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RESEARCH ARTICLE

PLASMA PROCESSES AND POLYMERS

Adhesion improvement on the inner side of LLDPE/PA tubular film exposed to DCSBD roll-to-roll plasma system from the outer side of the film

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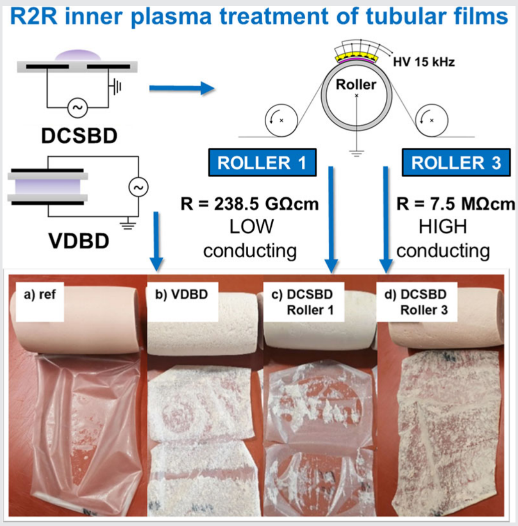
Abstract

Diffuse coplanar surface barrier discharge (DCSBD) was used to activate the opposite side of the plasma-exposed linear low-density polyethylene/polyamide (LLDPE/PA) tubular film of multilayer casing. We determined that conductive metal rubber roller in the DCSBD system allowed the formation of microfilaments perpendicular to the film surface, resulting in improved wettability and adhesion of inner LLDPE side of the tubular film. These findings were supported by increasing the concentration of polar functional groups. Based on these remarkable outcomes obtained after a very short plasma exposure time of 0.5 s, DCSBD roll-to-roll system in proper arrangement affords adhesion improvement of the opposite side of the treated film without any material damage, hence can compete with industrial corona in commercial sphere of plasma treatments.



KEYWORDS

DCSBD, film-to-meat adhesion, food packaging, LLDPE/PA tubular film, roll-to-roll reactor

1 | INTRODUCTION

The packaging industry of meat products offers a wide range of casings that are fundamentally differentiated to edible and not edible. The most common types of casings are natural, collagen, chitosan-based and plastic casings.[1–4] Besides natural casings, the packaging industry reaches continuous growth in the production of plastic casings due to plenty of benefits. The main advantages represent cost-effectiveness, good flexibility and machinability as well as the possibility to adjust the target features such as barrier properties, selective permeability and mechanical integrity to meet the specific requirements of the product.[5] Considering the processed meat products such as sausages, the control of resulting film diameter (calibre) is an additional beneficial feature of plastic casings over the natural ones.

New trends in the manufacture of synthetic polymer sausage casings were described by Savic.[6] The plastic casings are often manufactured from multiple layers due to the different properties of each polymer (thermal resistance, barrier and shrinking properties), because a single monolayer of polymer is not able to fulfil all requirements of food packaging industry.[7] The inner and outer layers of casings have different roles: the inner layer must be nonreactive with any food constituents and the outer layer should offer mechanical stability and printability, apart from barrier functions.[8] The typical polymer used as inner layer for processed meat packaging is polyethylene (PE), especially linear low-density PE (LLDPE), which is the most widely used.[5] PE has excellent moisture barrier properties and chemical inertness, but on the other hand has poor barrier properties against oxygen, flavour and aroma molecules.[9] One of the first mentions of LLDPE as a promising material for affordable food packaging comes from 1982.[10] Although LLDPE film is otherwise promising and a widely used material, for specific purposes, it is necessary to strengthen its functionality and adhesive properties. PE is characterised by low surface free energy and bad wettability as well as insufficient adhesion; thus, some surface modification including enhancement of adhesion of meat batter inside the sausage casings is necessary. The good adherence of inner film to meat batter prevents the so-called 'cook-out' effect, which is the undesired collection of liquid between the outer surface of the meat and the inner surface of the film.[11]

A sufficient adhesion of the meat batter to the surface of the film is the subject of several patents, which focused on production and development of multilayer tubular films for the meat industry.[11–13] Rosinski et al.[14] studied the effect of the meat batter composition and the ratio between raw and precooked meat on the adhesion to the packaging film. The adhesive force required to peel the film from sausage was measured directly during the peeling process. Another possibility of evaluating the film-to-meat adhesion of cook-in-the-film meat products is by examining peeled films using scanning electron microscopy (SEM). The procedure was described in detail by Clardy and Dawson.[15] The methods used for characterising and overcoming stickiness problems in food processing and storage operations were explained by Adhikari et al.[16] Moreover, a comparison between peeling modes 90° and 180° in quantifying the food adhesion was made in this study.

Considering the chemical inertness and poor adhesion ability of LLDPE film, it is necessary to perform specific surface treatment to ensure the required meat batter adhesion. Different ways of surface treatment such as ozone treatment, physical manipulations or chemical modification of films used in packaging industry are known from the literature.[17–19] Wet chemical modification methods using strong acids and bases produce hazardous waste and often affect the bulk properties of treated material. The advantages and drawbacks of various physical and chemical manipulations of packaging materials commercialised partly in the meat industry were compared by Lee et al.[18] Flame treatment, ultraviolet radiation, ion beam, electron beam irradiations and laser and plasma treatments are among the frequently used physical surface modification methods.[6] From the above-mentioned methods, plasma treatment can be successfully used for improving the wettability,[20] dye uptake,[21] printability,[22] and adhesion of polymers for appropriate application.[23,24]

An overview of the cold atmospheric-pressure plasma systems compared to well-established low-pressure plasma systems for treatment of films presented in this review provides a better understanding of emerging atmospheric plasma technologies.[25] An example of plasma treatment at low pressure was shown by Lee et al.[26] Bardos and Baranková.[27] achieved an increase in the surface tension of PE web after 1 s of plasma treatment with a radio frequency large-area plasma source operating at atmospheric pressure. Popelka et al.[28] applied the corona treatment in order of seconds to enhance the adhesion properties of LLDPE. The wettability as well as the peel resistance of LLDPE significantly increased even after 1 s exposure. Regarding the packaging industry, plasma treatment found application also in microbial decontamination of foods inside the sealed package while plasma was applied from the outside.[29] The so-called in-package plasma technology represents a new approach of surface sterilisation of food packaging.[30] and also provides a simple tool for modification of the inner side of the polymer film for improving its adhesion.

