DC AND AC NON-THERMAL PLASMA SOURCES FOR COLD SURFACE TREATMENT AT ATMOSPHERIC PRESSURE

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1. Introduction

"Cold" surface treatment, based on use of non-thermal plasma at low pressure, yields excellent results in different applications. However, the vacuum-based low-pressure plasma treatment technique has poor compatibility with industrial production lines, that results in high process cost. For this reason, non-thermal plasma surface modification at atmospheric pressure is a challenging problem for modern plasma science and technology. One of the complicated tasks therewith is to ensure cold plasma treatment with cheap gas mixtures and low specific energy consumption at short processing time. It is evident that progress in this field depends strongly on advances in the development of efficient atmospheric pressure cold plasma sources.

In general, a cold surface treatment at atmospheric pressure can be performed in two different manners. The first approach is called remote process and assumes that treated sample is located out of the non-thermal plasma source. In this first method, non-equilibrium cold plasma contacts the treated film without passing the discharge current through the material. This feature of remote processing is valuable and required for numerous practical applications. As a rule, the lifetime of most neutral and charged active species generated by cold plasma in dense gases is short (except ozone) due to abundant quenching and recombination processes under atmospheric pressure. It results in necessity to use fast gas flow with a velocity about several tens of m/s and short distance (about 1 cm or smaller) between the plasma source outlet and the treated surface.

A great merit of the remote process is the absence of a high electric potential on the treated material that results in absence of backside treating and pinholes in treated materials due to electro-thermal and -breakdown effects. Therefore, the first approach can provide mild surface treatment of delicate materials like thin films. However, at present there are no large-scale remote treatment industrial installations, for lack of appropriate cold plasma sources which could be scaled up easily to the needed sizes. In many cases, typical non-thermal plasma sources for remote treatment have a cylindrical shape and they generate a cylindrical plasma jet at the outlet. As a rule, the outer diameter of this source greatly exceeds the diameter of the outlet plasma jet, that is typically several mm. Such cylindrical plasma jet sources are best suited for 3-dimensional processing of non-flat subjects, but not for roll-to-roll treatment of broad (up to several meters) and fast moving (several hundreds of meters per min) films or fabrics. For this reason, there is necessity to elaborate new kinds of non-thermal plasma reactors for remote surface treatment at atmospheric pressure.

In the second method a sample is activated directly in a discharge zone (Fig. 1). Compared to the first approach, the second one ensures reduced losses of photons, charged particles, excited atoms and molecules and other chemically active species created by the plasma during their transport to the treated surface. In general therefore, a surface treatment in the second approach is of greater intensity than that in the first one. The second approach is widely used, for instance, in so called "corona treater stations" to treat plastic films, foils and paper at the time of extrusion and in-line of converting process. All of these "corona" installations generate a non-homogeneous AC barrier discharge in ambient air, with intensive streamers in a narrow gap.

Streamer barrier discharge (SBD) in air is easy to generate but this kind of discharge is a reason for different limitations of "corona treaters". First, SBD in air exhibits numerous thin current filaments or micro-discharges, which spread irregularly over the treated surface. Intensive streamers form high-density current spots on the surface, which can result in an inhomogeneous treatment and even cause local damage in the case of thin films. Once a streamer strikes the polymer surface, it leaves a local distortion, which in turn attracts the next streamer to the exactly same spot. Second, to initiate SBD in air, high voltage is required. This voltage can be high enough to induce a discharge on the back side of fast-moving webs, resulting in treatment of this back surface as well, an effect not desired in most cases. Third, to ensure high level of both the line speed of treatment and the energy dose per cm^2 of treated surface, it is necessary to enhance drastically the average power density of SBD, but this results in a great problem of thermal expansion of the electrodes. Fourth, "corona treaters" working with air generate a lot of ozone. All parts utilized in the treater stations therefore have to be made of corrosion- and ozone-proof materials, and equipped with a ventilator and filter system to eliminate ozone, which results in increase of cost of the "corona treaters".

