Comparing the effect of different atmospheric pressure non-equilibrium plasma sources on PLA oxygen permeability

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Abstract. Plasma technology is widely adopted for polymer surface modification. In this work polylactide (PLA) samples have been exposed to the plasma region generated by three different plasma sources operating at atmospheric pressure: a floating electrode dielectric barrier discharge (FE-DBD), a novel linear corona discharge and a DBD roller. The sources have been supplied with a high voltage generator capable of producing pulses with a rise rate in the order of several kV/ns in order to obtain diffuse plasma and avoid local damage to the membrane; air and argon have been used as working gases. Pure oxygen permeation tests in PLA films have been carried out by means of a closed-volume manometric apparatus working at 35°C with a pressure difference of pure O₂ of about 1 bar applied across the membrane. Tests have been performed shortly after the plasma treatment and also replicated at different times in order to investigate the durability of surface modification. The effects of voltage, pulse repetition frequency (PRF) and exposure time on the membrane surface characteristics and barrier property have been studied.

1. Introduction

In past decades petroleum-based polymers such as polystyrene, polyamide and polyethylene have been widely used because of their availability in large quantities at low costs [1]. However, driven by growing environmental concerns, new polymers based on renewable materials are being designed and developed to replace conventional polymers in different applications like food packaging [2].

One of the most promising of these eco-friendly polymers is polylactide (known also as polylactic acid or PLA). Polylactide is an aliphatic biodegradable, thermoplastic polyester derived from vegetal sources such as sugarcane, corn starch and tapioca, which are fermented to lactic acid and then polymerized. PLA can be processed like common thermoplastics and possesses good mechanical properties and high transparency. For these reason PLA is widely used in the packaging field for bottles, trash bags or disposable tableware [3]. In the human body PLA undergoes scission into lactic acid, a natural intermediate in carbohydrate metabolism [4]. PLA is therefore biocompatible.
and is used for many medical applications such as drug delivery, resorbable sutures, vascular devices and orthopedic implants [5].

Despite its excellent properties PLA presents a number of drawbacks that limit its broad application, such as its brittleness and thermal instability. Moreover, PLA barrier properties are worse than those of some oil-based polymers such as PET, and even if production cost is constantly decreasing it is still higher than those of common plastics. In order to enhance PLA properties and broaden its application field, new treatments and solutions must be developed. Chemical and physical properties on the surface have great influence on the final characteristic of the material; plasma treatment is one of the new inexpensive technologies able to achieve surface modification of the top layer (1-10nm) of polymeric materials without altering their bulk properties [6]. Furthermore plasma treatment proves to be an environmental friendly process, solvent free and with good energy efficiency [3]. While many publications have been dedicated to plasma treatment of polymeric materials using low pressure RF plasmas [1,10,11], only few investigate PLA modification using atmospheric pressure plasma sources [3,12,13].

In this work we report on the treatment of PLA films using three different non-equilibrium atmospheric pressure plasma sources; the effect on surface wettability, morphology, O₂ barrier properties and treatment durability have been analyzed for various operative conditions.

2. Experimental setup

2.1. Plasma treatments of PLA sample

Three different plasma sources have been used for PLA surface modification. The three sources have been alimented by a pulse generator (FID GmbH – FPG 20-1NMK) producing high voltage pulses with a rise time of few kV/ns, a peak voltage of 7-20 kV into a 100-200 Ω load impedance and a maximum pulse repetition rate of 1000 Hz. The circular PLA treated sample had a 2.5 cm diameter and a thickness of 40µm.

2.1.1. Floating Electrode – Dielectric Barrier Discharge (FE-DBD): this plasma source is widely adopted for the treatment of thermosensitive and biological materials since it relies on a dielectric layer between the electrodes to prevent the formation of an arc discharge and consequently limit the operating temperature (figure 1) [14]. In this study we used a DBD plasma source composed of a cylindrical copper electrode (diameter 30 mm, length 45 mm), a dielectric plastic material that covers the curved face of the electrode and a thin quartz disk (diameter 33 mm, thickness 0.5 mm) that covers the electrode plane surface where the plasma is generated. As the copper electrode diameter is larger (3 cm) than the PLA film circular sample (2.5 cm) a static treatment has been realized.

![Figure 1. Floating Electrode Dielectric Barrier Discharge](image-url)
2.1.2. **Linear Corona**: this source is based on the corona discharge principle, while instead of a pin the discharge is generated at the edge of a metal sheet with thickness lower than 1 mm (figure 2). The plasma region dimensions are limited by the electrode geometry, thus requiring handling for sample treatment. The distance between electrode and PLA samples has been controlled using two spacers fixed to the source.

![Figure 2. Linear Corona](image)

2.1.3. **DBD roller**: this source has been specifically designed for the treatment of films. The plasma generated between the two rollers has a long and narrow geometry, suitable to treat large foils. Two different configurations have been investigated: a direct treatment (figure 3-b) where the PLA was directly in contact with the plasma and an indirect treatment (figure 3-c) where the PLA foil was posed under the plasma region and handled with a motorised slit.

