source and a second plasma discharge gap, a cascaded dielectric barrier discharge (CDBD) set-up is built. The lower gap provides direct plasma exposure to the packaging foil and may be flowed by reactive or oxidative plasma gases. The efficient excimer UV source is emitting narrow-band UV light near to the packaging which results in high angles of incidence of the light. We compare spore reduction properties of “standard” DBD set-ups with one gap and of cascaded DBDs using different gas atmospheres. The CDBD showed to be more efficient in terms of treatment duration and power consumption compared to the “standard” barrier discharges.

## 1 Introduction

Dielectric barrier discharges are known for a long time and represent a effective way to create non-thermal plasmas at atmospheric pressure. Industrial applications for dielectric barrier discharges (DBD) range from generation of ozone to surface modification of plastic foils for better printing properties to generation of excimer UV light (Kogelschatz (2003)). There are various publications dealing with decontamination of substrates with low-pressure or atmospheric pressure plasmas (Moisan et al (2001)). Recently, the ap-

plication of plasmas for sterilisation of packaging foils was investigated (Feichtinger et al (2003)).

Polymer foils of different kind are commonly used as packaging material in the food processing sector. In aseptic packaging machinery the packaging and the food are sterilised separately and then brought together under sterile conditions. Packaging is usually sterilised by means of hydrogen peroxide, peracetic acid or by hot steam. The treatment duration is in the range of several seconds allowing output rates of some thousand packaging units per hour.

Sterilisation of polymer foils by dielectric barrier discharges is feasible as in this type of atmospheric pressure plasma several different inactivation pathways occur. The generation of UV light in the plasma is able to destruct cells by inducing strand breaks in the DNA due to a broad absorption maximum near wavelengths of 260nm. Impact of charged particles (electrons) may disrupt cells by generation of strong electric fields. Reactive particles created in the plasma, e.g. hydroxyl radicals, are able to attack cell membranes and will lead to cell inactivation via oxidative processes.

We have used standard dielectric barrier discharges with one discharge gap as well as a new type of discharge, the cascaded dielectric barrier discharge (CDBD), for sterilisation experiments.

## 2 Set-ups and Methods

### 2.1 Experimental DBD Set-ups

The standard DBD set-up for sterilisation of polymer foils is built into a closed housing (Fig. 1). It consists of an electrode system with gas supply and a moving carrier which holds the sample. Application of an AC high-voltage in the range of 5kV to 15kV leads to breakdown in the small gas gap between the alumina electrodes and the metal carrier with the sample. A mainly filamentary discharge plasma – composed of many individual discharge channels – is built up. Various gases (nitrogen, argon) can be fed into the system by a gas supply in between the two electrodes. The moving carrier is driven with a defined speed – up to 30m/min – through the discharge. The total energy input per unit area – the dose in J/cm² – can be determined by the number of passes through the discharge, the speed of the moving carrier and the power setting.

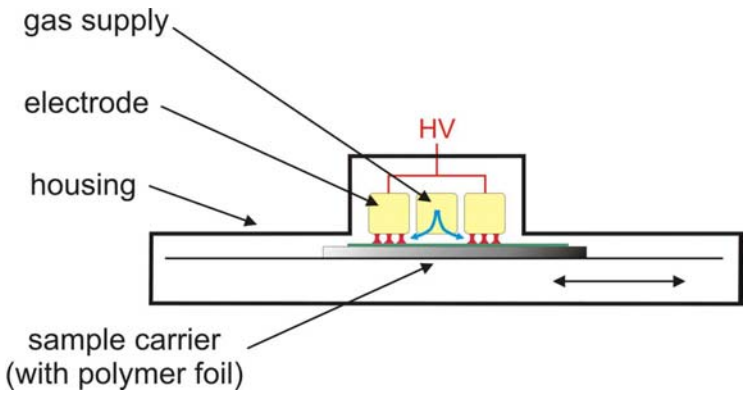



**Fig. 1** Sketch of standard DBD set-up in closed housing – two alumina electrodes are fixed next to a gas supply. Polymer foils (PET) are moved through the discharge with defined speed.