Hence, in spite of the existence of a broad spectrum of industrial "corona treaters" based on SBD in air, there is a need to offer other approaches for cold treatment using both new types of the plasma gases and AC discharges at atmospheric pressure. One of the attractive ways is to utilize electropositive gases like He, Ar, N_2, which do not produce harmful ozone and require lower voltage to sustain the AC discharge than that in air under the same operating conditions. To obtain a high line speed, a reasonable operating cost and acceptable quality of materials treated with AC discharges, it is reasonable to use metallic or resistive sharpened electrodes typical for true corona operation (Fig. 1b). In general, an electrode system with a sharpened electrode generates an AC discharge that combines properties of both barrier discharge and AC corona, which can therefore be named "AC barrier corona" (ACBC). The sharpened electrodes possess a strong electric field around them and provoke the formation of streamers under lower voltage across the inter-electrode gap than that in a classical barrier discharge. It follows that volume streamers in ACBC are weaker than those are in a barrier discharge between plane electrodes. Because of the lower voltage, one would expect that the sliding surface streamers in ACBC will be also weaker, and the local influence of mild surface streamers on the treated substrate will be of lower intensity than that in a barrier discharge generated with smooth electrodes. This circumstance can help avoid local damage of thin dielectric materials during cold plasma treatment.

We offer a new kind of atmospheric pressure plasma surface treater based on ACBC. This discharge is generated with sharpened electrodes which can produce ACBC with mild sliding surface streamers. A set of experiments with ACBC in ambient air and Ar at atmospheric pressure were carried out separately, and the gas-discharge conditions that correspond to strong increase in wettability of polymer films and fabrics after short cold plasma treatment have been investigated. We have succeeded also in developing a steady-state diffusive glow discharge in fast air flow at atmospheric pressure. This discharge can serve as the basis of a non-thermal plasma reactor for remote cold surface treatment, in particular, for fast roll-to-roll processing of wide films and fabrics. Atmospheric pressure glow discharge is easily scaled up transverse to the gas flow direction, to the extent needed for specific applications. This discharge has been applied to the remote surface treatment of polyethylene films and polyester fabrics.

2. Setup of DC atmospheric pressure glow discharge

A general scheme of our lab-scale plasma reactor based on DC volume diffusive glow discharge is depicted in Fig. 2. This source produces many chemically active species without significantly heating the background gas flow. A steady-state diffusive glow discharge is sustained by rectified high voltage (up to 30 kV), which is applied to the multi-pin cathode and plane anode, separated by a gap h about of 1 cm (Fig. 2). The distance between sharpened pins equals 3.5 mm. The pins were fabricated from stainless steel with a diameter of 1 mm. Each cathode pin is ballasted with a resistor of 1 MΩ. The electrodes are placed in a dielectric channel with a high flow of air. The exit cross-section h x l of the plasma source is 1.0 x (5-20) cm^2. In our case, the width l of the discharge zone transverse to the gas flow was varied from 5 to 20 cm; in principle, l can be increased as much as needed, up to the size of industrial installations for remote surface treatment. The length of the discharge chamber along the flow direction is short, not exceeding several centimeters.

Our gas discharge installation is specially equipped with a setup which allows pre-heating the background gas entering the plasma source to 65 °C, and varying the water vapor concentration in the process gas between 1.5 and 10 vol %. The gas velocity through the plasma source ranges from 0 up to 55 m/s. The high gas velocity limits losses of chemically active particles on their way to the surface, and thus intensifies the treatment.

The setup used allows a dynamic regime of remote treatment, which simulates some aspects of an industrial roll-to-roll process. A polymer sample of 10 cm length is placed on the surface of the 36 cm diameter cylinder. As a rule, the distance between the discharge chamber and cylinder surface was 10 mm.