The aim of the present study is adhesion improvement on the inner side of LLDPE/PA tubular film while the plasma treatment is carried out from the outside. The backside treatment effect on plasma-treated materials is quite common for volume dielectric barrier discharge (VDBD), because the plasma is produced through the sample due to the arrangement of the electrodes on both sides. Such plasma consists of hot filamentary microdischarges, which are perpendicularly oriented and randomly distributed along the treated material. However, this effect is highly undesired during the industrial processing due to subsequent problems associated with surface changes on the opposite side of the exposed material. To avoid the backside treatment, diffuse coplanar surface barrier discharge (DCSBD) represents a highly efficient plasma source generating very thin plasma, which affects only the thin layer of the treated surface. DCSBD.[31,32] generates visually homogeneous plasma, where the diffuse parts of the microdischarges are intensified while the filamentary elements are highly suppressed. This laboratory plasma source with possible scale up to roll-to-roll arrangement suitable for industry found applications in the treatment of a wide range of materials.[33–36] Despite in the case of DCSBD plasma source, the backside treatment was not monitored yet, we revealed that in the suitable configuration of the roll-to-roll system, the opposite side of the exposed material can be modified. We took advantage of this observation in the plasma treatment of a tubular multilayer film with LLDPE inner layer. Although DCSBD plasma is applied from the outside of the LLDPE/PA film, the surface changes on the inner side are observed to be dependent on the used arrangement of the roll-to-roll DCSBD system. The influence of various materials of the roller differing in conductivity are examined in the case of DCSBD system and the results are compared with commercially employed VDBD.[33,37–39] Since the industry aims for large volumes, low cost and high speed of treatment, roll-to-roll plasma represents a promising option for the rapid pretreatment of plastic films.[40,41] Accordingly, optimisation of plasma treatment procedure in terms of short exposure time, high treatment speed and appropriate input power is carried out concerning industrial demands. The examined properties of plasma-treated LLDPE/PA films include wettability and surface morphology, changes in surface chemistry, peel resistance improvement and film-to-meat adhesion used in the meat industry in the case of the cook-in-the-film meat products.

2 | EXPERIMENTAL PROCEDURE

2.1 | Material

Tubular multilayer films with LLDPE inner layer and polyamide 6 (PA6) outer layer used for the experiments are commonly utilised in the meat processing industry. The inner LLDPE layer of the tubular film is the subject of this study. Samples with a width of 16.6 cm were delivered in the form of a roll prepared for industrial processing. The LLDPE/PA tubular film weights were 53 g m^{-2}, and the thickness of the coextruded film was 0.1 mm. The melting temperature of PA6 was 220°C, and 121°C in the case of LLDPE.

2.2 | Plasma systems

Two types of dielectric barrier discharges were used in this study for the outside treatment of LLDPE/PA tubular film; both are applied in ambient air at atmospheric pressure. The outer PA layer of the tubular casing was exposed to plasma treatment, and the inner LLDPE nonexposed side of the tubular casing was in direct contact with the meat product after filling. First, the DCSBD with the concavely curved plasma unit was utilised for experiments. The second plasma system, VDBD, is often referred to as 'industrial corona'. VDBD has been used in the polymer film industry for the decades, although it has many limitations that DCSBD can address. Industrial corona is not suitable for thermally sensitive polymers as it often causes undesirable backside treatment, or possible damage of material due to the hot filamentary microdischarges.

The DCSBD produces a plasma layer with an effective thickness of 0.3 mm in ambient air,[42] and the area of produced nonequilibrium plasma is 8 cm × 20 cm. The square power density of DCSBD fluctuates in the range of 2.5–3.8 W cm^{-2} depending on the utilised input power of 400 or 600 W, respectively. An input power of 400 W is used as a standard in most applications, while a higher input power of 600 W is applied with the aim to shorten the exposure time. Plasma treatment of LLDPE/PA tubular film was performed using exposure times in the range of 0.5–2 s and the treatment speed varied in the range of 4–16 cm s^{-1} depending on the exposure time. The frequency of supply voltage used in experiments corresponded to ~15 kHz for an input power of 400 W and ~30 kHz for an input power of 600 W. DCSBD plasma source equipped with concavely curved plasma unit enables a continuous treatment of flexible materials at high treatment speed. The laboratory reactor, similar in principle to standard industrial roll-to-roll systems, consists of a roller and DCSBD unit with a concavely

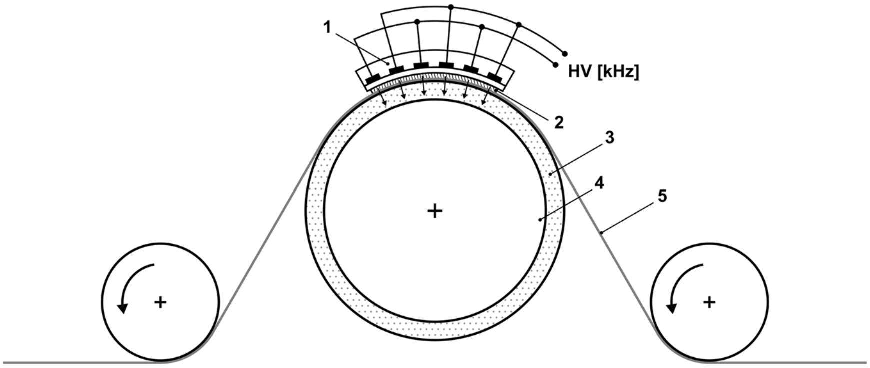


FIGURE 1 A scheme of a roll-to-roll reactor with the concavely curved diffuse coplanar surface barrier discharge (DCSBD) electrode system (1—DCSBD concavely curved plasma unit, 2—generated plasma, 3— an adhesive material (rubber) covering the metal core of roller, 4—metal core of roller and 5—treated tubular film). Parts 3 and 4 are related only to metal-rubber rollers and not to plastic roller.

curved electrode system. Figure 1 describes individual parts of the plasma system.

Experiments were performed using different types of rollers used in DCSBD plasma system manufactured by Roplass s.r.o. Three types of rollers, which differ in the material they are made from and, thus, in their electrical conductivity properties were compared.

Roller 1: Common metal-rubber roller with steel core covered with silicone rubber (thickness of rubber ~1 cm) has a resistance of 238.5 GΩcm. This type of roller is preferably used in the DCSBD roll-to-roll system.[35,43]

Roller 2: Plastic roller made of unplasticised polyvinyl chloride with almost zero conductivity and tremendous resistance.

Roller 3: Optimised metal-rubber roller consists of steel core covered with ethylene propylene diene monomer rubber (thickness of rubber ~1 cm). This type of roller has a resistance of 7.5 MΩcm.