A cascaded dielectric barrier discharge is characterised by the fact that two separated discharge gaps exist which are separated by a UV-transparent dielectric. The gaps can be either flowed with two different gases, or, alternatively, the upper gap is made of an excimer flat lamp fixed in a distance of few millimetres above the ground electrode (Fig. 2). It has been shown that such an arrangement can be more homogeneous than a standard DBD with one gap and that more UV light is emitted (Heise et al. (2004))

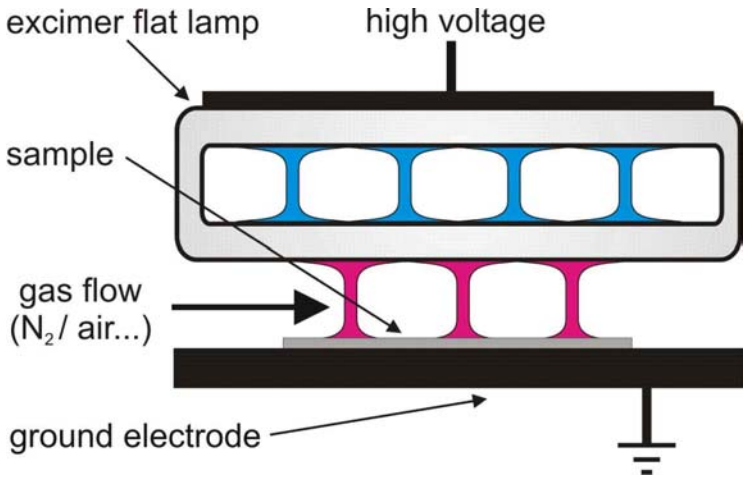
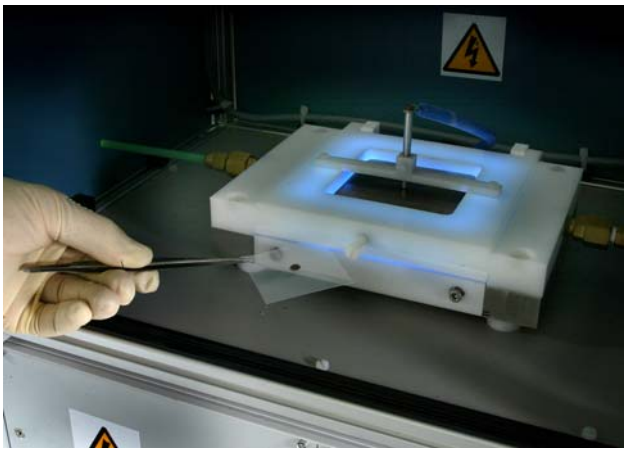



**Fig. 2** Sketch of cascaded DBD set-up with excimer flat lamp. The polymer sample is located in the lower gap which is flowed with a gas like nitrogen, oxygen or simply air.

Compact plasma devices were built which can be used in laminar flow benches in a microbiological lab and allow working under sterile environmental conditions. The reactors use the cascaded dielectric barrier discharge with excimer flat lamps at 282nm and 222nm wavelength respectively (Fig. 3). Flat samples up to 10cm x 10cm size can be treated. The intention is to perform so-called end-point tests with these devices, where a

large number of samples has to be treated. This facility is enhanced in a new system including an automatic process control.



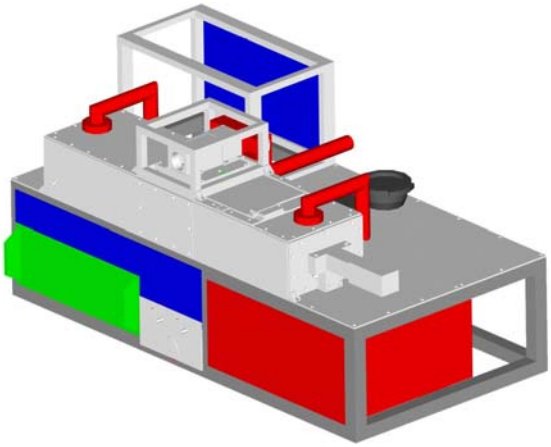


**Fig. 3** (left) The figure shows the CDBD electrode arrangement of an “end-point reactor” with the power supply switched on. The blue glow comes from the XeBr-excimer flat lamp in the CDBD emitting mainly at 282nm. In front, a polymer sample with drop contamination is shown. (right) Sketch drawing of a new “end-point-reactor” system with automatic process control for use in microbiological laboratories.

