Morphological and chemical analysis of PP film treated by Dielectric Barrier Discharge

E C Dell'Orto¹, A Vaccaro², C Riccardi¹
¹Dipartimento di Fisica, Università degli Studi di Milano-Bicocca, Piazza della Scienza 3, Italy
²Manucor S.p.A., 81037 Sessa Aurunca (Caserta, Italy)

Abstract. PP films have been activated by DBD, with different gases (air, N₂, H₂, CO₂) and at different energy treatments. Then film surfaces were analysed by AFM, contact-angle technique, ink test measurements and XPS, to explore modifications in surface topography, wettability, and oxidation state. After the treatments, it is possible to observe the formation of water-soluble low-molecular-weight oxidized materials (LMWOMs), which dimensions and spatial density are related to treatment parameters. Using AFM data it is possible to analyse the statistical distribution of the bubbles sizes. The analysis of XPS spectra shows the formation of oxidized polar groups on surface (e.g. C–O, C=O, COH) and allows to evaluate the extent and the nature of film oxidation, and how it influences surfaces properties. The relationship between surface chemical and morphological modifications and treatment parameters is pointed out. Then PP sample have been monitored in the time, to determine the ageing effects.

1. Introduction
Many industrial applications of polypropylene (PP) films, like printing or coating, request good adhesion properties, that are a high surface energy [1]. This characteristic is related both to the polar groups present on PP surface and to film morphology [2].

Dielectric Barrier Discharge (DBD) treatments could be used to modify surface properties, increasing wettability [3-4]. Plasma surface treatment of polymers primarily results in the oxidation of the surface, by the generation of functional groups such as C–OH (alcohol), H–C=O (aldehyde), C=O (carbonyl) and C–O–C=O (ester). Furthermore surface activation causes both a cross-linking of the polymer chains and a oxidative polymer chain degradation, for example the creation of more or less mobile chemical degradation products on surface areas of the polymer [5-6]. Thus it is possible to observe the formation of low molecular weight oxidized materials (LMWOMs). They appear as “droplets” on the treated surface that could be removed by wiping the film surface [7]. The size of this droplets results to be related to treatment dose.

Chemical modifications occurred on PP surface could be monitored by XPS measurements and FTIR/ATR measurements [8-9]. Using AFM technique it is possible to study surface topography of treated Biaxially Oriented PP (BOPP) films.

Even if in literature the effects of dose treatments on chemical and morphological modifications on PP are widely studied [10-12], here we propose a systematic study on DBD treatment of BOPP. We have analysed changes in surface energy, surface chemistry and surface topography as a function of treatment dose, and in relationship with gas used during treatments. Then aging of treated samples are monitored, to evaluate the causes of surface energy change after a storage time.
2. Experimental
The BOPP film used in this study is about 30 µm thick and has a total surface energy lower than 34 dynes/cm.

The DBD experimental setup is showed in figure 1. It consists of a stainless steel plate electrode coated by Polytetrafluoroethylene (PTFE), where samples to treat are placed on. Two rod electrodes (220 mm long, 8 mm diameter) coated with pure (>99.7%) Al₂O₃ synthesized ceramic dielectric (thickness 2 mm) are displaced in a mechanical arm, distant 20 mm from each other. The two rods are connected through an HV cable to the secondary coil of a transformer, whose primary circuit is connected to a power generator, providing the driving high voltage for the discharge. Distance between plate electrode and rod electrode could be varied between 0.5 mm to few millimetres. In our experiments it is fixed at 1 mm. During treatments the mechanical arm can move horizontally with a speed between 0.7 to 7 m/min. The electrical power deposited into the discharge could be varied until 450 W. For each treatment, the energy density, or dose, could be estimated by: \( D = \frac{P n}{vl} \), where \( P \) is the electrical power, \( v \) is the speed of rod electrodes, \( l \) is their length and \( n \) is the numbers of treatments.

A system of 2 mass flow controllers and a controlled evaporator and mixer allows mixing gas and vapours. The inlet fluxes are injected between the high voltage electrodes through an injection nozzle that ensures uniform fluxes on the whole width of the electrodes up to 20 l/min.