3. Setup of AC barrier corona (ACBC) at atmospheric pressure

The multi-pin ACBC was created within a dielectric chamber (cylinder 160 mm in inner diameter and 150 mm in length) between the multi-pin sharpened electrode and the plane metallic electrode, the latter being covered with dielectric material to be treated. The electrical scheme of this discharge is identical to that presented in Fig. 1b. The diameter of the metallic plate was 100 mm. The radii of the pin tips are 100 μm. The distance between the plane and sharpened electrodes was varied up to 35 mm. The number of pins depends on the type of plasma-producing gas and overall area under treatment. This electrode system is easily scaled up.

We used two power supplies; the first has a fixed frequency, 50 Hz, and voltage amplitude up to 35 kV. This power supply was used for excitation of ACBC in ambient air. The amplitude and frequency of the second power supply could be varied up to 4.5 kV, and from 50 to 10^5 Hz, respectively. The latter power supply was used for excitation of ACBC in Ar.

Experiments on treatment of polymer materials with ACBC were performed using of the described setup, the samples being static during treatment. Exposure time was varied with a programmable timer switching on/off the AC high-voltage generator.

4. Properties of steady-state glow discharge in fast air flow

The relation between the applied voltage U and the reduced current I is termed the Volt-Ampere Characteristics (VAC) of a discharge. A typical VAC of a steady-state multi-pin DC discharge in a fast air flow is presented in Fig. 3. Because the sharpened electrode system is close to pin-plane corona geometry, the initial region of the VAC (small currents and large increase in applied voltage) corresponds to the well-known corona with dark inter-electrode gap. The region of slow rising voltage corresponds to a new current regime named diffusive glow discharge, which is accompanied by intense light emission from the entire gap.

The fast gas flow prevents the formation of sparks. There is another crucial parameter that drastically influences the efficiency of producing chemically active species in the glow discharge, namely the absolute humidity of the background gas flow, that is, the concentration of water vapor in the process gas. The humidity impacts the average reduced electric field E/P. The appropriate experimental data are presented in Fig. 4.

The average reduced electric field E/P is a very important discharge parameter, determining the average kinetic energy of electrons T_e in discharge plasma. The higher E/P, the higher T_e, and therefore the higher (exponentially) is the efficiency of electrons in dissociation and excitation of background molecules like O_2 and H_2O, from which the chemically active species like O and OH radicals are formed. One can say, therefore, that operation of a glow discharge under high humidity (in another words, at high E/P and low currents) is energy-efficient. Besides, energy losses due to voltage drop across the cathode ballast resistors decreases as well, because of the lower discharge current in moist air. Additionally, the very low concentration of harmful ozone can provide environmental friendly operation without the need for expensive elimination of ozone.

5. Properties of AC barrier corona

Air. An AC discharge in air requires a higher voltage (more than tenfold) to sustain than that in Ar. The AC barrier corona appears almost homogeneous in the gas gap and above the surface of a dielectric film. In fact, ACBC in air has two different current modes, depending on positive or negative polarity of the applied voltage. These modes clearly reveal themselves in the waveform of the AC discharge current, representative examples of current and voltage oscillograms being presented in Fig. 5.

During the positive half-period, ACBC is non-uniform because it operates under a streamer regime. Each streamer strikes the surface and branches over it in the form of short sliding streamers. The streamer length in the bulk of the gap is much greater than those on the surface

The negative half-period of ACBC corresponds to a homogeneous glow regime without any spikes in the current oscillogram. There are two reasons why streamers are absent during the ACBC negative half-period. First, pins do not provoke streamers in a negative corona, and second, the uniform anode region formed near the dielectric film is highly tolerant to streamer initiation as well.

Argon. In comparison with air, Ar is an easily ionized gas. This results in strong differences in discharge properties between ACBC in air and Ar. There is a critical power frequency, f_{cr} (about 10 kHz), which separates two different current regimes of ACBC in Ar.

