

## Article

# Effect of Plasma Surface Modification on Print Quality of Biodegradable PLA Films

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**Abstract:** PLA films, as non-absorbent materials, require modification of the surface before the printing process in order to improve the wettability of the substrate and to obtain proper ink adhesion to the substrate. In this paper, the surfaces of two kinds of PLA films were modified using plasma activation with parameters enabling high surface free energy (SFE) values, and then the films were printed on using different kinds of flexographic inks. Two gases, oxygen and argon, were used for activation, as these make it possible to obtain good hydrophilicity and high SFE values while having different effects on the roughness, or the degree of surface etching. Plasma-activated films were subsequently subjected to the measurements of: contact angle with water, diiodomethane and three printing inks, roughness, weight change, strength properties, color and gloss change, and SFE was determined. Unmodified and activated films were flexographically printed in laboratory conditions and then the quality of obtained prints was analyzed. The results showed a strong effect of activation with both oxygen and argon plasma on the SFE value of the films and the contact angles of water and inks, with the gas used for plasma activation and the type of film significantly influencing the thickness of the fused ink layer and the resultant color. Moreover, plasma activation had a especially favorable and significant effect on the quality of prints made with water-based inks, while it had little effect when printing with solvent-based inks.

**Keywords:** plasma activation; PLA films; biodegradable polymers; water-based inks; solvent-based inks; flexographic printing; printability; print quality



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## 1. Introduction

Biodegradable materials are particularly relevant to modern world economies struggling with waste and environmental issues [1–3]. One of the key biodegradable plastics is polylactide (PLA) [4–6], which (as a non-absorbent substrate (biodegradable film)) can be printed using flexographic or gravure printing techniques commonly used in industry.

Flexography is one of the varieties of relief printing, where printing is done using flexible printing forms and liquid water-soluble, solvent or UV inks [7,8]. This technology enables high quality printing with an optimized selection of printing process parameters [9]. Print quality is influenced by many factors, such as the type of printing substrate, its finishing and preparation (coating or smoothing of paper substrates, modification of the surface layer of non-absorbent materials, etc.), the printing technique and the kind of printing inks [8,10–14].

PLA films, like other non-absorbent materials, require surface preparation prior to printing or finishing processes to improve wettability and to impart adequate hydrophilicity [15–18]. Plasma activation, in comparison to chemical activation, is an environmentally friendly alternative for modifying the surface layer of polymers prior to their further refinement and finishing processes. Other advantages include the high reproducibility and stability of the process and the possibility of obtaining diverse effects due to the use of different gases (O<sub>2</sub>, CO<sub>2</sub>, N<sub>2</sub>, NH<sub>3</sub>, air, H<sub>2</sub>, He, CF<sub>4</sub> and Ar) [19,20] or process parameters

(activation time, pressure, power, etc.) [21,22]. Plasma activation results in the formation of functional groups on the surface of the modified material, changes in surface hydrophilicity and surface free energy, changes in surface crosslinking, changes in surface morphology, the removal of impurities or the improvement of biocompatibility [23,24].

The surface free energy of the film is calculated using the contact angle of various measuring liquids. It is the basic parameter for good wettability of the substrate and its printing [25–27]. Even if the surface wetting is satisfactory and the ink can be applied, this does not guarantee good adhesion of the ink to the substrate [15]. Wettability is one of the basic characteristics of printing substrates, which depends on the chemical composition and morphology of the material, both of which affect hydrophilicity. On the other hand, the value of adhesion force is influenced by the impurities present on the surface of the material, the development of its surface, the surface free energy and the magnitude of the difference between the surface free energy of the substrate and the printing ink [16,28].