![Figure 1. Schematic view of DBD treatment apparatus](image)

Before treatments the samples are washed using acetone and then they are dried in air. After treatments PP films are characterized and then stored in air to evaluate aging affects. The analysis of discharge properties is not a purpose of this research, chemical and physical BOPP films modifications were studied in detail.

X-ray photoelectron spectra (XPS) were recorded using a 5500-PHI (Physical Electronics) apparatus, with a monochromatic Al-anode Kα source and an electron take-off angle of 45°. The analysed circular area had a diameter of 0.8 mm. The pressure in the chamber was around 10⁻⁶ Pa. The spectrometer was calibrated by using the Ag 3d5/2 peak and the resulting energetic resolution was 0.46 eV.

AFM characterizations were made using a Solver P47-PRO NT-MDT, operating in semi-contact mode. Mono-crystal silicon tip with a radius of curvature lower than 10 nm was employed. Contact angle measurements were performed using two different probe liquids: distilled water and 1-Bromonaphthalene 97% Sigma Aldrich (C₁₀H₇Br). Wettability was estimated using the standard test method described in literature [13], equivalent to ISO 8296.

The treatments were realized with different doses and different gas fluxes.
3. Results

3.1. Surface energy

First we have performed air treatments. Different doses have been tested, to evaluate the effect of energy density on surface energy. In Table 1 results are reported.

| Dose [W min/m²] | Surface energy [Dyne/cm] | Contact angle water | Contact angle C₁₀H₁Br |
|-----------------|---------------------------|---------------------|------------------------|
| BOPP            | <34                       | 109±1.5             | 49±0.8                 |
| 90              | 36                        | 74.1±2.5            | 32.9±1.8               |
| 180             | 40                        | 74±0.7              | 35.1±0.5               |
| 270             | 40                        | 79.3±1.4            | 34.1±2.1               |
| 540             | 40                        | 70±0.7              | 34.2±1.2               |
| 1100            | 42                        | 71.8±0.9            | 35.1±1.1               |
| 1400            | 44                        | 70.6±1.2            | 32.6±2                 |

It is possible to observe how wettability raises increasing treatment dose. Anyway there is a range of dose, from 180 W min/m² to 540 W min/m² where surface energy seems to remain the same. This could be related to the existence of threshold energy in activation process. The higher value of wettability is 44 dyne/cm, reached at 1400 W min/m². After treatments contact angles decrease, according to surface energy data. A clear decrease occurs just after the treatment at 90 W min/m², while for greater doses contact angle changes are less relevant, or not appreciable at all for C₁₀H₁Br.

To evaluate the effect of using different gases during treatments, we have fixed a dose of 1100 W min/m², and have performed treatments using a mixture of nitrogen and hydrogen (95:5), and carbon dioxide.

Results are reported in Table 2. Results show as using a different feed gas during treatments, surface energy increases. This improvement is more evident in CO₂ treatment. In fact wettability raises until 46 dyne/cm, while using N₂-H₂ it reaches 44 dyne/cm. Observed modifications could be related both to chemical and morphological modifications, in the next sections we examine in details the reasons of wettability change.

| Gas       | Surface energy [Dyne/cm] | Contact angle water | Contact angle C₁₀H₁Br |
|-----------|---------------------------|---------------------|------------------------|
| H₂-N₂     | 44                        | 67.4±1.1            | 34.8±1.5               |
| CO₂       | 46                        | 68.2±2.1            | 34.5±1.4               |

3.2. Surface AFM

It is well known in literature how plasma treatments on BOPP cause surface modifications through surface oxidation and scission, which combine and create water-soluble low-molecular-weight oxidized materials (LMWOMs). The presence of these materials could affect wettability, stability and adhesion properties of treated films.
The formation of LMWOMs is observable by morphological modifications on film surface. They create a typical “drop-like” structure, which could be detectable by microscopy techniques, like AFM. In figure 2 and 3 the images obtained analyzing BOPP samples treated in air different doses are reported. We have stated scan images obtained using different scan size, 10 µm and 2 µm. Observing the scans performed at 10 µm, it is possible to observe how the drops are uniformly distributed on the surface, and that drops diameter increase until 1100 Wmin/m², then it seems to remain constant. Then the scans executed at 2 µm, allow examining in details LMWOM structures. Starting from a dose of 540 Wmin/m², large spread bubbles are superimposed to join smaller ones. In table 3 the height and

![Figure 2](image1.png)

**Figure 2.** AFM images obtained on BOPP films treated in air at different doses, with a scan size of 10 µm. The formations of LMWOM are pointed out from the presence of “bubble” on the surface.