## 2.2 Microbiological methodology

Pieces of PET foil sized 10cm x 10cm were used as substrate. A spore suspension containing e.g. Bacillus subtilis (strain DSM2277) or Aspergillus niger (strain DSM1957) was sprayed homogeneously onto the samples within a diameter of 7cm. These types of spores are commonly used as test spores in hydrogen peroxide or UV decontamination. Bacillus subtilis is expected to be resistant against oxidative agents or environments and Aspergillus niger shows a strong resistance against UV light. The amount of spores can be controlled by weighing unloaded and loaded samples directly after the spraying process. For experiments with standard DBD and some experiments with CDBD, the samples were sent overnight in a cooled container to the lab where the plasma treatment was done. The samples were packed in PE-bags directly after the plasma treatment. The bags were filled with 100ml of Ringer solution, sealed, and were sent back to the microbiological laboratory. During transport the spores were washed away from the samples, which was ensured by mechanically working the PE-bags in a Stomacher device. A portion of the Ringer solution containing the spores was dispersed on agars and after incubation the number of colony forming units (cfu) was counted. The logarithmic reduction $R$ is defined as

$$R = \log N_0 - \log N \quad \text{or} \quad R = \log N_0 - \log \ln \frac{n_0}{n_{sterile}}$$

where $N_0$ is the number of spores before the treatment and $N$ is the number of survivors. The first definition holds for experiments where count reduction method is used, the second definition is valid for end-point method. In the second case the number of sterile samples after treatment $n_{sterils}$ is set into relation to the total number of samples $n_0$.

# 3 Results

## 3.1 Standard DBD

The inactivation efficiency of standard DBDs can be related to the (V)UV spectra of the gases used in the discharge (Heise et al. (2004), Franken et. al. (2003)). The number of spores of Bacillus subtilis is reduced by about five orders of magnitude within 7s treatment time if argon is used as plasma gas (Fig. 4). Increasing treatment times lead to a stable number of surviving spores, called “tailing”. Smaller reduction rates are observed with nitrogen. Nitrogen shows strong emission in the wavelength range from 210nm to 280nm which should be very efficient for inactivation of cells. As argon mainly emits at 308nm (see below) it is most probable that a second mechanism is the reason for the high reduction rate. This could be excimer emission from $Ar_2$ at 126nm. This radiation has a small penetration depth in air (vacuum UV), but due to the fact that it is generated in the plasma near to the packaging surface, it can reach and kill the bacteria spores.

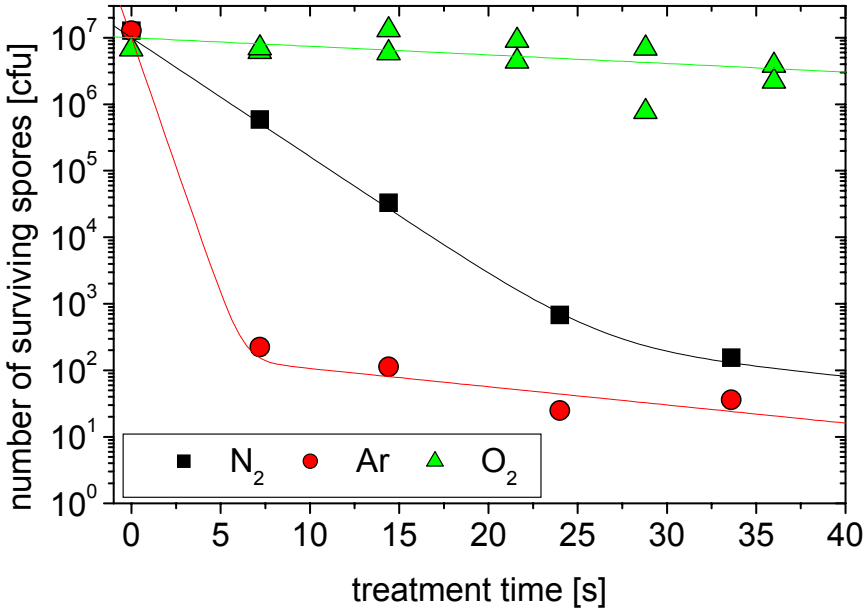



**Fig. 4** Inactivation of Bacillus subtilis spores with gases nitrogen, argon and oxygen in a standard DBD. With argon, fastest inactivation is obtained here, whereas oxygen shows almost no killing of spores.