Rollers 1 and 3 differ in the electrical resistance of rubber covering the metal core of the roller.

VDBD is a commercial plasma source from Ahlbrandt System GmbH company.[44] A schematic diagram of the device and a detailed information are presented in our recent study.[33] VDBD produces a nonequilibrium plasma with filamentary character and an effective area of 7 cm × 21 cm. The electrode system consists of four high-voltage (HV) strip electrodes and a grounded rotating cylinder isolated by a ceramic layer in the roll-to-roll arrangement. The exposure time of 1 s was used for comparative experiments with DCSBD, corresponding to a plasma treatment speed of 30 cm s^{-1}, and the distance between the treated sample and HV electrodes was set to 1 mm. An input power of 380 W corresponding to the same square power density as plasma produced by DCSBD at an input power of 400 W was used.[31,45,46] The square power density of VDBD fluctuates in the range of 2.6–3.9 W cm^{-2} depending on the input power of 380 or 570 W.

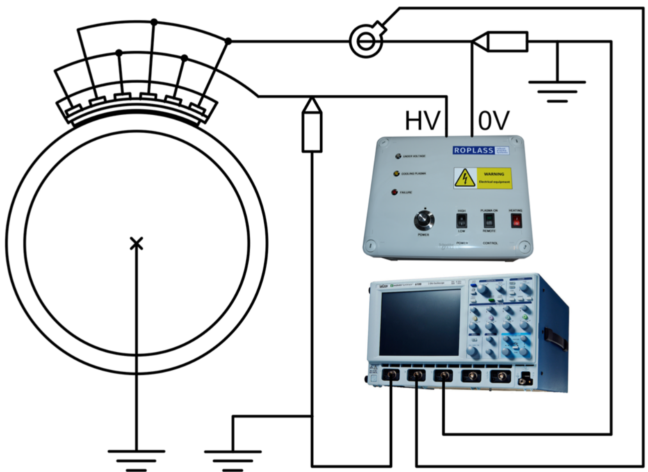


FIGURE 2 A scheme of the circuit during measurement of electrical characteristics using different probes. HV, high voltage.

2.3 | Analytical methods

2.3.1 | Electrical characteristics

The electrical characteristics of the DCSBD plasma unit were captured using two passive HV probes P6015A (Tektronix UK Ltd.), Rogowski coil, wideband current monitor 4100 (Pearson Electronics) and DC-coupled current probe TCP 202 (Tektronix UK Ltd.), connected to the channels of ecroy 6100A WaveRunner, 4-Channel, 1 GHz oscilloscope (LeCroy Corporation) (see Figure 2). The peak-to-peak values of voltage were measured by a passive HV probe connected to the HV electrode and a second passive HV probe connected to the grounded electrode. Wideband current monitor recorded the discharge current on the cable to the grounded electrode. We know that the power supply is not symmetric and the floating potential appearing on the grounded electrode is up to 1 kV. Therefore, a passive HV probe was applied to the grounded electrode. The instant discharge voltage was calculated as the difference between the voltage measured on the HV electrode and the voltage acquired on the grounded electrode.

The influence of the roller material was examined using Rogowski coil when the movement of roller was on. The velocity of roller rotation was $8\,cm\,s^{-1}$, corresponding to the plasma treatment time of 1 s. No film sample was attached to the roller during the measurement of electrical characteristics.

2.3.2 | Wettability and surface morphology

Wettability of LLDPE/PA film was tested with methylene blue solution p.a. (PENTA s.r.o.). A piece of film was soaked in a methylene blue solution diluted with distilled water in a 1:40 ratio. Images of film appearance with and without plasma treatment were captured.

Imaging of surface morphology was performed using SEM Mira3 (Tescan) with a maximum resolution of 1 nm and a maximum magnification of 1 000 000. A secondary electron detector and an accelerating voltage of 15 kV was used. LLDPE film surface was coated with 20 nm of Au/Pd layer to prevent charging of the sample. The surface morphology analysis was carried out with a magnification of up to 5000.

2.3.3 | Peel resistance

Static material testing machine AllroundLine Z010 TE (ZwickRoell GmbH & Co. KG) was used for peel resistance measurements. The 90° angle peel test for evaluating adhesion on plasma-treated LLDPE/PA film casing was realised using a component called 'Rotating German Wheel' for continuous peeling off the adhesive tape from the LLDPE side of casing. The sample was prepared by sticking a 19-mm wide piece of Scotch Magic® adhesive tape on the LLDPE film and ensuring 10 passes over a taped area with a rolling pin. The loading speed was set to $10\,mm\,min^{-1}$, and the load cell with a 1 kN range was used for adhesion measurements. Evaluation of measured peel resistance was conducted at a range of 20–70 mm. The average peel resistance was calculated from three measurements of samples treated under the same conditions.

2.3.4 | Film-to-meat adhesion tests used in the sausage industry

Meat emulsion was used for film-to-meat adhesion testing to estimate the degree of adhesion. Raw meat batter contains various ingredients depending on the type of meat emulsion. Expansive emulsion consists of a pork shoulder (24%), pork fat (24%), salt (2%), Top FOS (0.3%), nitrite salt (0.2%), soybean granulate (3%), water (39%), soy isolate (3%) and potato starch (5%). The output is an emulsified meat product similar to luncheon meat.

The preparation procedure is decribed as follows: (1) preparation of raw meat batter in a cutter according to the composition mentioned above; (2) filling of casings using the stuffing machine Handtmann VF 300 (Handtmann Group) and closing the sausages with a clipping machine Automatic Double-Clipper FCA 160 (Polyclip System GmbH & Co. KG); (3) cook-in-the bag processing, it means boiling in hot water for 160 min at a temperature of 80°C using Chamber Maurer ASR 2717 (Maurer-Atmos Middleby GmbH); (4) cooling under the shower for 30 min by maintaining the temperature of water at ~10°C and after that in the fridge for several hours at a temperature range of 3–5°C; (5) equilibration to the ambient temperature of ~18°C before testing of film-to-meat adhesion; and (6) peeling off the casings from sausages and evaluation of the film-to-meat adhesion.

The amount of meat emulsion used for a one cook-in-bag emulsified meat product was 2 kg and the diameter (calibre) corresponded to 12 cm; film-to-meat adhesion testing was performed in two repetitions. Film-to-meat adhesion tests were performed according to the internal standards of the testing company. All tubular film samples were not filled at once (two batches); therefore, there may be a slight difference in the composition of the meat emulsion.

