

# Fractal polymeric surfaces by plasma processing

C. Piferi<sup>1</sup>, M. Daghetta<sup>1</sup>, H.E. Roman<sup>1</sup>, C. Riccardi<sup>1</sup>

<sup>1</sup> *Dipartimento di Fisica, Università degli Studi di Milano-Bicocca, Piazza della Scienza 3,  
20126 Milano, Italy*

**Introduction** Nanostructures are today very interesting to generate new advance materials, having superior properties for environment [1], energy [2] and biomedical applications.

Among the different techniques cold plasma is able to functionalize different polymeric surface materials without to damage their bulk properties and processing the surface at nanometric level [3]. The plasma modification of the surface chemistry by grafting chemical groups can enhance the adhesivity of natural polymers for the generation of biodegradable compound [4], or tailor surfaces for environment applications such filtration [5] or enhance the adhesion to coatings for clothing [6]. Deposition of monomers on polymeric surfaces permits to achieve superior chemical functions [7] such super repellency, to control gas barrier properties [8] and to functionalize surfaces in view of biomedical applications. Most of the plasma processes are demonstrated to be stable in time [9].

More recently plasma are widely used for the modification of the surface morphology, in order to create nanotextures [9] having new interesting properties, such as for instance, antifouling properties having strong impact on the biomedical applications. Hierarchically nanostructures tailored for superhydrophilicity and hydrophobicity have been recently obtained by oxygen plasma on PET films and textiles [10].

This work deals with a study of nanostructures induced by oxygen cold plasma on two different polymers PET and PP investigating the plasma effects at the microscopic and macroscopic scales. This study demonstrates the plasma ability to tailor nanostructures in dependence on the polymeric chemistry. A discussion on the two main competitive plasma processes occurring on the surfaces, chemical etching and deposition, is based on SEM imaging. The balance between these processes gives rise to different microscopic nanotextures and macroscopic behavior of the two polymers.

**Equipment setup** The plasma is generated in a homemade vacuum chamber (Fig. 1a) using oxygen at a pressure of about 0.45 mbar, by means of a RF power generator (Advance Energy RFX-600) capacitively coupled to a planar antenna. Polymers which sizes are 6 x 6 cm<sup>2</sup> for the PET and 5 x 5 cm<sup>2</sup> for the PP, are placed on a grounded holder located in front of the antenna at

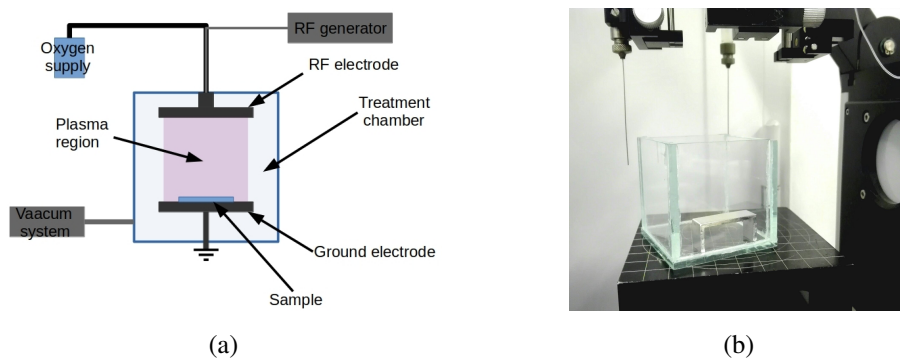


Figure 1: (a) Scheme of the plasma chamber. (b) Roll-off equipment setup.

variable distances between 5 and 20 cm. RF power can be varied between 100 W and 500 W to optimize the plasma processing avoiding the heating of the polymers. A matching box permits to transfer almost all the RF power to the coupling antenna system.

PET films can be treated up to 150 W for several minutes, between 2 and 30 min, while PP films are treated at 150 or 300 W between 2 and 20 min to avoid thermo degradation. Usually the temperature of the substrate, measured by a thermo couple, is well below 50°C. The microscopy properties have been analyzed by means SEM and AFM imaging, while the macroscopic ones by means of the water contact angle in air and the roll off angles in air and water.

For SEM analysis we used Zeiss 500, and for AFM Solver P47-PRO. For the evaluation of the contact angle and the roll-off angle we used DataPhysics OCA 20. We evaluated the contact angle of a water droplet in air and the roll-off angle of a  $\alpha$ -bromonaphtalene droplet in water. In order to do that, as can be seen in Figure 1b, we placed the polymeric sample in a box filled with water and we rotate the base till the oil droplet start to roll over the sample.