The effect of plasma activation on PLA properties has been the subject of previous studies [6,19,29–44]. They showed a good effect, using argon and oxygen to increase the surface free energy values and improve the wettability [22,29–31]. Upon activation with oxygen, various groups containing oxygen atoms are formed on the surface of the modified material, thus improving the hydrophilicity of the material [45,46], causing etching of the material surface [47,48], and slightly changing the surface roughness [34,44,49]. With argon activation, in addition to a significant improvement in material hydrophilicity and adhesion, there is a significant increase in surface roughness and the formation of free electron pairs at the carbon atom [29,37]. As a result of previous in-house studies, it was found that oxygen plasma activation is more effective than argon plasma activation and has a greater effect on improving the wettability of PLA films. Furthermore, it was shown that a longer activation time has no significant effect on the wetting angle in the case of argon plasma activation. On the other hand, in the case of oxygen activation, a longer activation time even has a negative effect on the wetting angle value [22,29,30]. Moreover, the type of gas used for plasma modification has been found to have a much greater effect on the wettability of modified substrates using solvent-based inks than in the case of water-based inks [22]; however, this study was limited only to the investigation of the contact angle of a modified substrate using three different inks without taking into account the printability of the substrate. The research carried out in this paper, on the other hand, will include an extensive study of the effect of PLA film activation and the kind of flexographic ink used for printing on print quality and the parameters used to evaluate it, such as ink adhesion to the substrate, gloss, CIELab color coordinates, optical density and relative contrast.

In this study, we attempt to determine the effect of the gas used during plasma modification of PLA film and the type of substrate and printing ink on the printability of the film and the quality of the prints obtained. The relevance of the plasma process before flexographic printing with various printing inks has been demonstrated. To the author's knowledge, there are no available studies presenting the influence of plasma activation on the printability of PLA films with a thorough analysis of parameters determining the quality of prints, which was realized in this study. Available publications addressing the issue of the effect of substrate activation on printability deal with other materials, other printing technologies and other activation processes [50–54] or are only an introduction to the issue [22]. On the other hand, publications dealing with printability of PLA films do not consider plasma modification of the substrate [55–58].

## 2. Materials and Methods

### 2.1. Materials

Two types of polylactide films were used for this study: Nativia BOPLA NTSS (Taghleef Industries GmbH, Holzhausen an der Haide, Germany) and EarthFirst PLA BCP (Plastic Suppliers, Inc. EarthFirst, Ghent, Belgium), with thicknesses of 20 and 50 micrometers, respectively. Both materials are commercially available, biodegradable and compostable films based on polylactide. A more detailed characterization of the films is

shown in Table 1. Both films used for this study were supplied as A4 sheets. The film samples were conditioned in an air-conditioned laboratory room under standard ambient conditions (ISO 187:1990) (temp.  $23 \pm 0.5$  °C, HR  $50 \pm 1.5\%$ ) before treatment and were printed immediately after treatment under the same conditions.

**Table 1.** The characteristics of the films used in the study.

	Nativia BOPLA NTSS	EarthFirst PLA BCP
Abbreviation used	NTSS	BCP
Surface free energy (mJ/m <sup>2</sup> )	37	38
Gloss (GU)	80 (45°)	125 (60°)
Haze (%)	1.5	7.0
Moisture vapor transmission rate		
MVTR (g/m <sup>2</sup> /d)	440	155
Oxygen transmission rate O <sub>2</sub> TR		
(cm <sup>3</sup> /m <sup>2</sup> /d)	1100	450
Tensile strength MD/TD		
(N/mm <sup>2</sup> )	105/205	55.16/55.16

Three different black, flexographic inks were used to print on NTSS films and water-based ink was used for BCP films (see Table 2). The viscosity (Ford cup, 100 mL,  $\phi$ 4 mm) of all of the printing inks was 18 s.

**Table 2.** The characteristics of the inks used in the study.

	Ink 1	Ink 2	Ink 3
Trade name	FlexiWet (Chespa)	Urania (Chespa)	Wiflex (Chespa)
Kind of resin	Acrylic	PA	NC/PU
Kind of ink	water-based	solvent-based	solvent-based

## 2.2. Plasma Treatment

Plasma activation was performed using a vacuum chamber with a Diener Nano low-pressure plasma system (Diener Electronic, Altensteig, Germany). One half of PLA films was exposed to low pressure oxygen plasma (100% O<sub>2</sub>), while the other half was treated with argon plasma (100% Ar). The device was operated at the following settings: radio frequency 40 kHz, power 1000 W, pressure 0.5 mbar (50 Pa), gas pressure control, fixed gas delivery time 2 min and exposure time 2 min. Activation time and pressure were determined based on previously completed studies [21,22,29,30] as optimal for obtaining high surface free energy (SFE) values.