The cross-section of higher frequency barrier corona (HFBC) generated with a single sharpened electrode is smaller than that in air, and it practically remains unchanged with varying applied voltage. Serious problem with ACBC in Ar at higher frequency is that it is difficult to uniformly distribute the total current of the HFBC over the multi-pin electrode system. Consequently, the average current density at the polymer substrate is too high, and it can damage a thin film due to thermal effects.

The current waveform in lower frequency barrier corona (LFBC) (Fig. 6) has almost symmetrical shape, with many sharp current spikes in each half-period. It means that streamers occur in LFBC during both positive and negative half-periods. Our observations show that the length of sliding surface streamers in LFBC in Ar are much greater than the length of volume streamers, that is, LFBC in Ar spreads over a surface very readily. This is a distinctive property of ACBC in Ar, which is extremely important for surface treatment. The effective diameter occupied by mild surface streamers is nearly 10 cm at f=50 Hz and U=3 kV. To the naked eye, this area looks like a dense web of many thin, faint whitish filaments running chaotically and rapidly over the polymer film. In contrast to low frequency barrier corona in air, the cross-section of surface streamer area in LFBC in Ar does not depend on, h, the length of inter-electrode gap; the effective diameter of LFBC in Ar increases with amplitude and decreases with frequency powering the ACBC.

6. Results of atmospheric pressure “cold” treatment

These results will be demonstrated at oral presentation of the report.

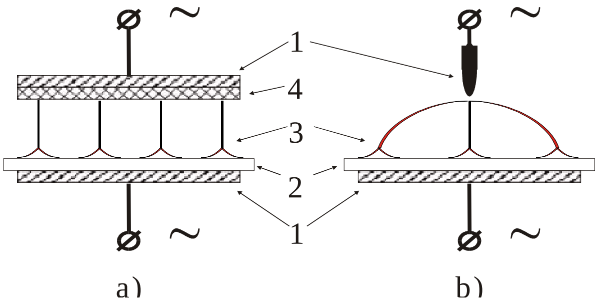
7. Conclusions

DC glow discharge remote treatment with high line speed, up to 500-600 m/min (similar to a roll-to-roll regime) appears possible. Such rapid processing can be realized with an attractive linear power density of about 20 W/cm, which is 2 to 2.5 times lower than that in large-scale industrial AC “corona” treaters at the same line speed.

Low frequency barrier corona in atmospheric pressure argon induces many mild surface streamers, which readily slide over a large area of the treated substrate. This regime of ACBC is energetically favorable, and provides gentle treatment of substrates at a low level of the reduced power density, about 0.1 W/cm^2, without damage to a thin polymer film. ACBC in argon is powered with a much smaller (by a factor of 10) amplitude of the applied voltage, in comparison with a barrier discharge in air. This low voltage reduces the danger of back side treatment, usually highly undesirable.

Cold plasma processing with ACBC in Ar creates a long-lasting treatment effect at low energy dose, and this attribute of streamer processing in Ar makes it attractive from a practical application point of view. Lastly, a comparison between ACBC in Ar and ACBC in N_2, He shows that LFBC in Ar provides a better treatment effect at lower consumed energy.

8. Figures



a) b)

Fig. 1. Schematics of cold plasma treatment in the discharge zone: a) classical barrier discharge; b) AC barrier discharge with sharpened electrode(s). 1: metallic electrode; 2: treated film; 3: streamers; 4: barrier.

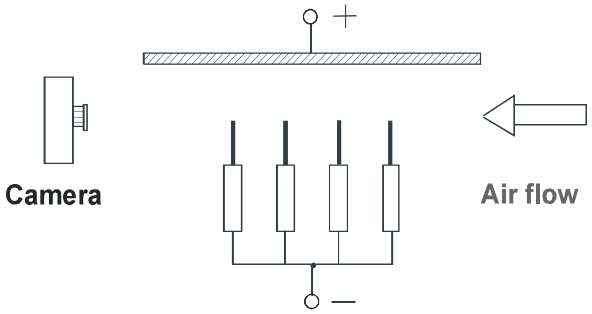


Fig. 2. Sketch of a multi-pin electrode system used for generating a volume diffusive glow discharge in air flow at atmospheric pressure.