2.3.5 | X-ray photoelectron spectroscopy

The X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCALAB 250Xi X-ray Photoelectron Spectrometer (Thermo Fisher Scientific) at a take-off angle of 90°. The system is equipped with a 500-mm Rowland circle monochromator with a microfocused Al Kα X-ray source. An X-ray beam with a power of 200 W (650 μm spot size) was used. The survey spectra were acquired with a pass energy of 50 eV and an energy step of 1 eV. High-resolution scans were acquired with a pass energy of 20 eV and an energy step of 0.1 eV. To counterbalance charges on the surface, an electron flood gun was used. The base pressure in the analysis chamber was in the 10^{-9} mbar range. After the acquisition, spectra were aligned to the lowest binding energy peak assigned to C–C/C–H, which is an arbitrary set at 284.8 eV. Spectral calibration, processing and fitting routines were carried out using Avantage software.

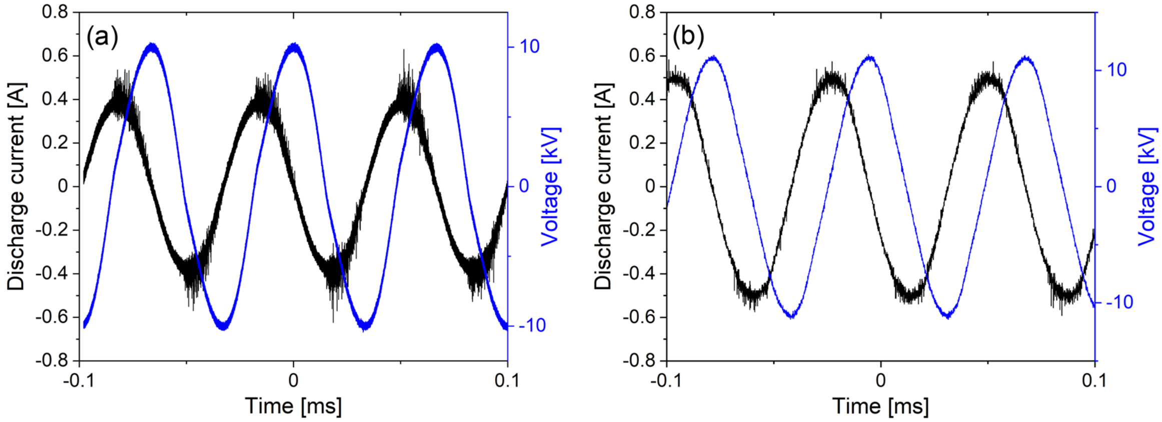


FIGURE 3 Voltage and discharge current waveforms of curved diffuse coplanar surface barrier discharge (DCSBD) plasma unit in configuration with (a) plastic roller with zero conductivity (Roller 2) and (b) metal-rubber roller with a resistance of 7.5 MΩcm (Roller 3). Input power of 400 W and frequency of ~15 kHz were used.

3 | RESULTS AND DISCUSSION

3.1 | Electrical characteristics of DCSBD

Typical voltage and discharge current waveforms of the DCSBD unit are shown in Figure 3. Here, the electrical characteristics of DCSBD plasma unit in configuration with plastic roller (Roller 2—Figure 3a) and metal-rubber roller (Roller 3—Figure 3b) are compared. Corresponding measurements for configuration of DCSBD plasma unit with Roller 1 were omitted due to similar development of voltage and current waveforms to Roller 2. In Figure 3, we observed a typical phase shift between the current and voltage corresponding to $\pi/2$ rad value. On the maxima of the current sinusoidal waveform are visible typical sharp peaks representing the filamentary component of the DCSBD plasma. It has been experimentally verified that a nonconductive roller constructed from plastic does not allow the surface discharge to be superimposed by microfilaments generated perpendicular to the film surface in contrast to metal-rubber roller (Figure 3a). Therefore, sharp peaks on the maxima of the current sinusoidal waveform are more intensive and higher in configuration with a plastic roller than with a metal-rubber roller, where a part of the discharge current is transformed to the microfilaments generated perpendicular to the film surface. The different appearance of the curves in Figure 3a,b reflects various materials of the roller with different conductivity and resistance. The finding that the effect of roll-to-roll plasma treatment is strongly dependent on the material of the roller is protected by the Utility model number 33294: Device for plasma treatment of tubular foils.[47] Therefore, different types of rollers mounted in roll-to-roll plasma systems were used in the experiments.

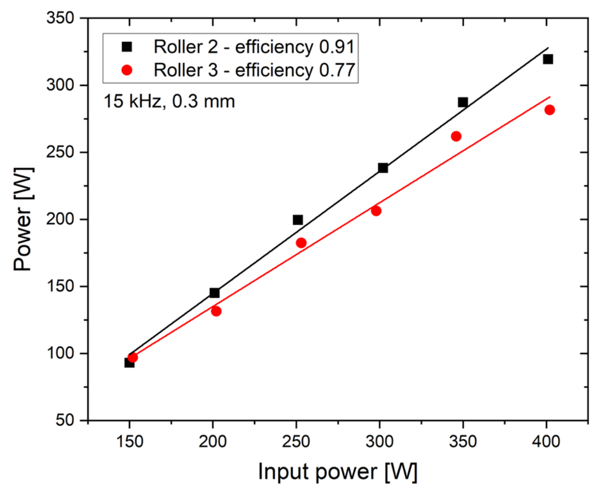


FIGURE 4 Electrical efficiency—comparison of discharge power and input power for a plastic roller with zero conductivity (Roller 2) and metal-rubber roller with a resistance of 7.5 MΩcm (Roller 3).

The electrical efficiency of the DCSBD plasma unit for different materials of the roller is presented in Figure 4. Discharge power and input power were measured for several values by maintaining a distance of 0.3 mm between the roller surface and DCSBD ceramics. The resulting linear regression was applied to calculate the electrical efficiency. The electrical efficiency of the plasma system with a plastic roller corresponds to 0.91, and lower electrical efficiency of 0.77 was calculated for a metal-rubber roller. These results follow typical voltage and discharge current waveforms presented above (Figure 3). It means, in the case of metal-rubber roller, the microfilaments generated perpendicular to the exposed material are more intense in comparison to the plastic roller. By applying an input power of 400 W, the difference in power between the metal-rubber roller and the plastic roller is ≈40 W.

