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Surface Modification of Polyethylene Terephthalate (PET) By Corona Discharge Plasma

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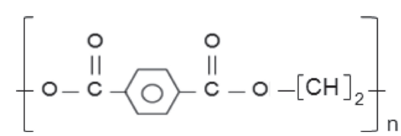
ABSTRACT

Surface modification of polyethylene terephthalate (PET) was studied by corona discharge plasma at different exposure times using air as working gas. The modification of the surface properties are characterized, those are morphology and wettability. Corona plasma treatment was found to modify the PET surface in both morphology and wettability. The corona discharge at atmospheric pressure is a heterogeneous with multiple current pulses, which generates an asymmetric pattern of erosion on the PET surface. The corona discharge treatment erodes the surface and therefore modifies the surface morphology. The roughness of the PET surface increases in the impact point of the corona discharge on the PET surface. An increase in the wettability of PET was also observed after corona discharge treatment at atmospheric pressure.

1. Introduction

PET is a linear thermoplastic polymer with a wide range of properties, which makes it suitable for processing through multiple transformation processes and gives it a vast applicability [1-2]. Its excessive use has become environmental pollution problem, due to the inadequate disposal of its waste. As an example, the great quantities of PET bottles used in the soft drink industry. According to the UN, four out of every five PET bottles used go directly to landfills. This means that only 20% of the used PET is recycled, which is true in countries with high ecological awareness such as Germany. In countries like ours, where it is estimated that only 7 to 9% are recycled, there is a need to exhort an ecological conscience to promote technical and innovative solutions that make it possible to reintegrate back this material after being used into the production chain, after being used. PET is a polyester resin synthesized from ethylene glycol and terephthalic acid. Said polymer is classified according to intrinsic viscosity, which is directly proportional to its molecular weight, whose modification influences the crystallization rate and melting point. It is classified as a thermoplastic synthetic resin or a semi-crystalline thermoplastic polymer. The chemical structure of PET is as follows:



The physical properties of PET and its ability to meet various technical specifications have been the reasons why it has reached a great demand in the production of a great diversity of packaging, in particular, in the production of commercial beverage containers.

Among the most important features it presents are:

- Good behavior under static stress
- High resistance to wear and corrosion
- Low friction coefficient
- Good thermal properties
- Fully recyclable
- Lightweight
- High strength and stiffness
- Good strain resistance
- High surface hardness
- Great dimensional stability
- Good electrical insulator

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This polymer is not affected by acids or atmospheric gases, so it has good weathering stability. Even so, when the containers have prolonged exposure to the open air they lose their molecular integrity, they fragment and disperse, so, buried bottles last longer. The time weather exposure that the containers must have in order to present fragmentation is not known exactly. According to weathering tests carried out of plates and components made of recycled PET at the Experimental Center for Economic Housing in Argentina, PET proved to be a material with excellent resistance to the effects of weathering [3]. The plates and components were exposed for two years, subjected to rain, sun and other inclement weather, without presenting dimensional alterations or apparent damage. Due to the results obtained, Argentine researchers carried out an accelerated aging test on elements made with PET in the Laboratory of the National Institute of Industrial Technology, using the panel method in the ultraviolet light accelerated weathering tester (Q.U.V tester). The result obtained showed that the elements tested are resistant to the action of ultraviolet rays and humidity cycles, observing a decrease in compressive strength after time aging of the order of 25%.

PET is also a material resistant to degradation by microorganisms (biodegradation) since they do not have mechanisms to attack it. Due to this characteristic is not a suitable medium for the proliferation of fungi, parasites or rotting bacteria. It is resistant to the attack of moths, rodents and insects. As it is not a biodegradable element, it maintains its inalterability over time, which provides a long service life. In addition to this, PET is odorless, recyclable and does not contain toxic components like other plastics.

Recent studies carried out in different countries indicate that, in a short time, a new form of degradation of PET containers by a microbiological pathway will become reality. At the Kyoto Institute of Technology, researcher Kohei Oda got PET containers degraded in just eight weeks by a consortium of bacteria and, was identified a specific bacterium isolated from that consortium capable in reduce the degradation time at half. The bacteria identified is capable of metabolize polyesters such as PET [4].

In Mexico, scientists from the Professional Interdisciplinary Biotechnology Unit (UPIBI) of the National Polytechnic Institute, led by Dr. Claudio Garibay Orijel, achieved through in vitro tests that consortia formed by fungi and bacteria degraded one of the main compounds of PET: teraphthalic acid [5].