![Figure 3](image2.png)

**Figure 3.** AFM images of BOPP films treated in air at different doses, with a scan size of 2 µm.
the width of the bubbles are reported, discerning, where present, the bigger structure from smaller ones. Observing data reported in table 3, it is possible to note as the bubbles are low and wide, the ratio between the diameter and the height is about 10 for all samples. This characteristic will be useful to analyze samples profile.

| Dose [W min/m²] | Bigger structures | Secondary structures |
|-----------------|-------------------|----------------------|
|                 | Diameter [nm]     | Height [nm]          | Diameter [nm] | Height [nm] |
| 270             | 100-200           | 15-20                | -             | -           |
| 540             | 200-300           | 30-40                | 100           | 10-15       |
| 1100            | 300-500           | 50-70                | 100-200       | 10-30       |
| 1400            | 300-500           | 50-70                | 150-200       | 15-30       |

Figure 4. Histograms of the surfaces of the scans showed in figure 3, obtained with a scan size of 2 µm. In the table on the right, roughness values are reported.

Focusing on the analysis of distributions shape, it is possible to examine the contributions of different LMWOMs structures. In figure 5 we have reported the height distributions relative to treatments
performed at 540 and 1100 W/min/m², and the numerical fits obtained using two Gaussian distributions. The peaks of the Gaussian distributions corresponds roughly to the values reported in table 3, those were extrapolated from profile scans. Then peaks intensity allows to estimate the relative presence of “drop-like” structures with different heights on the same surface.

After the analysis of the effect of dose on morphology, it is interesting to evaluate the effect of using gas during treatments. In figure 6 AFM images performed on CO₂ treated BOPP (D = 1100 W/min/m²), are reported. Also in this case, it is possible to observe the typical “drop-like” structure, even if in this case the smaller drops are not so well defined. The drops heights are about 20-40 nm, the diameters are about 200-400 nm.

Figure 6. AFM images performed on CO₂ BOPP treated at 1100 W/min/m².

LMWOMs are soluble in polar liquids, such as water used in contact angles measurements. We have tested the effect of water on film morphology. The results have showed that, during contact angle measurements, the amount of water is to small and the time interval is to short, to cause morphological modification, and then contact angle values.

In this paragraph we have analysed morphological modifications that occur on BOPP surface after DBD treatments. These modifications turn out to be related to treatment dose. We have pointed out in previous sections how also energy surface modifications are related to treatment dose. However the relationship between surface morphology and wettability properties is not so simple to understand. Observing data it is possible to note that, even if wettability doesn’t change performing a treatment with a dose of 270 or 540 W/min/m², samples surface appears different. At the same time, the change in wettability that occurs between 1100 and 1400 W/min/m² is not reflected in a change of morphological structure. It emerges how more than one cause occur in alter wettability.

The next paragraph analyse chemical variations that take place on the surface as a consequence of DBD treatments.

3.3. Surface chemistry

XPS measurements have been performed on the following samples: untreated BOPP, air treated BOPP at 270 and 1100 W/min/m², to evaluate the effect of dose on chemical modifications, and CO₂ treated BOPP at 1100 W/min/m², to evaluate the effect of feed gas. Table 4 shows the atomic percentage of elements determined on these sample. After all treatments the amount of oxygen increases, and this increase is more relevant, as treatment dose rises. So it is possible to state a relationship between dose intensity and the presence of oxygenated functional groups on sample surface. In the CO₂ treated sample, a small amount of nitrogen has been detected.