3.2 | Wettability and surface morphology

We conducted a simple test with methylene blue water solution to visualise the effect of DCSBD plasma on the inner LLDPE side of the tubular film, while the plasma treatment was performed from the outside of the film. Three types of rollers were used in the DCSBD electrode system and were tested; the best result was achieved with Roller 3. Treatment of LLDPE/PA tubular film for a duration of 1 s was enough for a significant wettability change on the inner side of LLDPE (Figure 5). Untreated film surface repelled methylene blue solution, and tiny drops were created on the surface (Figure 5a). LLDPE/PA film sample treated by DCSBD unit with Roller 3 is entirely and uniformly covered with methylene blue solution (Figure 5b). Unlike the positive wettability results with Roller 3 in the DCSBD plasma system, methylene blue solution did not wet the film so markedly in the case of other DCSBD configuration (Roller 1 and Roller 2). This simple test has shown evident wettability improvement of the LLDPE film surface observable with the naked eye.

A similar test using wetting inks was carried out by Bárdos and colleagues on polyethylene web treated by radiofrequency plasma source at atmospheric pressure for 1 s when the surface tension increased significantly

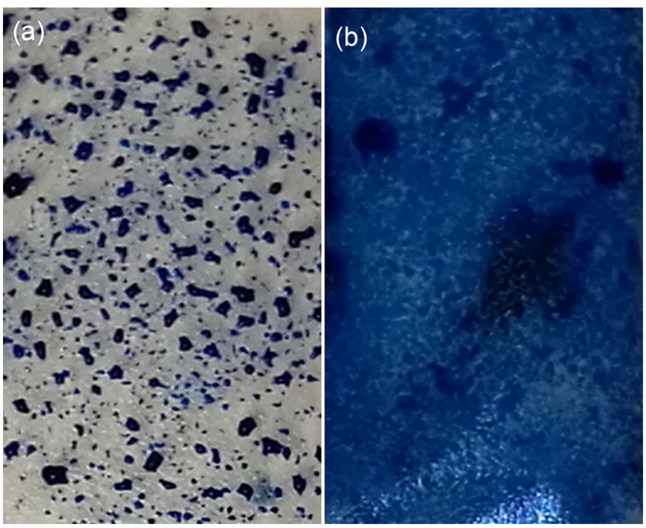


FIGURE 5 Linear low-density polyethylene film surface after soaking in a methylene blue water solution (a) untreated and (b) diffuse coplanar surface barrier discharge treated using Roller 3 for 1 s by input power of 400 W.

(from values <34 mN m^{-1} to values ≥56 mN m^{-1}) after the plasma treatment.[25,48] Quantitative results of surface tension could be achieved due to the flat substrate without texture. In our case, only qualitative test was applicable due to the fibrous nature of the film surface, which is not suitable for using wetting inks.

To demonstrate the potential damage of the surface induced by plasma, plasma-treated samples with the longest exposure time at higher input power and Roller 3 were chosen for surface morphology analysis using SEM. If changes are not noticeable under these 'most extreme' conditions within this study, then they are unlikely to be observable at shorter times and at lower input power. The SEM images taken on the film samples exposed to a plasma exposure time of 2 s and at a higher input power of 600 W in the case of DCSBD and 570 W in the case of VDBD are presented in this study. The surface structure of the LLDPE film is inhomogeneous with an irregular pattern due to the foaming process used during fabrication. There is no indication of noticeable traces from microdischarges or other undesirable changes on the LLDPE film surface after the plasma treatment, as is evident from Figure 6. Here, we show that the microdischarges are generated differently for these two types of discharges. DCSBD works in continuous mode where the surface discharge is dominant. Some parasitic microdischarges are generated perpendicular to the surface in the case of DCSBD using Roller 3, but apparently in a much smaller amount and with much lower power, that is, with a lower temperature than for VDBD. In contrast to DCSBD, the VDBD generates hot microdischarges acting only perpendicular to the treated material. Therefore, the probability of possible material damage is higher in the case of the VDBD treatment.

3.3 | Peel resistance improvement

Peel resistance of untreated LLDPE/PA film was so low that it was unmeasurable, and the adhesive tape almost did not stick to the surface of the LLDPE film. The effect of DCSBD plasma treatment using plastic Roller 2 and metal-rubber Roller 3 on peel resistance improvement was observed and it was found to be similar to that in the case of electrical characteristic evaluation described in Section 3.1. The influence of exposure time in the range of 0.5–2 s and the conductivity of a roller on peel resistance value is presented in Figure 7. With exposure time prolongation, there was an increase in the peel resistance when treated with both types of rollers, although higher values of peel resistance were obtained for the LLDPE/PA film treated with a metal-rubber roller. In the case of 0.5 s of exposure time, there was a

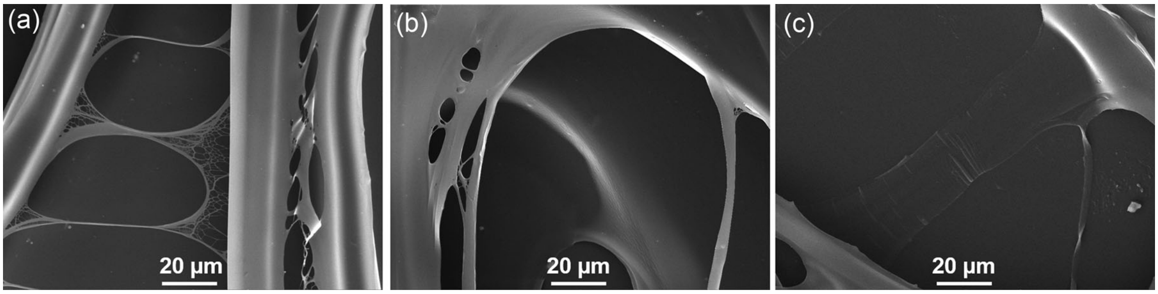


FIGURE 6 Typical morphology of linear low-density polyethylene film surface obtained from scanning electron microscopy imaging: (a) untreated, (b) diffuse coplanar surface barrier discharge treated for 2 s at 600 W, and (c) volume dielectric barrier discharge treated for 2 s at 570 W. Magnification of 2000 was applied.