At present, the most widely used recycling process is the mechanic, in which, after a process of selection and preparation of the material, it is crushed to mix it with virgin PET and produce new parts, which have the disadvantage of offering inferior properties that those made with virgin PET [6-7]. The chemical recycling process has become a viable option. Different processes have been developed in this direction, of which methanolysis and glycolysis are carried out on an industrial scale. Other chemical processes are: hydrolysis, aminolysis and oxidation, among others [8]. In general, PET can theoretically degrade in order to obtain the monomers used in its synthesis: a diacid and a dialcohol. Of the aforementioned processes, degradation by hydrolysis in a temperature range of 100 °C to 120 °C is 5000 times faster than the oxidation degradation process and 10000 times faster than the thermal degradation process [9]. In the last two decades there has been a rapid increase in the research of discharges at atmospheric pressure. Among its applications is the surface modification [10], gas treatment of chimney [11-13], the plasma-assisted combustion [14-16] and the most recent in medicine plasma [17-19]. A wide variety of devices have been developed so far, like discharges volume (dielectric barrier or corona type) and surface discharges, jets, micro-discharges; all of them have the characteristics of being highly transient and not be an equilibrium process despite of domino collisions, they are processes strongly influenced both by post-discharge and surface phenomena.

Atmospheric pressure plasma discharges are of great interest because of the lower cost and simplified operation in comparison with low pressure plasma process and also because of the potential applicability to non-vacuum compatible materials and processes [20]. A requirement for many of these applications is non-thermal plasma. Non-thermal plasmas (also called non-equilibrium plasmas or cold plasmas) are characterized by a non-equilibrium distribution of energy between different degrees of freedom, different excited states and different particles. Usually the classification can be simplified a little, assuming that energy distribution can be described by several temperatures such as the electron temperature (T_e), electronic excitation temperature (T_{elex}), vibrational temperature (T_{vib}), rotational temperature (T_{rot}) and translational temperature (T_{trans}). In non-thermal plasmas created by externally applied electric fields typically $T_e > T_{elex} > T_{vib} > T_{rot} = T_{trans}$. The non-equilibrium nature allows for the creation of active species without generating excessive heat which may damage substrates or cause excessive dissociation. Also the chemical processes which occur in the non-equilibrium plasma are beyond those which are accessible by the addition of only thermal energy.

In this work, the corona discharge treatment was done in order to study the PET transformation and/or degradation. The properties of the treated surface are characterized by: contact angle measurement and scanning electron microscopy (SEM).

2. Experimental Setup

The experimental setup is shown in Figure 1. The atmospheric plasma jet is generated in a setup of a needle cathode and a plate copper anode. The needle with a diameter of 3.5 mm and with 22º tip it is electrically connected to a DC power source with a maximum voltage of 20 kV and peak current of 150 mA. The copper electrode it is connected to ground through a small resistance.

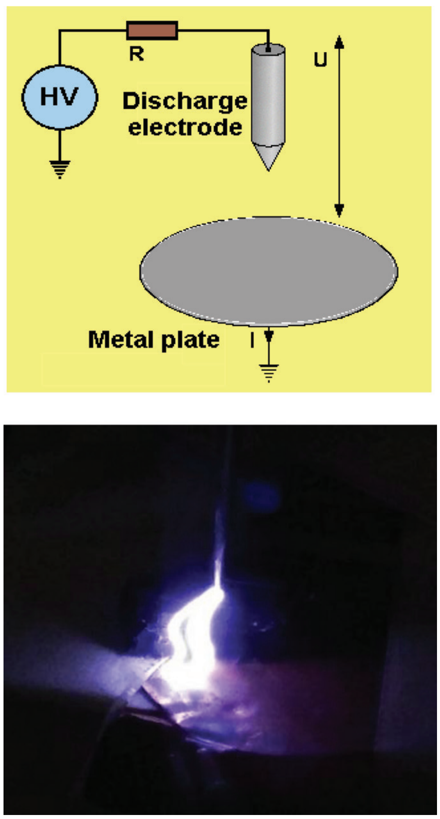

Figure 1: Experimental setup and corona discharge.