The results of the high resolution C1s and O1s peak deconvolutions are summarized in table 5. In the table the assignments are reported too [14]. Plasma treatments on BOPP have the effect to increase the quantity of carbon atoms that are singly or doubly-bonded to oxygen. In detail, the creation of C-O groups is favored over the formation of C=O groups. The small amount of nitrogen, detected in case (c), could be due to chemical reaction between air and BOPP surface, immediately after the treatment.
Table 4. Atomic percentage of elements, for studied samples: untreated BOPP; (a) air treated BOPP (D = 270-1100 W/min/m²); (b) air treated BOPP (D = 1100 W/min/m²); (c) CO₂ treated BOPP (D = 1100 W/min/m²).

| Sample | O₁s  | C₁s  | N₁s |
|--------|------|------|-----|
| BOPP   | 2.5  | 96.9 |     |
| (a)    | 13.1 | 86.9 |     |
| (b)    | 18.1 | 81.9 |     |
| (c)    | 17.0 | 82.5 | 0.5 |

Table 5. High resolution XPS C₁s and O₁s peak deconvolutions for studied samples: untreated BOPP; (a) air treated BOPP (D = 270-1100 W/min/m²); (b) air treated BOPP (D = 1100 W/min/m²); (c) CO₂ treated BOPP (D = 1100 W/min/m²).

| Center [eV] | ∆E [eV] | Assignment | % Area |
|-------------|---------|------------|--------|
| C₁s         |         | 92.5       |        |
| 285.0       | -       | C-H, C-C   |        |
| 286.7       | 1.7     | C-O        | 6.2    |
| 288.3       | 3.3     | C=O        | 1.2    |
| 289.7       | 4.7     | O-C=O      | -      |
| O₁s         | 532.7   | C-O, C=O   | 2.4    |

3.4. Ageing

All the characterizations that have been discussed before, have been monitored during a storage time of up to more than one month, on BOPP treated in air at 270 and 1100 W/min/m² and BOPP treated in CO₂ at 1100 W/min/m². Measurements of surface energy and contact angles are plotted in figure 7.

![Figure 7. Surface energy and contact angles measurements on treated BOPP, as a function of storage time. Straight and dotted lines are guides for eyes.](image)

The observed decrease of hydrophilic properties on treated samples could be attributed to several factors, such as diffusion, agglomeration or sublimation of LMWOM, modification in polymer chains and migration of additives from the bulk to the surface [15-16]. To better understand the origin of detected “hydrophobic recovery”, morphological and chemical properties of treated films were examined during the storage period.

AFM images obtained on stored samples (figure 8) don’t show relevant modifications after three month from the treatment. So morphology of treated BOPP gives information about the amount and the size of LMWOMs, and these properties affect wettability. However the lack of hydrophilic properties is not related to morphology changes.
Figure 8. AFM images of: (a) air treated BOPP (D = 270-1100 Wmin/m$^2$); (b) air treated BOPP (D = 1100 Wmin/m$^2$); (c) CO$_2$ treated BOPP (D = 1100 Wmin/m$^2$). Images are obtained with a scan size of 2 µm.

Table 6. Atomic percentage of elements for studied samples: untreated BOPP; (a) air treated BOPP (D = 270-1100 Wmin/m$^2$); (b) air treated BOPP (D = 1100 Wmin/m$^2$); (c) CO$_2$ treated BOPP (D = 1100 Wmin/m$^2$). Data are reported at different storage time.

| Sample | O1s | C1s | N1s |
|--------|-----|-----|-----|
|        | 0 day | 1 week | 1 month | 0 day | 1 week | 1 month | 0 day | 1 week | 1 month |
| BOPP   |       |       |       | 2.5   | 96.9   |       |       |       |        |
| (a)    | 13.1  | 12.3  | 11.6  | 86.9  | 86.8   | 88.3   |       |       |        |
| (b)    | 18.1  | 13.8  | 13.0  | 81.9  | 86.2   | 86.2   | 0.5   | 0.8   | 0.6    |
| (c)    | 17.0  | 16.4  | 13.9  | 82.5  | 81.6   | 85.3   | 0.5   | 0.8   | 0.6    |

Table 6 reports XPS data collected at different storage time. All samples show a decrease in oxygen percentage. This decrease however is not enough to explain the change in wettability. For example CO$_2$ treated sample shows, after 1 month, an oxygen percentage of about 13.9%, greater respect to air treated BOPP at D= 270 Wmin/m$^2$, however its wettability is lower. The explanation of this result could be the phenomena of the polymer chain migration toward the film bulk and chain reorientation. In this way, the functional groups can be still detected by the XPS analysis, since its penetration depth is of the order of few nanometers, but they don’t influence the surface energy, since they are not exposed to air.