![Figure 3. DBD roller: (a) DBD roller on, (b) direct PLA treatment (c) indirect PLA treatment](image)

2.2. **Diagnostic apparatus**

In this work we investigated plasma modification of PLA samples in terms of oxygen barrier properties, wettability and surface morphology.

Change in wettability has been monitored with a drop shape analysis system (KRUSS DSA30) for the measurement of static water contact angle. PLA sample were placed on a horizontal plane with the plasma treated surface upwards. A distilled water drop of 5 µl was deposited on the sample surface. Measurements of contact angle were done immediately after the plasma treatment.

Pure oxygen permeation tests in PLA films were carried out at 35°C by means of a closed-volume manometric apparatus [7] which resembles the one described in ASTM D 1434. The oxygen permeability $P$ of a sample of thickness $l$ is the ratio between the steady state gas molar flux, $J_{ss}$, divided by the gas pressure gradient across the sample $\Delta p/l$. The flux is estimated as a function of the pressure $p_d$ in the downstream volume $V$, the sample area $A$, the universal gas constant $R$, the temperature $T$, according to the ideal gas law:
\[ P = \frac{J_{SS}}{\Delta p/l} = \left( \frac{dp_d}{dt} \right)_{SS} \frac{V}{RTA} \frac{l}{\Delta p} \]  

Permeation experiments were carried out with a pressure difference across the membrane of about 1 bar, although the oxygen permeability does not depend on pressure in this range. In order to assess the repeatability of the permeability data, all the measurements were replicated at least twice (the resulting deviation is around 1%).

Morphological investigations have been carried out by means of Atomic Force Microscopy (AFM). Areas of 10x10 µm have been sampled in different positions on the surface for every PLA sample investigated.

![Manometric apparatus used for oxygen permeation measurements](figure4.png)

**Figure 4.** Manometric apparatus used for oxygen permeation measurements

### 3. Results

#### 3.1. Contact angle

Contact angle measurements have been performed on PLA samples treated with both FE-DBD and the DBD roller sources. For each plasma source three different operating conditions were considered. Images and values of the contact angle measurements are shown in table 1 for the treated samples and an untreated PLA sample used as a reference for comparisons.

The contact angle of untreated PLA sample is 69.3°. After 1 minute of FE-DBD plasma treatment, static contact angle of PLA has shown a decrease to 48.2°. A continuous decrease in contact angle value has been observed for increasing treatment times, down to 33.7° after a 5 minutes treatment. Plasma generated by DBD roller has caused less straightforward effects on PLA samples; indeed, after 1 minute of plasma treatment static contact angle was still 64.1°. Instead, after 2 minutes, this parameter has increased up to 69.7°. Decreasing the peak voltage from 20kV to 18kV has produced a static contact angle of 63.7° for a 2 min treatment time.
3.2. Pure oxygen permeability

The effect of treatment time over the variation of the oxygen permeability has been investigated for different plasma sources (FE-DBD, Linear Corona and DBD roller). In order to maximize discharge uniformity we have adopted different sets of operating condition depending on the plasma source:

- **FE-DBD**: voltage 16 kV, PRF 125 Hz, gap 2 mm
- **Linear Corona**: voltage 16 kV, PRF 1 kHz, gap 2 mm, flow rate (He) 5 slpm
- **DBD roller**: voltage 20 kV, PRF 330 Hz, distance from the discharge 11 mm

Results for this measurements are presented in figure 5. The effect of the plasma treatment depends strongly on the plasma source.

In the case of FE-DBD the oxygen permeability increases linearly with treatment times up to 180 s; for longer treatment times no further variation is observed.

PLA treated with Linear Corona shows a decrease in permeability for exposure times shorter or equal to 120 s; permeability values close to pristine PLA have been measured for longer exposure times.

| Operative conditions | Drop image | Average value |
|----------------------|------------|---------------|
| **UNTREATED**        |            | 69.3°         |
| **FE-DBD**           | ![Drop image](image) | ![Drop image](image) |
| Treatment time: 1 min| PV: 16 kV, PRF: 125 Hz | 48.2° |
| Treatment time: 3 min| PV: 16 kV, PRF: 125 Hz | 39.8° |
| Treatment time: 5 min| PV: 16 kV, PRF: 125 Hz | 33.7° |
| **DBD ROLLER**       | ![Drop image](image) | ![Drop image](image) |
| Treatment time: 1 min| PV: 20 kV, PRF: 330 Hz | 64.1° |
| Treatment time: 2 min| PV: 20 kV, PRF: 330 Hz | 69.7° |
| Treatment time: 2 min| PV: 18 kV, PRF: 330 Hz | 63.7° |

Table 1. Static contact angle measurements
The treatment with the DBD roller has achieved the most significant alteration in PLA oxygen permeability. A maximum increase in permeability (15%) has been obtained with 60 s of treatment time. A similar, but slightly lower oxygen permeability has been obtained for a 120 s treatment time.