The corona discharge is maintained by a DC high voltage of both polarities applied onto the metal electrodes with a corona geometry forming a non-homogeneous electric field. The gap length (d) between the needle tip and the plate electrode copper can be adjusted in the range between 3 to 16 mm [21]. The applied voltage is measured by a high voltage probe (Hipotronics 50) that has its own display. The discharge current is measured with a little resistance (R=1 MΩ) connected in series with the grounding electrode. The discharge current is measured by a Rogowski coil connected to an oscilloscope. Here we show the effects of a DC discharge generated with 10 mm in gap length (distance between the needle electrode tip and the PET surface) using a well-known streamer corona (SC)at an high voltage of 4 ± 0.5 kV, and a current amplitude I_{max} = 150 ± 0.6 mA.

From waste PET commercial container were cut squared coupons of 1 cm of arista (area = 1 cm^2). Before the exposure to the atmospheric plasma discharge the PET surfaces were cleaned with absolute ethyl alcohol. The cleaned sample was placed on the copper electrode in order to expose to the corona discharge. After the treatment time elapsed, the samples were analyzed by optical microscopy (OM) and by scanning electron microscopy (SEM).

In order to determine the wettability behavior of the sample after corona discharge, the sessile drop technique was used to measure the contact angle (CA) using a distilled water drop (volume = 5 µL). Using a USB digital microscope (Model Px-537) the contact angle was determined in both areas of the surface unaffected and affected zone. The contact angle was calculated by analyzing the images of the drops with the ImageJ® program.

In order to observe the change in the surface morphology due to corona discharge, the samples were analyzed by Scanning Electron Microscopy (SEM). Images were taken at different magnifications and at different points to characterize the surface morphology. The equipment used was a SEM JEOL JSM-5900LV located at USAII, UNAM.

3. Results

The characterization by optical microscopy shows that initially the surface of the PET shows evidence of slight surface damage and that it is slightly curved (given the origin of the PET), see Figure 2.

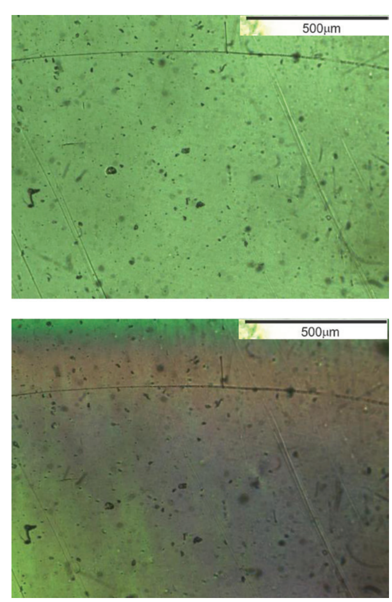

Figure 2: PET observed by OM. It is observed with slight damage to the surface. In the second, the change observed with polarized light is due to the curvature of the samples obtained from wasted bottles.

An image of the footprint generated by the corona discharge on the PET surface is shown in Figure 3.

The point of impact of the atmospheric corona discharge is on the right side of the image and the damaged region becomes wider as it approaches the edge of the sample, left side of the image.

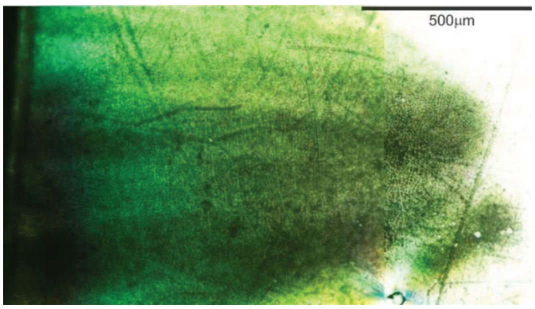

Figure 3: Footprint generated by the corona discharge on the PET surface.

Figure 4 shows an image obtained using polarized light. A cellular topography can be seen with greater erosion on the right side compared to that observed on the left side of the image. This pattern could be associated with the structure generated by the spherulites of PET.

In Figure 5 (a-f) the surfaces eroded by the corona discharge are shown, in (a) the surface is shown without interaction with the discharge. From (b) to (f) erosion is increasing as it approaches the point of impact of the discharge (f). This shows that the effect of the discharge is not uniform.

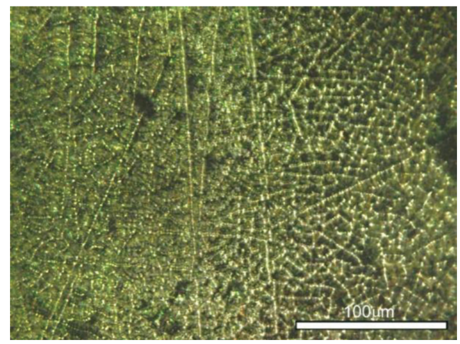

Figure 4: Detail of the OM image of polarized light where the morphology generated by the corona discharge is observed.