4. Conclusion
We have performed a systematic study to compare the effects of treatment dose and used gas on BOPP properties. We have pointed out how these parameters affect wettability, and how it is possible to relate the increase in energy surface to chemical and morphological modifications. Then we have monitored surface properties during time, to observe the hydrophobic recovery. We have point out how this recovery is related to variations in polymer chains, not to sublimation or reorganization of LMWOMs.

5. References
[1] Uehara T., 1999. Corona discharge treatment of polymers, MATERIALS ENGINEERING-NEW YORK, 14, 191-204.
[2] Overney R M, Guntherodt H-J, Hild S, 1994, Corona-treated isotactic polypropylene films investigated by friction force microscopy, Journal of Applied Physics 75, 1401.
[3] De Geyter N, Morent R, Leys C, Gengembre L, Payen E, 2007, Surface and Coatings Technology, 201(16), 7066-7075.
[4] Strobel M, Jones V, Lyons C S, Ulsh M, Kushner M J, Dorai R, Branch M C, 2003, A comparison of corona-treated and flame-treated polypropylene films, Plasmas and Polymers, 8, 1, 61-95.
[5] Grossman R F, Beasley W A, 1959, Effects of corona discharge upon polyethylene, J. Appl. Polym. Sci. 2, 163.
[6] Kim C Y, Evans J, Goring A I, 1971, *Corona-induced autohesion of polyethylene*, J. Appl. Polym. Sci. 15, 1357.
[7] Overney R M, Luthi R, Haefke H, Frommer J, Meyer E, Gu’ntherodt H-J, Hild S, Fuhrmann J, 1993, *An atomic force microscopy study of corona-treated polypropylene films*, Appl. Surf. Sci., 64, 197.
[8] Suzer S, Argun A, O. Vatansever O, Aral O, 1999, *XPS and Water Contact Angle Measurements on Aged and Corona-Treated PP*, J. Appl. Polym. Sci., 74: 1846–1850.
[9] Massines F., Gouda G, Gherardi N, Duran M, Croquesel E, 2001, *The Role of Dielectric Barrier Discharge Atmosphere and Physics on Polypropylene Surface Treatment*, 6, 35-49.
[10] Kostov K G, Hamia Y A , Mota R P, dos Santos A L R, Nascente P A P, 2014, *Treatment of polycarbonate by dielectric barrier discharge (DBD) at atmospheric pressure*, Journal of Physics Conference Series 05/2014, 511, 012075.
[11] Jones, V., Strobel, M., & Prokosch, M. J. (2005). *Development of poly (propylene) surface topography during corona treatment*, Plasma Processes and Polymers, 2(7), 547-553.
[12] Mix R, Friedrich J, Rau A, 2009, *Polymer surface modification by aerosol based DBD treatment of foils*, Plasma Processes and Polymers, 6, 9, 566-574.
[13] ASTM International, *Standard Test Method for Wetting tension of Polyethylene and Polypropylene Films*.
[14] Beamson G, Briggs D, 1992, High resolution XPS of Organic Polymers: The Scienta Acta ESCA 300 Database, John Wiley, Chichester.
[15] Strobel J M, Strobel M, Lyons C S, Dunatov C, Perron S J, 1991, *Aging of air-corona-treated polypropylene film*. Journal of Adhesion Science and Technology. 5, 119-130.
[16] Morent R, De Geyter N, Leys C, Gengembre L, Payen E, 2007, *Study of the ageing behavior of polymer films treated with a dielectric barrier discharge in air, helium and argon at medium pressure*, Surface and Coatings Technology, 201(18), 7847-7854.