Parametric study on the effectiveness of treatment of polyethylene (PE) foils for pharmaceutical packaging with a large area atmospheric pressure plasma source

Marco Boselli1, Vittorio Colombo1,2, Emanuele Ghedini1,2, Matteo Gherardi1, Romolo Laurita1, Anna Liguori1, Filippo Marani1, Paolo Sanibondi1 and Augusto Stancampiano1

Alma Mater Studiorum – Università of Bologna
1 Department of industrial engineering (DIN)
2 Industrial Research Center for Advanced Mechanics and Materials (C.I.R.I.-M.A.M.)
Via Saragozza 8-10, 40123 Bologna, Italy

Abstract: The effects of a Dielectric Barrier Discharge plasma source operating at atmospheric pressure in ambient air on a polyethylene polymer foil commonly used for pharmaceutical packaging are investigated. To evaluate the uniformity and the effectiveness of the treatment the variation induced on water contact angle and the preservation of polymer foil weldability are considered. Results show that it is possible to achieve a uniform treatment while maintaining a good weldability of the treated material.

Keywords: Atmospheric pressure plasma, DBD, polyethylene, wettability, weldability, treatment uniformity

1. Introduction

Atmospheric pressure plasmas have been proven an effective tool for many material treatments such as cleaning [1] and activation of surfaces [2], polymer deposition [3] and interaction with in-vivo and in vitro tissues [4] and disinfection and sterilization of surfaces [5][6][7].

The wide and constantly expanding range of possible applications is due to the great variety of sources and operating conditions for the plasma generation [8]. Moreover plasma technology is environmentally friendly, as no chemical compounds are required [9].

Though low pressure non-thermal plasma is already an established technology in the field of material modification, atmospheric pressure plasmas are rising interest because of their easy handling, effectiveness and low operational costs.

An interesting use of non-thermal atmospheric pressure plasma is the sterilization of polymer foil for packaging applications.

One of the most employed polymers worldwide is polyethylene [10] due to its limited cost, easy processing, chemical inertness and durability.

The sterilization of polymer foil is an attested potential of atmospheric cold plasma [11][12]. However as plasma has the potential to induce surface modification of the top layer (1-10 nm) of polymeric materials [13] is essential to investigate the possible reduction of the weldability of the polymer because is an essential property in many industrial processes.

The future challenge is therefore to develop a uniform treatment able to sterilize while maintaining a good weldability of the polymer foil.

In this work we have focused on establishing the effectiveness of a plasma treatment with a DBD source on a polyethylene foil by considering the induced modifications on wettability and weldability characteristics. The first has been evaluated, through water contact angle (WCA) measurements, to establish the uniformity of the treatment. The second has been investigated by mean of T-peel test to establish the feasibility of introducing the plasma treatment in an online industrial process including a welding stage.

2. Experimental setup

The plasma source adopted in this study is designed for the treatment of foils with dimension up to 30x20 cm and can be easily scaled up to support the treatment of larger foils. The plasma source (Fig. 1) is a planar Dielectric Barrier Discharge (DBD) with a steel high voltage electrode, a 1 mm dielectric layer of polyoxymethylene (pom-c) covering a grounded aluminum electrode and an air gap of 2 mm.

![Fig.1 Schematic of the DBD plasma source (a); picture of the DBD plasma source during operation (b)]
The plasma source is powered with a high voltage bipolar square wave with a slew rate of 750V/µs (Fig. 2) and operated in ambient air at atmospheric pressure.

The treated material is a polymer foil, commonly employed in the manufacturing of pharmaceutical packaging, composed of three different layers:
- Polyvinyl chloride - PVC (200 µm)
- Polyvinylidene chloride - PVDC (23 µm)
- Polyethylene - PE (50 µm)

The treated sample dimensions are 30x16 cm and the plasma treatment was performed on the PE side of the foil.

To evaluate treatment uniformity, wettability of the PE substrate after the plasma treatment is evaluated at different positions; advancing and receding water contact angles (WCA) is measured with the sessile drop method using a Kruss Drop Shape Analysis System DSA 30. First, a drop of distilled water is deposited on the sample surface by a micrometric syringe; then the volume of the drop is increased, forcing the drop to advance on the sample, until a constant contact angle is observed, representing the advancing water contact angle (A-WCA). Then the drop is progressively shrunk until a drop radius decrease is observed and a constant angle is measured, representing the receding water contact angle (R-WCA) [14].

The weldability of the PE foil is evaluated by means of T-peel test measurement (Instron 4465 with load cell 1kN and speed of 110 mm/min). To prepare the test specimens (Fig. 3) the treated samples have been folded so that the PE layer faced itself and then welded using a laboratory welding machine (130°C, 2s, 230 kPa).

### 3. Results

The effects of plasma treatment on PE foil are evaluated by means of WCA measurements and welding tests with the aim to investigate the variation of polymer weldability and wettability after plasma exposition. The investigation of weldability modification is carried out because it is a fundamental property in many industrial processes including packaging applications. WCA measurements are used to investigate the change of polymer wettability which is a good indicator of the plasma effect and allows consideration on the uniformity of the treatment and therefor of the polymer sterilization. Advancing and receding WCA are measured in different points of the same sample to test the uniformity of plasma treatment and, then, of the sample sterilization.