## 2.3. Testing of Selected Film Properties before and after Plasma Treatment

The contact angles of distilled water, diiodomethane 99% CH<sub>2</sub>I<sub>2</sub> (Sigma-Aldrich, Taufkirchen, Germany) and ink were measured. Measurements were made using a DSA 100 drop shape analysis system (Krüss, Hamburg, Germany) using the tangent method and sessile drops of the liquids deposited using 0.5 mm diameter needles before and immediately after treatment. The results presented are the average of five measurements. The surface free energy of the film as well as its polar and dispersion components were calculated based on contact angle measurements with water and diiodomethane. The Owens–Went method was used for these calculations [27,29].

Surface roughness were analyzed using a Sensofar Plμ Neox microscope (Sensofar Metrology, Terrasa, Spain). The following parameters for topographic images were used: objective 50 × 0.95 N in white light, measured area 768 × 576 pixels (254.64 × 190.90 μm<sup>2</sup>), layer thickness 15.2 μm, threshold 15%. The analysis was performed on the surface in three areas.

Weight change analysis of the samples was performed using a Sartorius LE 225D-OCE semimicrobalance (Sartorius, Göttingen, Germany). Samples of 50 × 50 mm were weighed immediately before and after activation, and the average of four determinations was reported as the mass change value.

More details of the measurement runs are reported in earlier works [29,30].

Determination of tensile properties of films was carried out according to ISO 527-3 using a static testing machine Roell (ZwickRoell GmbH & Co. KG, Ulm, Germany) and testXpert software. The reported results are the average for the five tested samples.

The change in color and gloss of the film due to activation was evaluated using a spectrophotometer SpectroEye (GratagMacbeth/X-Rite GmbH, Neu-Isenburg, Germany) and triple angle gloss meter PicoGloss 503 (Erichsen GmbH & Co. KG, Hemer, Germany), respectively. Spectrophotometric measurements were performed under the following instrument operating parameters: light source D65, observation angle 2° and no filter. Gloss was determined according to the EN ISO 2813 standard. 20° measurement angles were used, because the measurements made at a 60° angle were greater than those made at 70 GU.

#### 2.4. Flexographic Printing Process

The prints were made using flexographic technology on a laboratory machine FLP-21. A special flexographic photopolymer printing form with a test print containing full-surface and raster fields (80%) was used for printing. A raster cylinder (anilox) with a line count of 140 L/cm was used for printing with cell volumes of 10 and 8 cm<sup>3</sup>/cm<sup>2</sup> for water-based ink and for solvent-based inks, respectively.

#### 2.5. Evaluation of Prints

Evaluation of the quality of the prints included spectrophotometric measurements of color coordinates L\*, a\*, b\* and optical density of fields with 100 and 80% coverage, as well as gloss measurement and adhesion tests [59].

Spectrophotometric measurements were performed using a SpectroEye spectrophotometer (GratagMacbeth/X-Rite GmbH, Neu-Isenburg, Germany) where the color coordinates CIELab were measured with the following parameters: illuminant D50, standard observer 2°, polarization filter and Abs, and for optical density measurements a standardized white substrate (paper settings) was used. For each print, measurements were taken at 3 different points and the average value was reported as the result. To obtain the color change, the color difference defined by  $\Delta E$  was calculated from L\*, a\*, b\* color coordinate values [7,59].

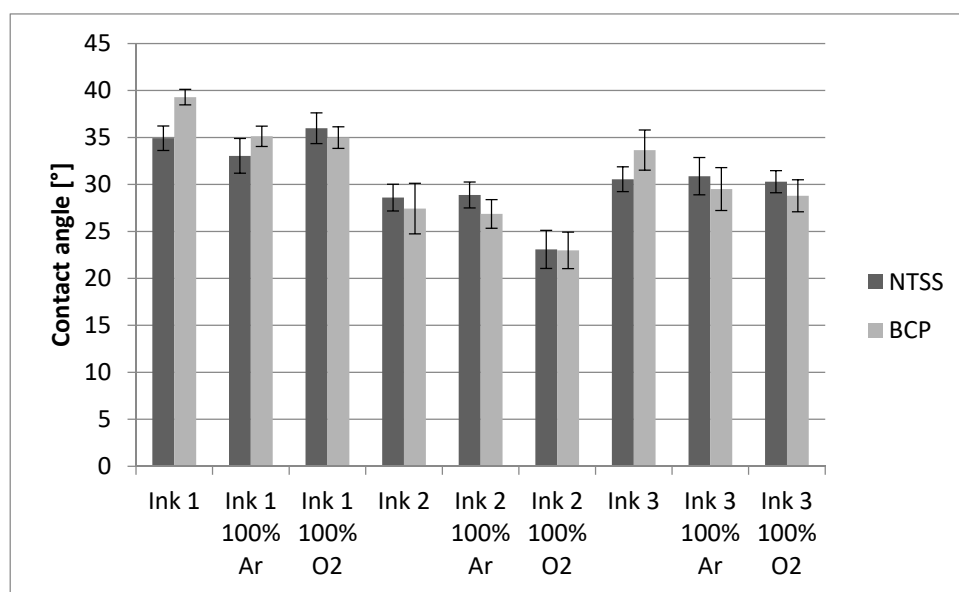
Gloss was determined with gloss meter PicoGloss 503 (Erichsen GmbH & Co. KG, Hemer, Germany) according to the EN ISO 2813 standard. The 60° measurement angle was used for all prints, and additional measurements were made at the 20° measurement angle for prints made with solvent-based inks due to the high gloss value. Presented results are the average of six measurements.