Oxygen doesn't emit noteworthy amounts of UV light in a DBD but could cause chemical oxidation of spores. However, oxygen shows the lowest reduction rates here. Even at a treatment time of 36s, no more than 0.5 orders of magnitude reduction is observed. That does not mean that oxidative effects on spores are weak in general, but they may be prevented due to strong ozone formation in the plasma. Ozone is formed by electro-negative oxygen radicals and this molecule is rather stable and not reactive compared to the oxygen radicals.

### 3.2 Cascaded DBD

The spectrum of a cascaded dielectric barrier discharge is composed of the spectrum of the excimer flat lamp and the spectrum of the gas in the lower gap (Fig. 5). The excimer lamp – filled with KrCl - in this case emits at 222nm. The lower gap which was flowed with Argon shows emission at 308nm which can be allocated to ArO*. Additionally, lines from nitrogen and nitric oxide can be seen which is an indication of impurities of air.

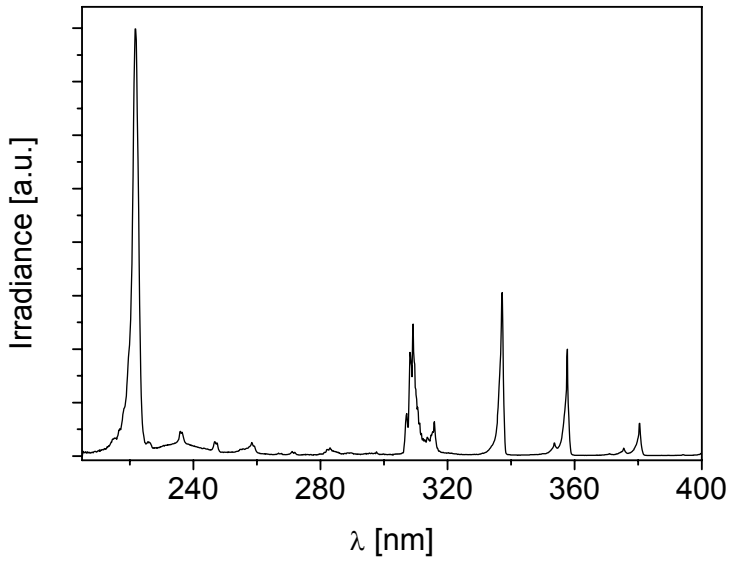



**Fig. 5** Spectrum of CDBD with KrCl-excimer flat lamp and argon in the lower gap. The spectrum is composed of excimer emission at 222nm, second positive system of nitrogen (317nm – 385nm), γ-system of nitric oxide (225nm – 260nm) and ArO* (308nm) emission.

A variety of micro-organisms was used in experiments with the compact CDBD device (Fig. 6) to establish a resistance library. Among spores which are used as bio-indicators for hydrogen-peroxide sterilisation (B. subtilis) or for heat sterilisation (Geobac. stearothermophilus), pathogenic micro-organisms like Clostridium botulinum and E. Coli were treated. This work had to be performed in a microbiological lab for security reasons. The CDBD had an XeBr-excimer lamp (282nm) and used room air in the lower gap, treatment time was 1s and 3s respectively. For all micro-organisms, at least four orders of magnitude reduction could be reached within this time. Data for the two treat-

ment times do not differ significantly. The most resistant cells are B. subtilis, Geobac. stearothermophilus and A. niger, in all other cases the reduction exceeds the mentioned level of four. In several cases the spore number is reduced below the detection limit where the average number of colony forming units (cfu) per foil is a fraction of one.