![Figure 5. Pure oxygen permeability measurements](image)

3.2.1. Ageing of PLA sample

After plasma treatment polymeric materials tend to recover their pristine properties in a process often referred to as ageing [2, 13]. In this work we investigate the effect of treatment time on the ageing of PLA permeability, measuring this property at different times after the treatment.

Results obtained for the Linear Corona source are reported in figure 6; for 30 s and 240 s treatment times no evident recovery effects has been appreciated up to 10 days after the treatment. Instead, samples treated for 120 s show a strong aging effect and measured oxygen permeability is very close to the original value after 8 days.

The samples treated with the FE-DBD and the DBD roller have also been investigated but show no apparent effect of recovery within 10 days.

![Figure 6. Aging of PLA sample treated with the Linear Corona plasma source](image)
3.3. **Morphological investigation with AFM**

In this paragraph we present the morphological characterization of samples treated for 5 min with the DBD roller source (peak voltage 20 kV, pulse repetition frequency 125 Hz) in the direct configuration. AFM images of PLA surface are presented in figure 7; images for the treated PLA refer to the surface exposed to the high voltage electrode during plasma modification. The untreated PLA surface (figure 7-a) appears smooth and characterized by a mean roughness ($S_a$) and a mean square roughness ($S_q$) of few nanometers. On the other side, plasma treated PLA surfaces (figure 7-b,c) show many morphological structures similar to bubbles, uniformly distributed on the sample area. These “bubble” structures, with a diameter in the range of 100-2000 nm, are visible in all the sampled areas of the treated PLA surface, proof that an uniform plasma treatment was achieved with the DBD roller. The measured mean roughness and mean square roughness of the modified PLA are an order of magnitude higher than for pristine PLA and uniform on the whole treated area.

![AFM images](image)

**Figure 7.** AFM images: (a) untreated PLA, (b) treated PLA surface sample 1, (c) treated PLA surface sample 2

### 4. Conclusions

In this paper we have reported on non-thermal atmospheric pressure plasma treatment of PLA, underlining the influence of the plasma source on the final surface modification.

Measurements performed on PLA samples treated with the FE-DBD have shown the highest increase, among the adopted plasma sources, in PLA wettability, without reducing significantly the oxygen barrier properties.

Very small alterations of the PLA oxygen permeability (below 2%) were noted for the samples exposed to the Linear Corona plasma source, and samples treated for 2 minutes tend to recover the original permeability after approximately 1 week.

DBD roller treatment results have shown that indirect treatment with this source was ineffective for the modification of the water contact angle and induced a considerable increase in the PLA oxygen permeability that indicates a deep deterioration of the surface. Direct DBD roller treatment has resulted in a uniform modification of PLA surface morphology; bubble like structures of variable size have been observed using AFM.

The nature of these bubble structures and their formation mechanism will be object of future investigations, together with the analysis of the apparent stability over time of samples treated with FE-DBD and DBD roller plasma. Since each of the tested plasma sources has shown the ability to differently modify PLA surface characteristics, future works will be directed towards their tailoring to specific applications and improvement of treatment performance.
References

[1] Chaiwong C et al 2010 Surf. Coat. Technol. 204 2933-2939
[2] Guinault A et al 2010 Int. J. Mater. Form vol.3 suppl 1:603-606
[3] Vergne C, Bunchheit O, Eddoumy F, Sorrenti E, Di Martino J, Ruch D 2011 J. Eng. Mater. Tech. 133 10.1115/1.4004156
[4] Drumright R E, Gruber P R, Henton D E 2000 Adv. Mater. 12, 1814
[5] Slager J, Domb A J 2003 Adv. Drug Delivery Rev. 55, 549
[6] Alves C M, Yang Y, Marton D, Carnes D L, Ong J L, Sylvia V L, Dean D D, Reis R L, Agrawal C M, 2008 J. Biomed. Mater. Res., Part B:Appl. Biomater., 87(1), pp. 59–66.
[7] Minelli M, De Angelis M G, Doghieri F, Marini M, Toselli M, Pilati F 2008 Eur. Polym. J. 44(8), 2581-2588
[8] Forch R, Zhang Z, Knoll W 2005 Plasma process Polym. 2, 351
[9] Renò F et al 2012 Plasma Process. Polym. 9, 10.1002/ppap.201100139
[10] Dreux F et al 2003 Mat. Res. Innovat. 7:183-190
[11] Inagaki N et al 2002 J. Appl. Polym. Scie. Vol. 89, 96-103
[12] Morent R et al 2010 Plasma Chem. Plasma Process. 30,525-536
[13] Liu C et al 2004 Surf. Coating Tech. 185, 311-320
[14] Fridman A 2008 Plasma Chemistry Cambridge Uni. Press.