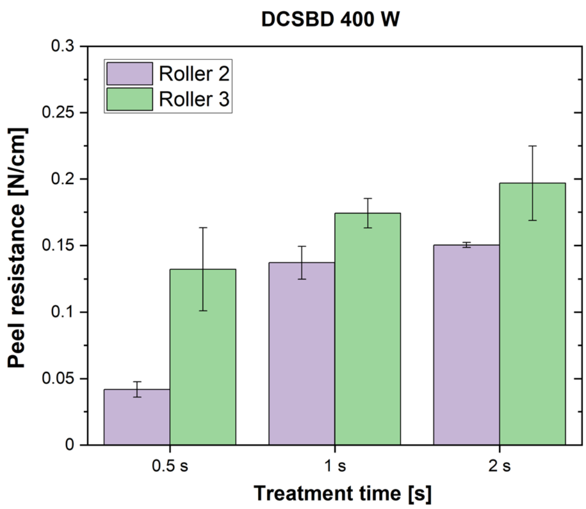


FIGURE 7 Values of peel resistance measured on linear low-density polyethylene/polyamide film treated by diffuse coplanar surface barrier (DCSBD) plasma unit using Roller 2 and Roller 3 showed dependence on treatment time. Input power of 400 W was used for the experiment.

three times increase in peel resistance in the metal-rubber roller than in the plastic roller. However, after 1-s plasma treatment, the value of peel resistance for plastic Roller 2 (0.14 N cm^{-1}) came close to the value of peel resistance achieved for Roller 3 (0.17 N cm^{-1}). Best results were obtained for 2 s plasma exposure, where the peel resistance reached using the metal-rubber roller was 31% higher than for the plastic roller.

Commercial VDBD plasma source, often referred to as industrial corona, was used for adhesion improvement besides the DCSBD plasma unit. As previously mentioned, the effect of plasma treatment was observed on the inner side of tubular film treated only from outside. This phenomenon is typical for VDBD and is based on the physical nature of this discharge, where the sample is placed between the HV and grounded electrodes, and hot microfilaments are generated through the sample. However, this feature is also the main disadvantage of the VDBD, as it can damage heat-sensitive materials (pinholing effect) and lead to inhomogeneity of the treatment. Whereas at the DCSBD plasma source, a thin layer of diffuse nonequilibrium plasma is generated on the surface of dielectrics. Curved DCSBD in configuration with Roller 3 produces surface discharge, partially superimposed by fine microfilaments burning perpendicular to the tubular film, characterised by substantially lower current values than typical for industrial corona.

The same treatment time of 1 s was used to compare the effect of various plasma sources (DCSBD, VDBD) on peel resistance value (Figure 8). The best results were obtained for DCSBD using a metal-rubber roller (0.17 N cm^{-1}) in comparison with VDBD (0.15 N cm^{-1}), and the lowest peel resistance was achieved in the case of a plastic roller (0.14 N cm^{-1}).

3.4 | Film-to-meat adhesion tests

This test aimed to estimate the degree of the film-to-meat adhesion, where a degree of 1 represents zero adhesion and a degree of 5 corresponds to the best-off adhesion. The stronger the film-to-meat adhesion, the better the film adheres to the meat emulsion. This fact prevents an undesirable formation of air bubbles or liquid, the so-called purge, under the film surface and prolongs the durability of a product.

Film-to-meat adhesion tests were carried out with differently treated LLDPE/PA tubular films. Previously, we compared Roller 2 and Roller 3. It was found that the effect of the plastic roller (Roller 2) on the inner side of examined tubular films was least pronounced due to the nonconductivity of the roller material, that is, when no microdischarges were generated against the roller. Therefore, for this analysis in addition to Roller 3 we also used Roller 1, which is often part of the large R2R DCSBD system suitable for processing large amounts of material (hundreds of metres) of various types. A comparison of (a) reference, (b) VDBD treated, (c) DCSBD treated using Roller 1 casings, and (d) DCSBD treated using Roller 3 casings after the peeling off is presented in Figure 9. The same plasma treatment time of 1 s was used in all configurations. No adhesion of the expansive emulsion to LLDPE film surface was observed for untreated film (Figure 9a); therefore, the degree of adhesion 1 corresponds to this sample. A slight improvement of adhesion occurred with LLDPE/PA film treated on a DCSBD plasma unit using Roller 1. However, the adhesion was incoherent, as can be seen in Figure 9c.

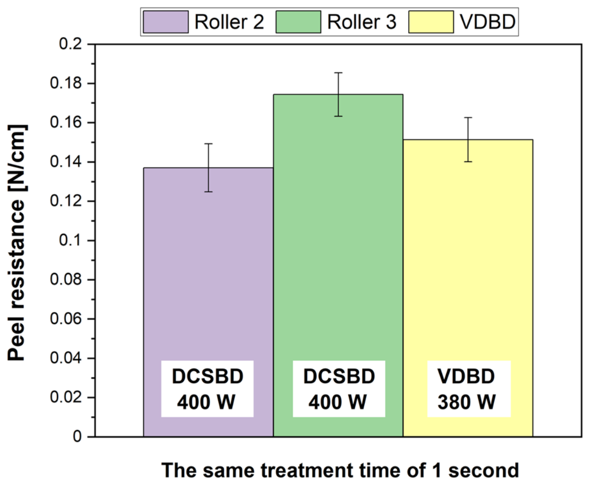


FIGURE 8 Effect of various plasma sources (diffuse coplanar surface barrier discharge [DCSBD], volume dielectric barrier discharge [VDBD]) and rollers used in combination with DCSBD on the peel resistance by the same exposure time of 1 s.

Best adhesion was achieved for LLDPE/PA film treated with VDBD or DCSBD plasma unit using Roller 3. These samples were comparable and corresponded to the degree of adhesion 5 (Figure 9b,d). The effect of roller conductivity is evident when comparing peeled off films in Figure 9c,d; although the same DCSBD plasma unit was applied, only the roller differed. Significantly better film-to-meat adhesion was observed for the DCSBD plasma unit using a metal-rubber roller with a resistance of 7.5 MΩcm (Roller 3) than for the metal-rubber roller with a resistance of 238.5 GΩcm (Roller 1). This result could be attributed to the low resistance of the roller, which means higher conductivity when the surface discharge is superimposed by microfilaments generated perpendicular to the film surface. Therefore, this type of roller (Roller 3) was used for further tests when the influence of exposure time and effect of one/both outer side treatment was studied (Figure 10).