Adhesion of ink to the substrate was evaluated using an adhesive tape test [13,59].

### 3. Results and Discussion

#### 3.1. Effect of Plasma Activation on Film Properties That Can Affect Printability

The parameter that enables printing of the film is its appropriate wettability by the printing ink. The smaller the contact angle is, the better the liquid wettability is. Figure 1 shows the variation of the contact angle of the two tested films, before and after plasma activation, with the three flexographic inks used subsequently for printing.

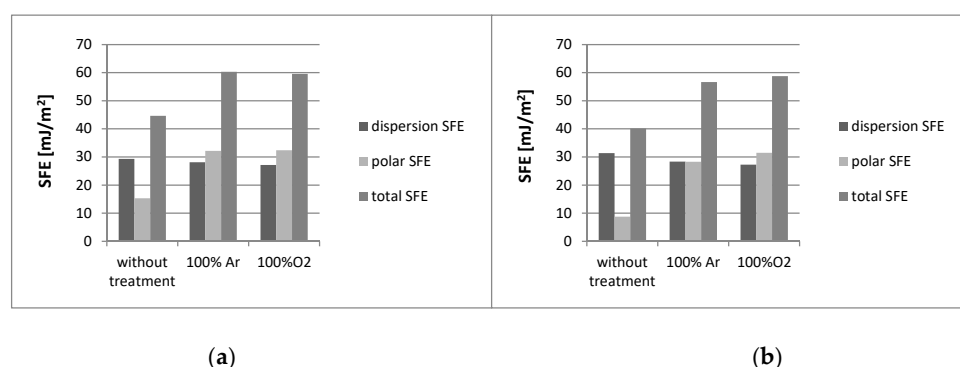


**Figure 1.** Changes in contact angles for inks.

The BCP film had a higher contact angle before modification than the NTSS film, which was 72.6° and 62.5°, respectively. Activation with both oxygen and argon plasma resulted in a significant reduction in the water contact angle for both materials (24° and 25° for NTSS films, and 33° and 29° for BCP film, respectively), indicating a significant improvement in the wettability of both films.

Analyzing the data obtained, it can be concluded that plasma activation, both oxygen and argon, had a beneficial effect on the wettability of BCP film by printing inks, while for the other film the effect is not conclusive. This may be due to the fact that the NTSS film is a corona-modified production material by the manufacturer, which affects its wettability and printability, and despite an SFE value comparable to the film without surface pretreatment, the film morphology, roughness and surface development may be altered. The type of gas used for activation has only a minor effect on ink wettability, although slightly better results as in previous studies performed for another PLA film [22], were obtained using oxygen activation. By far the more important factors determining wettability are the kind of ink and substrate. Obviously, solvent-based inks show better wettability than water-based inks due to the surface tension of these inks. In water-based ink, the solvent is water, which has a high surface tension, which translates into ink properties [60].

PLA films, like all films made of biodegradable or plastic materials, must have a surface free energy higher than the surface tension of the printing ink in order to be flexographically printed. The higher this difference, the better the wettability and adhesion of the ink to the substrate [15,16,28]. Based on the film contact angle studies, before and after activation using water and diiodomethane as two measuring fluids with different polar and dispersion properties, the values of SFE and its polar and dispersion components were calculated (see Figure 2).