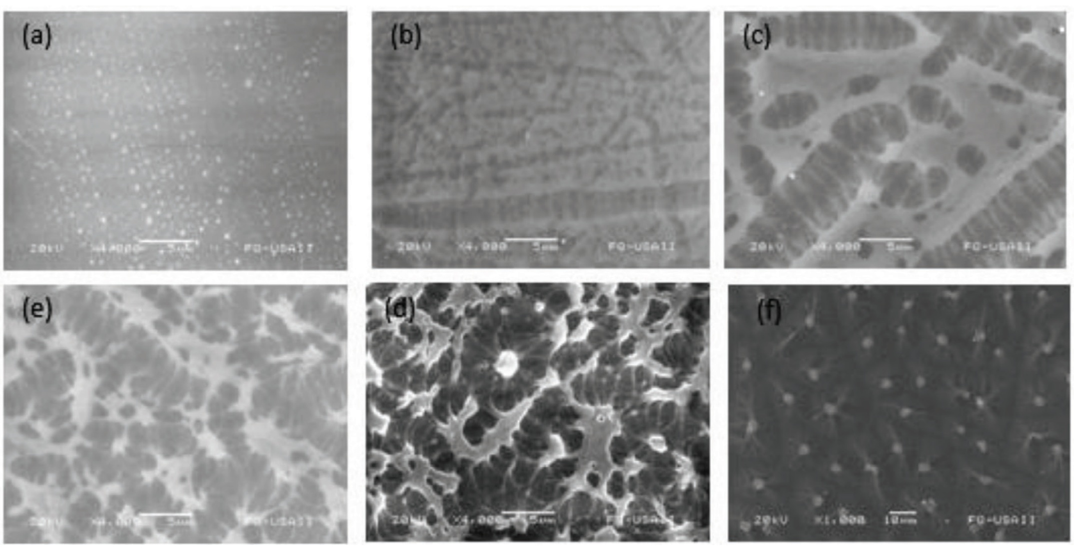

Figure 5: Image sequence of eroded surface by the corona discharge, from the area without erosion (a) to the area of greatest erosion (f).

The cellular pattern observed in Figure 5f is shown in greater detail in Figure 6. The X-ray scattered energy analysis (EDX) shows that the elements identified by the analysis (Spec A) of the area shown in Figure 5f correspond to those shown in Table 1. Spec 1 analysis corresponds to a region enriched with Cu, while region 2 (Spec 2) shows a composition very similar to the general analysis (Spec A). The region 1 shown shows less erosion than its surroundings, this may be associated with the concentration of Cu.

Table 1: Semi-quantitative analysis by EDX.

Element	Spec A	Spec 1	Spec 2
C	67.1	67.2	68.4
O	32.0	30.4	30.9
Cu	0.7	2.2	0.6
Al	0.1	0.1	0.1

The contact angle measured on the surface of the PET is 52°, while in the eroded region it is 45°. That is, the wettability increases once the discharge is made.

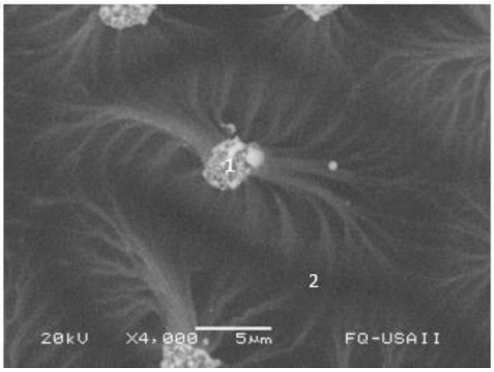

Figure 6: Detail of the cell pattern observed in Figure 5f. Semi-quantitative analysis obtained by EDX in the indicated regions.

4. Conclusions

The air corona discharge at atmospheric pressure is a heterogeneous discharge with multiple current pulses, which generates an asymmetric pattern of erosion on the surface of the PET.

Corona discharge treatment erodes the surface and therefore modify the surface morphology. The surface roughness increases as it approaches to the point of impact of the corona discharge on the PET surface.

Nanometric particles of Cu were identified, apparently forming micrometric clusters, which are more resistant to erosion by corona discharge. The origin of these particles requires further study.

An increase in the wettability of PET was observed after corona discharge treatment in air at atmospheric pressure.

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