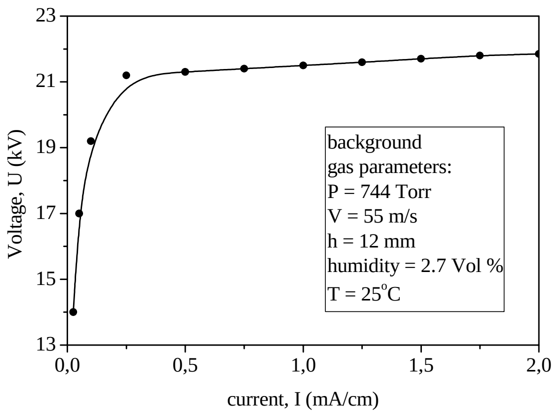


Fig. 3. Volt-Ampere Characteristic for reduced current per 1 cm in transverse direction of a multi-pin steady-state diffusive discharge in fast air flow.

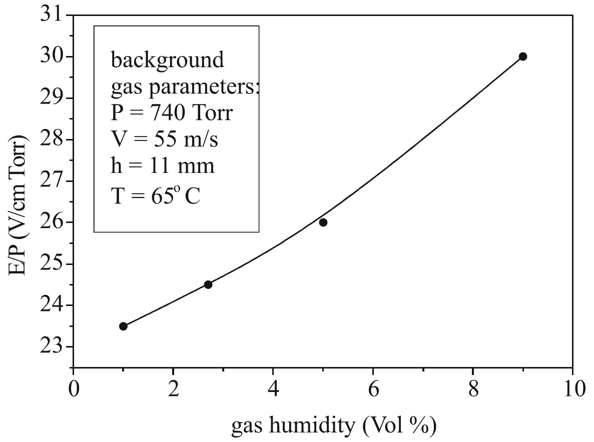


Fig. 4. Impact of air flow humidity on average reduced electric field, E/P, in the bulk of the glow discharge.

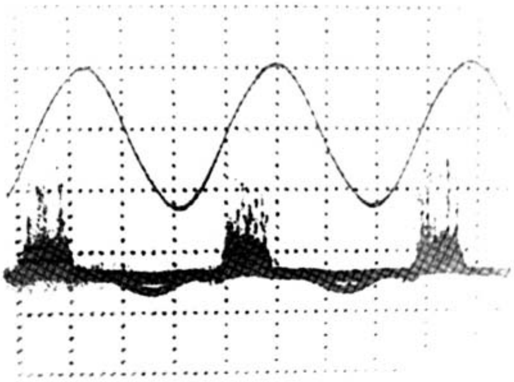


Fig. 5. Typical voltage (above) and current oscillograms of ACBC in air with sharpened electrode and barrier of PE-film. Power frequency is 50 Hz. Time scale is 5 ms/div. Voltage amplitude is 32 kV.

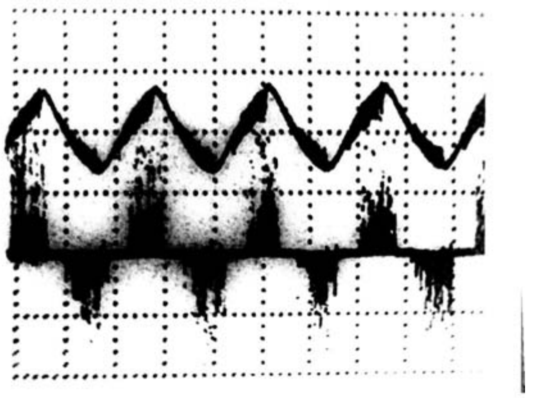


Fig. 6. Typical voltage (above) and current oscillograms of ACBC in Ar with sharpened electrode and barrier of PE-film. Power frequency is 400 Hz. Time scale is 1 ms/div. Voltage amplitude is 3.2 kV.