Different operating conditions are tested in order to relate the modification of PE wettability and weldability properties with the electric operating parameters (peak voltage, repetition frequency) and the treatment time. Aging tests to evaluate the persistence of plasma treatment effects on PE samples are also carried out.

The most important results of wettability and weldability analysis are highlighted and discussed in the following subparagraphs.

#### Wettability analysis

The advancing and receding water contact angle values for the unmodified PE sample obtained with the sessile drop dynamic method are 107°±2° and 90°±3° respectively. To evaluate the uniformity of plasma treatment on the polymer film, advancing and receding WCA are measured on five samples, having a size of 2x2cm, extracted from five different positions of the treated PE film as reported in Fig. 4.

![Fig.4 Schematic representation of the five samples considered for the WCA measurements](image)

Fig.4 Schematic representation of the five samples considered for the WCA measurements

To investigate the effects of peak voltage and repetition frequency on the modification of the WCA values, treatment time is fixed to 3 s, peak voltage is increased from 10.5 kV to 15 kV while repetition frequency from 100 Hz to 300 Hz.

Fixing the repetition frequency to 300 Hz and increasing the peak voltage from 10.5 kV to 15 kV for a treatment time of 3 s any important differences can’t be noticed comparing the advancing and receding WCA...
measured on the samples of the two different plasma treated films. For a peak voltage of 15 kV and a treatment time of 3 s, the increase of pulse frequency from 100 Hz to 300 Hz doesn’t cause a relevant variation of the WCA values, as observable comparing the WCA values measured on the samples of the two different treated films.

Comparing the advancing and receding WCA obtained on the different samples of the PE films treated for 3 s with those of untreated samples a drastic decrease of the angle values is registered and therefore a relevant increase of polymer hydrophilicity is achieved also for very short treatment time. Moreover a relevant hysteresis of the material is noticed after only 3 s of plasma treatment.

In Table 1 the advancing and receding WCA measured on the five samples of the each treated film are reported. Three different operating conditions are tested.

<table>
<thead>
<tr>
<th>TREATMENT TIME</th>
<th>ELAPSED TIME</th>
<th>A-WCA</th>
<th>R-WCA</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 sec</td>
<td>10 min</td>
<td>63° ± 3°</td>
<td>20° ± 2°</td>
</tr>
<tr>
<td></td>
<td>1 h</td>
<td>65° ± 3°</td>
<td>19° ± 4°</td>
</tr>
<tr>
<td></td>
<td>4 h</td>
<td>67° ± 2°</td>
<td>22° ± 2°</td>
</tr>
<tr>
<td>30 sec</td>
<td>10 min</td>
<td>57° ± 3°</td>
<td>16° ± 3°</td>
</tr>
<tr>
<td></td>
<td>1 h</td>
<td>59° ± 3°</td>
<td>10° ± 2°</td>
</tr>
<tr>
<td></td>
<td>4 h</td>
<td>57° ± 3°</td>
<td>13° ± 4°</td>
</tr>
<tr>
<td>60 sec</td>
<td>10 min</td>
<td>51° ± 4°</td>
<td>12° ± 3°</td>
</tr>
<tr>
<td></td>
<td>1 h</td>
<td>49° ± 4°</td>
<td>11° ± 3°</td>
</tr>
<tr>
<td></td>
<td>4 h</td>
<td>54° ± 3°</td>
<td>14° ± 5°</td>
</tr>
</tbody>
</table>

Weldability analysis

To investigate the persistence of plasma treatment effects the same samples considered for the evaluation of the treatment time influence are used for aging tests. Measurements are carried out after 1 hour and 4 hours from plasma treatment and the results are compared with those obtained after 10 min from the exposition. From the comparison the persistence of plasma treatment effects after 4 hours from the exposition is demonstrated observing the unimportant differences of WCA values obtained after 10 minutes and 4 hours from the plasma treatments.

The results for different treatment time and elapsed time are reported in Table 2.
Fig. 5 Percentage change of treated sample weldability from that of untreated sample

Because of the obtained results have an uncertainty of 20%, a comparison between the weldability resistance of the samples subjected to plasma discharges generated with different operating conditions is not feasible or significant.

To investigate the aging of welding properties after plasma treatment, different samples treated in the same operating conditions (15 kV, 300 Hz, 3 s) are welded after 4 hours and 28 hours from the plasma treatment and subjected to T-peel test after 4 hours and 28 hour from the plasma exposition. Results are highlighted in Fig. 6.

Fig. 6 Aging of welding properties after plasma treatment

4. Conclusions

The planar DBD plasma source has demonstrated to be a reliable mean to treat uniformly a polymer foil with a surface up to 30x16 cm. The plasma treatment induces a hydrophilic behavior on the previously hydrophobic polyethylene layer already after just 3 s of treatment.

There is an evident weldability reduction induced by the plasma treatment but it remains confined in a range between 21 and 39% of the untreated welding resistance.

There is no evident correlation between the weldability reduction and the treatment time or operating conditions.

In conclusion we may affirm that the tested planar large area DBD plasma source is a feasible mean for online polyethylene polymer foil disinfection in assembly chain as long as the weldability reduction induced is acceptable for the final product characteristics.

References