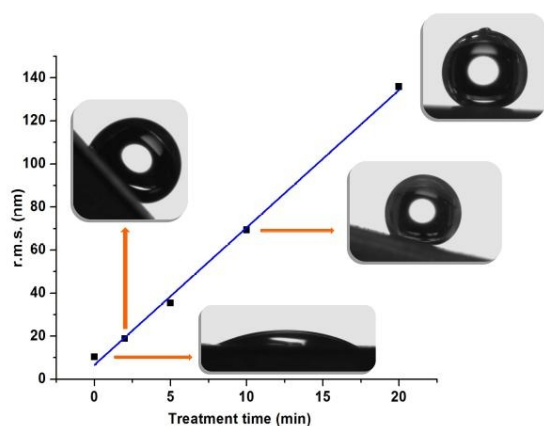


Figure 2: Roughness vs treatment time and rolloff angle at the same treatment time.

**Results and discussion** By oxygen plasma treatments PET films increase their hydrophilicity in air. The non-treated PET film exploits a water contact angle of about 140° and after a plasma time exposure of 20 min the water contact angle assumes value of the order of 5°. To this increase of wettability corresponds a morphology modification. In Fig. 2 the film roughness, evaluated by the AFM images, as r.m.s. of the surface heights, is reported as a function of

the plasma treatment time. The r.m.s. linearly increases with the time exposure. In the same figure the images of the roll-off angles of bromonaphtalene in water on the films is reported for some treatment times. When a oil droplet is put on the surface of the non-treated PET film, the droplet stiks on the polymeric surface and does not roll on the polymeric surface. The droplet maintains its spherical shape on the treated plymers, and the roll-off angle strongly decreases for the treated PET film as a function of time.

This phenomenon is due to the presence of nanostructures promoted by plasma etching of the polimeric chains. When the plasma treated polymer is put in water, nanostructures are filled by the water and the oil droplet floats on the top of the nanostructures.

A more detailed analysis of the spatial scale distribution of the nanostructures, shows a fractal-like behavior [10]. In this recent paper has been demonstrated that this morphological property is ascribed to two competitive plasma processes, the chemical etching occurring by the oxygen interaction with the polymeric surface and the deposition of low weight polymeric chain clusters produced during the plasma surface interaction. Increasing the nanostructures around 100-1000 nm the oil droplet roll-off angle decreases to zero.

To study in detail the oxygen plasma ability in the nanosizing and nano-structuring polymeric surfaces, a comparison between the plasma effects on different polymers should be provided. Here we report a comparison between PET and PP films [9], having different chemical polymeric nature. We expect to find different morphologies for the two plasma treated polymers because oxygen interacts differently with the chemistry of the polymeric chains. Here we report two SEM images of PP films. The non-treated sample of Fig. 3a was magnified for 24k times and turns out flat, on its surface no nanostructures are highlighted. In Fig. 3b an oxygen plasma treated PP film SEM image reported with the same magnification, exploits a completely different morphology. Grains which size are of the order of 50 nm appear on the surface top, revealing the formation of island-like structures. These grains seem excavated on the surface.

In the majority of the PP plasma treated films no evidence of cluster deposition are highlighted, suggesting that plasma promotes mainly a chemical etching and no deposition processing occurs.

A comparison between the two polymeric morphologies after plasma treatments can be observed looking at Fig. 3c-d, where a SEM image of a PET film non treated and treated by plasma has been reported. Along the etching processes on a larger spatial scales, some nanostructures can be observed probably due to a deposition of low weight molecular polymers.