**Figure 2.** Changes in surface free energy for (a) NTSS film; (b) BCP film.

Regardless of the type of gas used for activation, very high SFE values were obtained for both films. It is worth noting that the increase in the SFE value was due to the increase in the value of its polar component, which more than doubled. Moreover, the obtained SFE values are much higher than those considered to enable satisfactory print quality given in the literature [13,57,59]. In general, the higher the SFE value and the lower the water contact angle value, the more hydrophilic the film is and will be more susceptible to ink wetting. While the gas type did not significantly affect the total SFE value, it did affect its components. Higher values of the polar component are possible with oxygen plasma, which should have a beneficial effect on print quality.

Table 3 shows the results of the surface roughness and weight change of the samples due to film activation. From these, it was found that the surface roughness of both films decreased slightly with oxygen plasma activation, with the surface uniformity also decreasing. With plasma activation with argon for both films, an increase in surface roughness was observed. The obtained roughness changes are consistent with observations obtained in other studies [29,34,37,44,49].

**Table 3.** Changes in roughness and weight of the film due to plasma activation.

Measured Parameter.	BCP	NTSS
Surface roughness (without plasma) (nm)	130.22 ± 37.09	107.32 ± 13.07
Surface roughness (100% Ar plasma) (nm)	150.02 ± 16.23	244.64 ± 14.01
Surface roughness (100% O <sub>2</sub> plasma) (nm)	130.07 ± 48.19	89.62 ± 47.61
Weight difference (100% Ar plasma) (mg)	0.280 ± 0.071	0.405 ± 0.064
Weight difference (100% O <sub>2</sub> plasma) (mg)	0.355 ± 0.007	0.425 ± 0.064

From the results obtained (Table 3), it can be concluded that the type of gas used for plasma activation has a significant effect on the surface roughness and weight change of the sample. The change in sample weight can indicate the removal of impurities from the material surface, oxidation of the material and etching of the material [61]. As in other studies [29,34,37,44,49], the results obtained also confirm a slight change in roughness and significant etching of the sample due to activation with oxygen and a lower degree of etching, but the significant changes in roughness are due to activation with argon.

Changing the roughness affects the printing properties of the films by changing the surface wetting by the ink, which is confirmed by the contact angle results. Despite similar SFE values for different films activated with different gases, the obtained ink contact angle results differ, which may be due precisely to the different level of etching of the material layer and differences in surface roughness. The correlation between the substrate roughness and its water contact angle has long been studied [62]. The film roughness results obtained by the author exceed the value of 100 nm, for which the effect of roughness on the contact angle was found to be significant. Since the obtained water contact angle



values for both films activated with both gases were less than  $60^\circ$  (they were  $37.5^\circ$  and  $38.3^\circ$  for the activation with argon and oxygen, respectively, for the NTSS film, and  $43.4^\circ$  and  $39.6^\circ$ , respectively, for the BCP film), the roughness causes a decrease in the contact angle. In summary, it can be concluded that plasma activation with oxygen produced slightly better film wettability than with argon.

Flexographic printing is carried out on high-speed web machines [8,14,55]. In order to ensure the continuity of the printing process and eliminate the problem of tearing of the web of printed material, it is necessary to ensure certain strength properties of the material. It is important that the modification of the substrate does not have a significant effect on these parameters. Table 4 shows the effect of plasma activation on the measurement results for two basic strength parameters: tensile strength and elongation at break in the machine direction (MD) direction. The results obtained were different from those reported in the material specifications from the manufacturers but showed an analogous relationship demonstrating that the strength of NTSS films despite the lower thickness being significantly higher. Both types of plasma activation positively affected the breaking strength of BCP films, increasing it by more than 1.5 times. Such changes may be due to processes such as recombination and cross-linking associated with the formation of free radicals due to plasma activation on the modified material surface [43,63]. Plasma activation with argon had an equivalent effect on the NTSS film, while activation with oxygen decreased the value of the breaking strength, although it was still relatively high. The BCP film showed lower elongation at break than the NTSS film, which was significantly reduced by plasma activation regardless of the gas type. In the case of NTSS film, the changes depended significantly on the type of gas, with argon activation increasing the elongation value at break many times, while modification with oxygen plasma caused a very significant decrease in elongation at break. In conclusion, it can be stated that oxygen plasma activation has a negative effect on the tensile properties of NTSS films, while argon plasma activation has a lesser effect, and in the case of BCP films, it is even positive for both gases. In conclusion, the type of film is crucial when it comes to the effect of plasma activation on the strength properties of the modified material, and for each new substrate it would be suggested to determine such an effect.