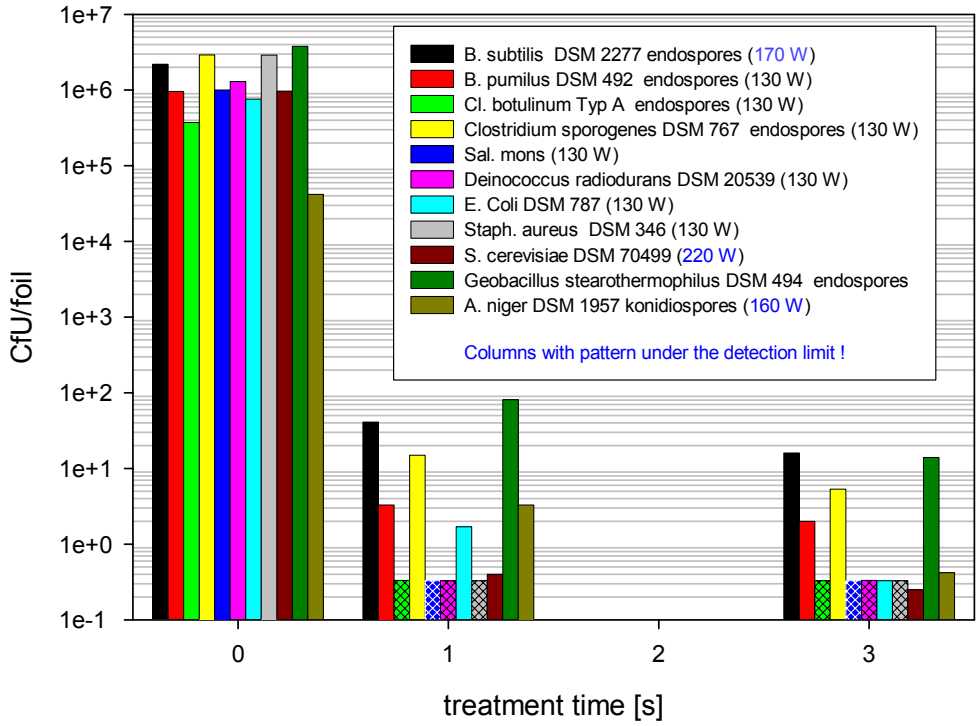



**Fig. 6** Resistance library – Initial number and number of surviving cells against treatment time; the graph contains data for typical test spores as well as pathogenic micro-organisms. All samples were treated with CDBD (282nm and air)

Results from end-point experiments with this arrangement show similar results (Table 1). The initial spore load is lower compared to count-reduction experiments and is usually varied over several decades. In this case, only one spore density was tested and 50 samples were used for treatment. The figures from end-point method and count-reduction method are in good conformance. This represents the small statistical scattering between the samples. More than four orders of magnitude reduction can be achieved. Independent of the kind of inoculation, the reduction of B. subtilis spores is near to $R = 5$ within 3 seconds. As A. niger is more resistant against UV light, the samples need to be treated for 5s to reach a level of $R = 4.3$. Another reason might be the slightly higher initial load of $1.3 \cdot 10^5$cfu.

**Table 1** Average logarithmic spore reduction of B. subtilis and A. niger with a CDBD at 282nm combined with air plasma. 50 samples were treated in each case.

| | **spray inoculation B. subtilis (3s)** | **drop inoculation B. subtilis (3s)** | **spray inoculation A. niger (5s)** |
|---|---|---|---|
| **initial load [cfu]** | $7.2 \cdot 10^4$ | $3.9 \cdot 10^4$ | $1.3 \cdot 10^5$ |
| **average logarithmic spore reduction / end-point method** | 5.0 | 4.7 | 4.3 |
| **average logarithmic spore reduction / count reduction method** | 4.7 | N.A. | 4.2 |

## 4 Conclusions

Standard DBDs and cascaded dielectric barrier discharges are suited to decontaminate flat polymer materials used for food packaging. The decontamination efficiency of standard DBDs can be related to the (V)UV spectra of the used gases. Longer treatment times are required for standard DBDs compared to CDBDs. The latter achieve logarithmic reduction greater than $R = 4$ within 1s of treatment for several different types of micro-organisms, among them pathogenic ones. The results from first end-point experiments with a reduced number of samples meet the requirements for standard decontamination processes in industrial application.

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