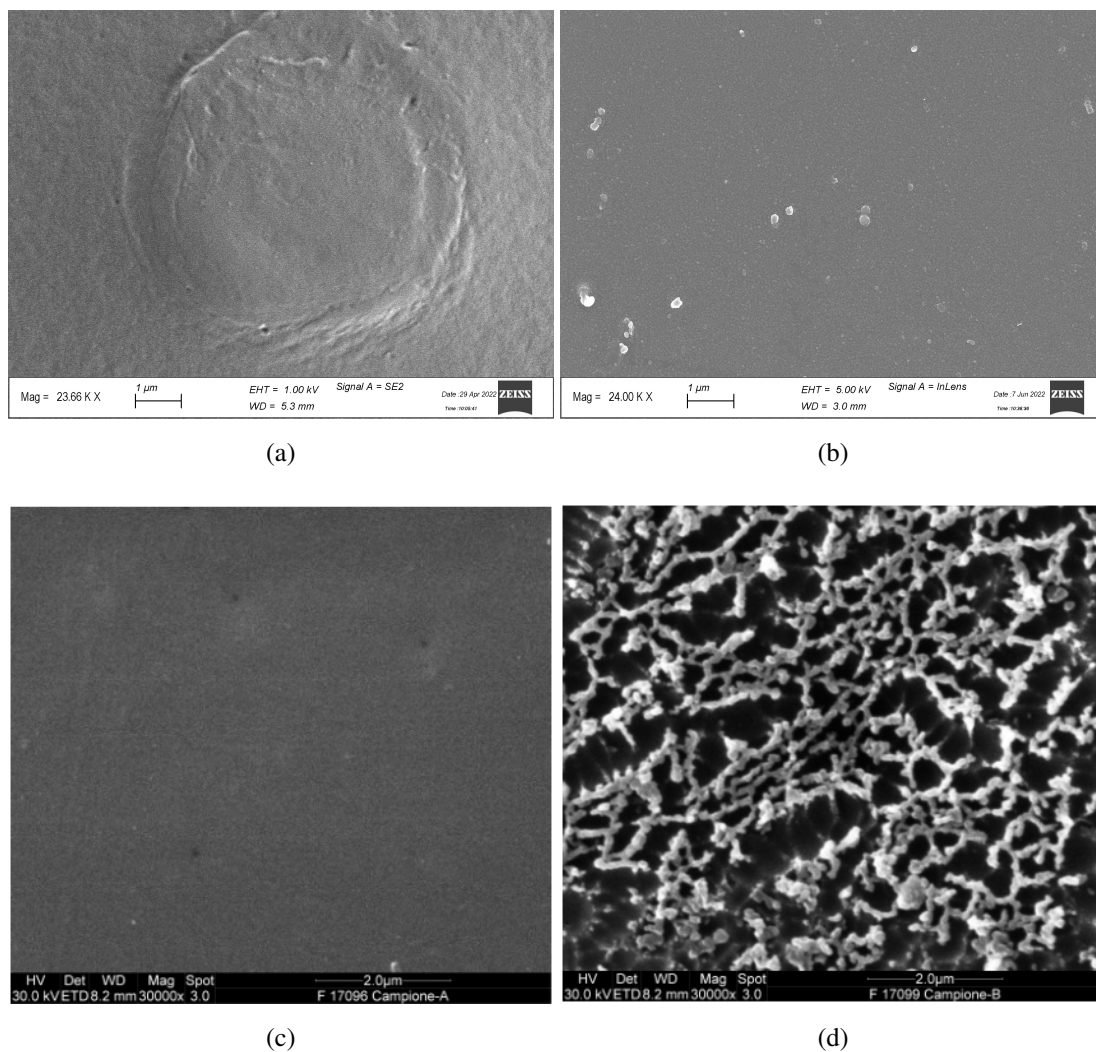


Figure 3: SEM images of (a) untreated PP, (b) treated PP, (c) untreated PET and (d) treated PET.

## References

- [1] Dell'Orto E.C., Caldirola S., Sassella A., Morandi V., Riccardi C., Applied Surface Science, 425, pp.407-415 (2017)
- [2] Trifiletti V., Ruffo R., Turrini C., Tassetti D, Brescia R., Di Fonzo F., Riccardi C., Abbotto A., Journal of Materials Chemistry A, 1 (38), pp. 11665-11673 (2013)
- [3] Zanini S., Freti S., Citterio A., Riccardi C., Surf. Coat. Technol., 292, pp.155 - 160,(2016)
- [4] Zanini S., Riccardi C., Canevali C., Orlandi M., Zoia L., Tolppa E., Surf. Coat. Technol. 200,1-4 SPEC. ISS., 556-560 (2005)
- [5] Zanini S., Massini P., Mietta M., Grimoldi E., Riccardi C., J. Colloid Interface Sci 322, 2, 566-571 (2008)
- [6] Zanini S., Grimoldi E., Citterio A., Riccardi C, Applied Surface Science 349, 235 – 240 (2015)
- [7] Zanini S., Zoia L., Della Pergola R., Riccardi C., Surf. Coat. Technol., 334, pp. 173-181 (2018)
- [8] Barni, R., Zanini, S., Riccardi, C., Advances in Physical Chemistry, 2012, 2012, 205380 (2012)
- [9] Dell'Orto C.E., Vaccaro A., Zanini S., Journal of Physics: Conference Series, 550 (1), 012032.2014 (2014)
- [10] Piferi C., Bazaka K., D'Aversa D.L., Di Girolamo R., De Rosa C., Roman H.E., Riccardi C., Levchenko I., Adv. Mater. Interfaces, 8(19), 2100724 (2021)