**Table 4.** Tensile properties of the film due to plasma activation.

Measured Parameter	BCP	NTSS
Tensile strength (without plasma) (MPa)	$27.54 \pm 6.35$	$59.84 \pm 5.72$
Tensile strength (100% Ar plasma) (MPa)	$44.64 \pm 23.09$	$102.10 \pm 11.44$
Tensile strength (100% O <sub>2</sub> plasma) (MPa)	$41.24 \pm 16.60$	$38.51 \pm 5.72$
Elongation at break (without plasma) (%)	$6.68 \pm 2.80$	$16.70 \pm 17.09$
Elongation at break (100% Ar plasma) (%)	$3.62 \pm 0.79$	$146.00 \pm 15.17$
Elongation at break (100% O <sub>2</sub> plasma) (%)	$3.66 \pm 0.52$	$3.24 \pm 0.82$

Changing the substrate color and gloss could affect the user's perception of the print and the final color of the print. If the substrate became yellowed, it would adversely affect the quality of the print and translate to the range of colors reproduced [59]. Regarding gloss, prints with higher gloss are generally perceived to be of higher quality. Table 5 summarizes the results of calculating the color change ( $\Delta E$ ) of the film due to plasma activation of the film using oxygen and argon as gases and the calculated values of the gloss difference. The color changes due to plasma activation with both oxygen and argon plasma are insignificant. The  $\Delta E$  values indicate that the color change is not noticeable to the film user [59]. The NTSS film obtained a significant increase in the gloss value for the modified films under all conditions considered, while the gloss of the BCP film decreased as a result of plasma activation. Nevertheless, it should be noted that both before and after activation, regardless of the type of gas used, both materials exhibited high gloss.

**Table 5.** Change in color and gloss of the film due to plasma activation.

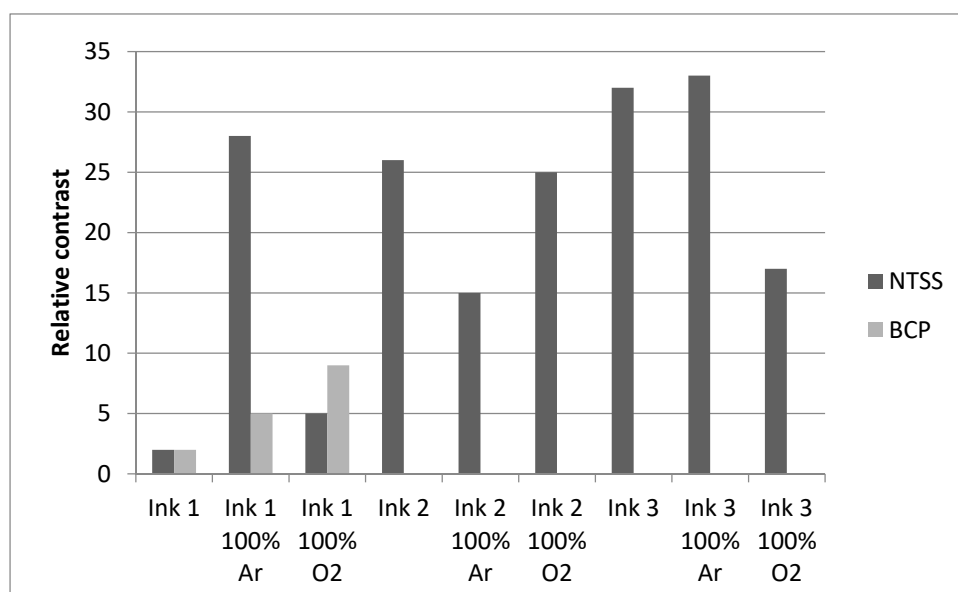
Measured Parameter	BCP	NTSS
$\Delta E$ (100% Ar plasma)	0.61	0.48
$\Delta E$ (100% O <sub>2</sub> plasma)	0.71	0.50
Gloss difference (100% Ar plasma) (GU)	−27.68	23.82
Gloss difference (100% O <sub>2</sub> plasma) (GU)	−31.81	33.47

### 3.2. Effect of Plasma Activation on Print Quality

One of the key parameters determining the quality of the print is the adhesion of the ink to the substrate. Without good adhesion, it is impossible to obtain a high-quality print. As a result of plasma activation, irrespective of the type of gas used for modification, very good adhesion of the ink to the film was obtained for each of the tested inks. However, for unmodified films, good adhesion was obtained for solvent-based inks, while it was not fully satisfactory for water-based inks. Water-based inks are more difficult to print than solvent-based inks and can create problems with ink adhesion to the substrate due to their composition and surface tension [13,15,58].