It was found that the influence of plasma treatment duration in the range of 0.5–2 s is minimal, and the degree of adhesion is similar for all plasma-treated samples using this type of roller. Even a very short exposure time of 0.5 s is enough to change the adhesion on the inner side of the film (Figure 10e), which is essential for industrial application. It was proven that the one-side treatment was sufficient for the adhesion improvement (Figure 10b,d) when plasma is applied on one outer side of the tubular film, as treatment of tubular film on both outer sides provided similar adhesive results

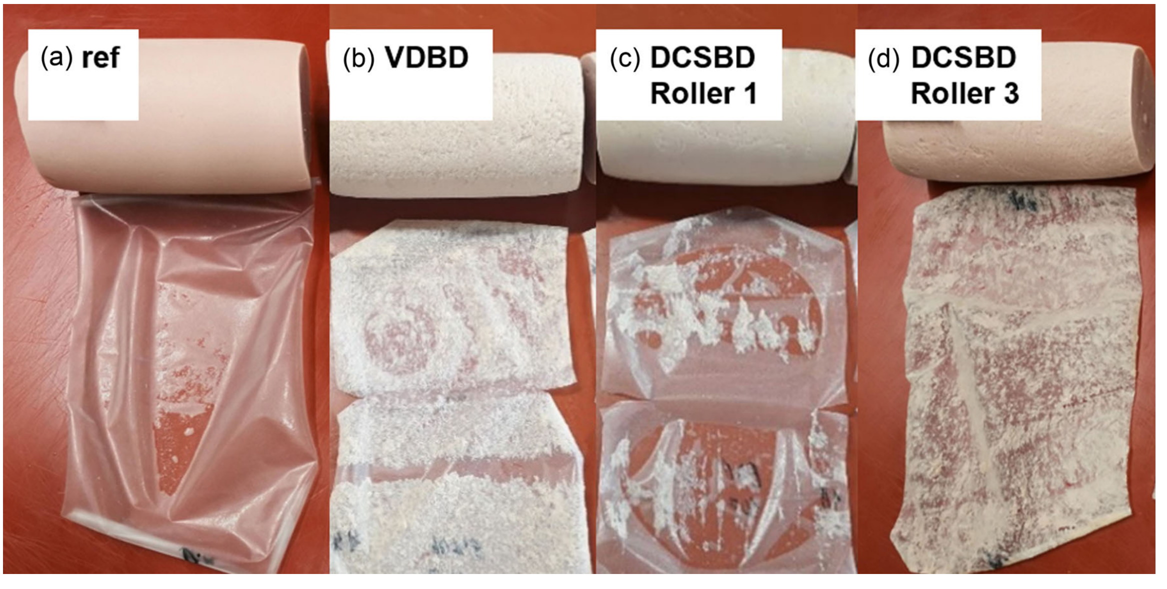


FIGURE 9 Film-to-meat adhesion tested on the linear low-density polyethylene/polyamide films (a) without treatment, (b) volume dielectric barrier discharge (VDBD) treated, (c) diffuse coplanar surface barrier discharge (DCSBD) treated using Roller 1, and (d) DCSBD treated using Roller 3 when the plasma exposure time was 1 s for all configurations.

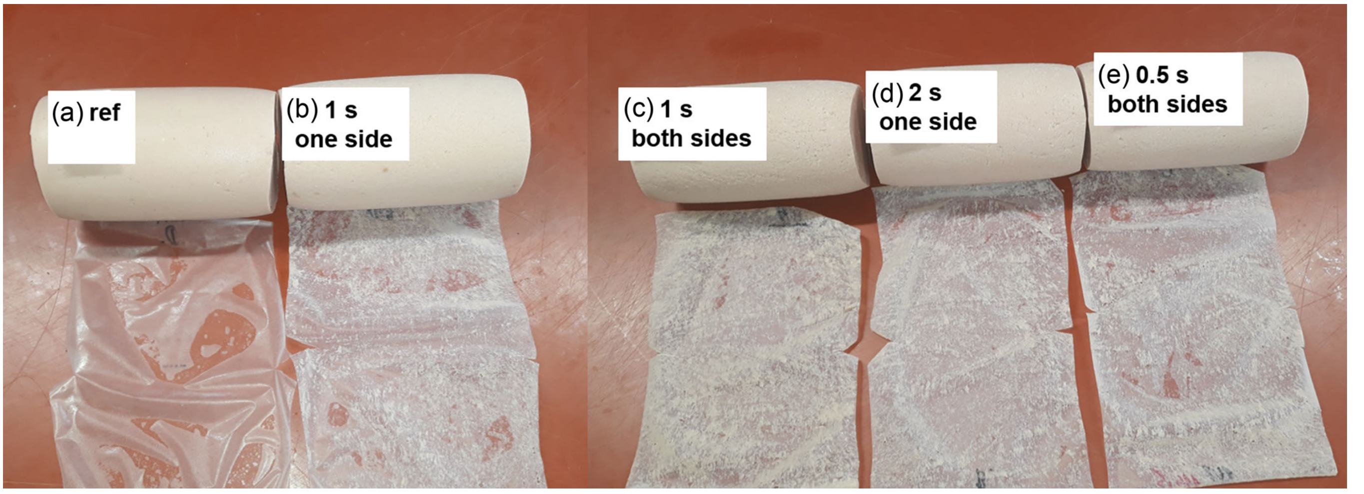


FIGURE 10 Film-to-meat adhesion tested on the low-density polyethylene/polyamide films treated with diffuse coplanar surface barrier (DCSBD) plasma unit using Roller 3 at 400 W for (a) 0 s, (b) 1 s (one outer side), (c) 1 s (both outer sides), (d) 2 s (one outer side), and (e) 0.5 s (both outer sides).

(Figure 10c,e). The benefit of a one-sided treatment of tubular film is timesaving. The results obtained from this film-to-meat adhesion testing indicate that DCSBD only in combination with Roller 3 is able to compete with industrial corona (VDBD) in respect to achieving the plasma effect on the inner side of tubular film treated from the outside.

3.5 | Surface chemical analysis

XPS analysis was used to evaluate plasma-induced chemical changes at the LLDPE surface. Based on the results from film-to-meat adhesion testing, we applied XPS analysis on samples treated with DCSBD plasma unit using Roller 3 and VDBD for standard and higher input powers in both cases. The elemental composition of untreated and plasma-treated LLDPE/PA film is summarised in Table 1. The untreated LLDPE film surface contains 94 at% of carbon, 4 at% of oxygen and 2 at% of silicon. Plasma treatment induced oxidation of LLDPE surface; therefore, an increase in oxygen has doubled and quadrupled compared to the original value. This finding reflects the O/C ratio representing the relative concentration of oxygen and carbon on the surface. Changes in surface chemistry after plasma treatment were observable already at an input power of 400 W in the case of DCSBD and 380 W in the case of VDBD. DCSBD plasma treatment of 1 s at an input power of 600 W promoted the highest increase of O/C ratio to a value of 0.21 from the initial value of 0.05 that was achieved for untreated LLDPE/PA film. The amount of carbon slightly decreased after the plasma treatment,

TABLE 1 Elemental composition of LLDPE film surface measured by XPS before and after plasma treatment (exposure time of 1 s was used) and calculated O/C ratio.