Contrast is an alternative to the measurement of tonal value gain. It is determined from the optical density of the fully covered field (100%) and the raster field (80%—recommended for black ink). High quality prints should have the highest possible print contrast, which is possible due to the high optical density of the fully covered field. For all prints made with solvent-based inks, whether the NTSS film was plasma activated or not, the relative contrast was very high [58,63] (see Figure 3). In contrast, both untreated films printed with water-based inks exhibited very low relative contrast values, with both oxygen and argon plasma activation having a beneficial effect in increasing contrast values. For solvent-based inks, the contrast values are many times higher than those for water-based inks. In addition, for water-based inks, where two different printing substrates were used, the type of film affects the results. The highest contrast values were obtained for printing with solvent ink 3 and water-based ink 1 on NTSS film activated by argon plasma (33 and 28, respectively) and for prints on untreated NTSS films printed with solvent inks 2 and 3 (26 and 32, respectively). The fact that for some prints the contrast decreased as a result of activation and did not increase further can be explained by the fact that an increase in the optical density value is associated with an increase in the thickness of the fused ink layer, which is only possible up to a certain limit and thus limits the further possibility of contrast increase due to halftone dot filling [64]. Furthermore, the change in the thickness of the ink layer transferred to the NTSS film may have been influenced by changes in the substrate roughness due to plasma activation with different gases.

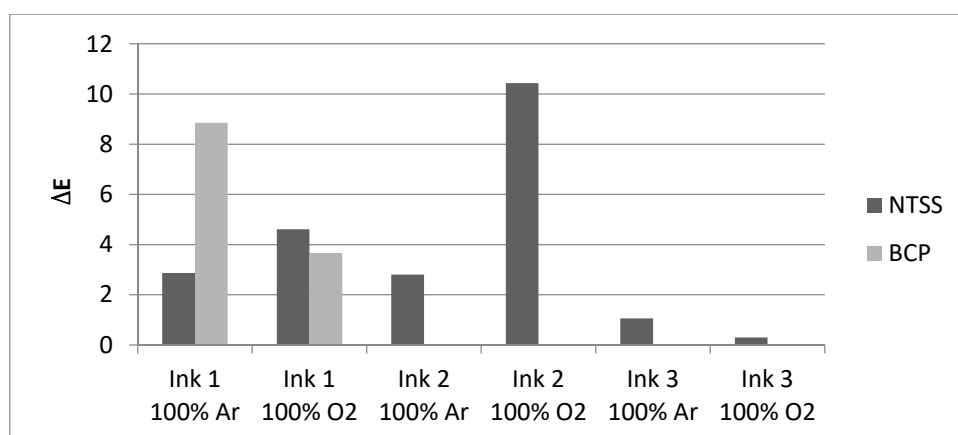




**Figure 3.** Changes in relative contrast of prints as a function of ink kind, substrate and kind of plasma activation.

In summary, the key influence on the relative contrast value is the kind of ink that was used to print the substrate. Films printed with solvent-based inks have significantly higher relative contrast than films printed with water-based inks. In the case of printing with water-based inks, plasma activation with both oxygen and argon positively increases the value, while a significant effect of the substrate on the results is observed.

Figure 4 shows the results of the color difference ( $\Delta E$ ) between the prints made on the substrate not activated before printing and activated by plasma activation using oxygen and argon as determined by the color coordinate measurements  $L^*$ ,  $a^*$ ,  $b^*$ . The  $\Delta E$  values obtained for ink 3 are the smallest and imperceptible to the observer. For this ink, the substrate contact angle values were only slightly different from each other, resulting in a similar amount of ink being transferred and fixed to the activated and nonactivated substrates, giving similar color coordinate values and little color difference. In the case of prints made with water-based and solvent-based ink 2, a significant effect of plasma activation regardless of the type of gas used on the color change of the prints was noted, an observation that can be explained by the change in thickness of the ink fixed on the print.