Sample	C (at%)	O (at%)	Si (at%)	O/C ratio
Untreated	94	4	2	0.05
DCSBD 400 W	90	9	1	0.1
DCSBD 600 W	81	17	2	0.21
VDBD 380 W	87	11	2	0.13
VDBD 570 W	84	14	2	0.16

Abbreviations: DCSBD, diffuse coplanar surface barrier discharge; LLDPE, linear low-density polyethylene; O/C ratio, oxygen/carbon ratio; VDBD, volume dielectric barrier discharge; XPS, X-ray photoelectron spectroscopy.

while silicon concentration stayed stable within the 1–2 at % range, regardless of plasma treatment. Changes in elemental chemical composition were similar for both plasma sources (DCSBD, VDBD). Moreover, it was observed that higher input power is beneficial for O/C ratio increase.

The deconvolution of C1s high-resolution spectrum of untreated LLDPE/PA film demonstrated the presence of two principal components attributed to C–C/C–H (binding energy = 284.8 eV) and C–O (286.3 eV) chemical bonds. After the plasma treatment, other peaks corresponding to C=O (287.7 eV) and O–C=O (289 eV) functional groups were detected. Growth or formation of polar C–O, C=O and O–C=O bonds responsible for hydrophilic properties of material was promoted by plasma treatment (Table 2). An increase in polar bonds after DCSBD plasma treatment was more significant than after VDBD treatment. Concentration of C–O bonds

TABLE 2 Concentration of functional groups before and after 1-s plasma treatment achieved from C1s high-resolution spectra measured by XPS.

Sample	C–C/C–H (%)	C–O (%)	C=O (%)	O–C=O (%)
Untreated	94	6	0	0
DCSBD 400 W	74	16	6	3
DCSBD 600 W	70	21	6	4
VDBD 380 W	88	8	3	1
VDBD 570 W	80	13	5	3

Abbreviations: DCSBD, diffuse coplanar surface barrier discharge; VDBD, volume dielectric barrier discharge; XPS, X-ray photoelectron spectroscopy.

increased from the initial 6% to 16% after DCSBD treatment at 400 W in contrast with the value of 8% achieved after the VDBD treatment at 380 W. DCSBD plasma exposure in only 1 s was sufficient to increase C=O and O–C=O bond concentrations from 0% to 6% and 3%, respectively. The decrease of C–C/C–H bond concentration was monitored from an initial 94% to 80% after VDBD plasma treatment at 570 W, and to 70% after the DCSBD plasma exposure at 600 W, respectively. Formation of polar functional groups along with the wettability improvement on the inner side of tubular film treated by plasma from the outer side confirm the presence of parasitic microdischarges, which penetrate perpendicularly through the treated film.

4 | CONCLUSION

The aim of this study was to efficiently modify the inside of the LLDPE/PA tubular film when exposed to plasma from the outside and to demonstrate that DCSBD can be engaged as an alternative to the industrial corona possessing the insufficient homogeneity and reproducibility of the treatment. Even though the DCSBD plasma source generates very thin diffuse plasma with highly suppressed filamentary elements, here we showed that in the suitable configuration of the DCSBD roll-to-roll system, microfilaments can slightly penetrate through the film. As a result, the inner side of the exposed material can be modified. By testing the several types of the rollers used in the DCSBD roll-to-roll system, we revealed that the rollers differing in material electrical resistance had a different effect on plasma activation of the film inside. Measured electrical characteristics of plasma discharge verified that a nonconductive roller constructed from plastic (Roller 2) does not allow the surface discharge to be superimposed by microfilaments generated perpendicular to the film surface in contrast to a metal-rubber roller (Roller 3). This finding was proven by a higher achieved value of electrical efficiency for plastic Roller 2 (0.91) compared to metal-rubber Roller 3 (0.77). The visible evidence of wettability improvement of the inner LLDPE layer of tubular film was observed by immersion of the film in a methylene blue water solution. While the untreated film repelled the solution, plasma-treated film using Roller 3 in DCSBD plasma system led to entire film wetting. XPS data confirming the growth or formation of polar C–O, C=O and O–C=O bonds responsible for hydrophilic properties of material underlined the improved wettability of inner LLDPE layer of the tubular film. More significant surface chemical changes were achieved by DCSBD treatment in comparison with VDBD treatment; moreover, the O/C ratio increased up to four times due to the plasma treatment. Additionally, we observed an increase in peel resistance for all plasma system configurations; however, achieved values were quite comparable. The best results were obtained for DCSBD using a metal-rubber Roller 3 (0.17 N cm^{-1}) in comparison with VDBD (0.15 N cm^{-1}), and the lowest peel resistance was measured for plastic Roller 2 (0.14 N cm^{-1}). Investigation of film-to-meat adhesion of meat emulsion to various treated LLDPE/PA casings revealed that the resistance of the roller in DCSBD plasma system had a tremendous impact on this parameter. Plasma treatment by DCSBD with Roller 2 having higher value of resistance (238.5 GΩcm) induced very weak and incoherent film-to-meat adhesion. On the other hand, Roller 3 with lower resistance (7.5 MΩcm) provided excellent adhesion of meat batter to film due to higher conductivity of the roller. Comparable adhesion was achieved by VDBD treatment. No adhesion of the expansive emulsion to LLDPE film surface was observed in the case of untreated film. Moreover, it was proven that one-side DCSBD treatment of tubular film is sufficient for the adhesion improvement also of the opposite LLDPE layer. Even a very short exposure time of 0.5 s was enough to change the adhesion on the inner side of the film, which is essential for industrial application. The results showed that DCSBD plasma system in configuration with metal-rubber roller having suitable conductivity is able to gently modify the inner side of the treated film by plasma exposure from outside.

AUTHOR CONTRIBUTIONS

Vlasta Štěpánová: Investigation; funding acquisition; writing – original draft; writing – review and editing. **Petra Šrámková**: Investigation; writing – original draft; writing – review and editing. **Slavomír Sihelník**: Investigation; writing – review and editing. **Miroslav Zemánek**:

Investigation. **Jana Jurmanová**: Investigation. **Monika Stupavská**: Investigation. **Dušan Kováčik**: Conceptualisation; funding acquisition; investigation; writing – review and editing.

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DATA AVAILABILITY STATEMENT

Data are available on request from the authors.

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