**Figure 4.** Color difference values between prints made on a substrate not activated before printing and activated by plasma activation using oxygen and argon.

Figure 5 shows the gloss of prints made using different inks on modified and unmodified films. Due to the very high gloss values obtained for solvent-based inks when measured with a 60° geometry, these were supplemented with results obtained for a 20° measurement geometry (Figure 5b). There was no significant influence of the type of plasma activation and the gas used on the gloss of the prints. However, the type of printing ink is a decisive parameter for the results obtained. Prints made with water-based inks show significantly lower gloss than those made with solvent-based inks. The change in gloss of the substrate caused by activation did not affect the obtained print gloss values.

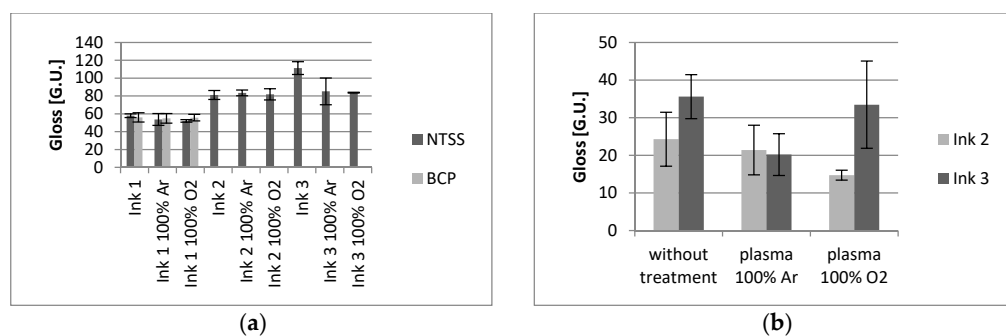


Figure 5. Gloss of prints measured with different geometry: (a) 60°; (b) 20° for very high gloss prints.

#### 4. Conclusions

The wettability of PLA films by flexographic printing inks, both water-based and solvent-based, can be effectively improved by modifying the substrate with cold plasma involving oxygen as well as argon. At the same time, the type of gas used does not have as significant an effect on the wettability improvement as the type of ink and the printing substrate. Nevertheless, the reason for the observed change in ink wetting may be the change in film roughness due to plasma activation.

A significant effect of the type of gas used for plasma activation on surface roughness and sample etching was observed. Activation with oxygen leads to minimal change in roughness and more etching of the sample, while activation with argon resulted in significant changes in roughness and less etching of the samples.

Moreover, plasma activation, regardless of the gas type, increased the SFE values to 57–60 mJ/m<sup>2</sup>, which is well above the minimum value needed for high quality prints. The change in SFE was due to the increase in the polar component of SFE. It is worth noting that a greater increase in the polar component was observed for oxygen plasma-activated films.

Plasma activation affected the strength properties of the films, with the effect depending on the type of gas and material. Generally, the breaking strength improved, while the elongation at break decreased. However, the observed changes should not affect the printing process.

Regarding the visual alteration of the film, the color of the film did not change significantly due to both oxygen and argon plasma activation. However, the gloss changes were dependent on the type of modified film rather than the gas used for plasma activation.

Analyzing all the data for the modified films, it can be concluded that the use of oxygen plasma for activation resulted in slightly better wettability of the films than using argon plasma. The improvement in substrate wettability as a result of the plasma activation of the films translates to the quality of the prints produced. Plasma activation with both oxygen and argon allows for very good adhesion of all printing inks to both substrates.

The relative contrast value is mainly influenced by the type of printing ink and, to a lesser extent, by the type of printing substrate and the way it is modified before printing. Plasma activation plays a significant role when printing with water-based inks, while its influence is insignificant in the case of solvent-based inks.

As far as the color changes of the print are concerned, here not only the type but also the composition of the ink and the substrate influence the magnitude of the observed

changes. Plasma activation of the film had a significant effect on the printability with water-based and solvent-based polyamide inks, as indicated by the  $\Delta E$  values obtained. On the other hand, there was no significant effect on the gloss of the prints, which depends mainly on the type of printing ink.

In conclusion, the changes occurring in PLA films as a result of plasma activation favorably influence the printability of these substrates. Several parameters simultaneously have a significant influence on the results obtained, namely the kind of material modification, the kind of printing ink and the kind of film.

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