

A Comparative Study of Plasma Effects on the PET Surfaces

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Poly(ethylene terephthalate) (PET) films were treated with two different helium plasma sources, i.e. a dielectric barrier discharge working at atmospheric pressure and a capacitively coupled discharge at low pressure. After exposure in these two environments, the polymer films have an improved hydrophilic character; the magnitude of the effects is different. The increase of the surface energy was found to be almost entirely due to the increase of the polar component, whereas the dispersive component remains unmodified. The surface chemistry, analyzed by the ATR-FTIR technique, is not modified during the treatment. Thus, in the treated polymers spectra new absorbance bands are not identified. Still some variations of the PET characteristic bands were found. In the UV-Vis spectral range the modified polymers have modified absorption bands, associated with electronic transition in C=C and C=O bonds.

Keywords: poly(ethylene terephthalate), plasma treatment, surface energy

From laboratory to industry plasma treatments are widely used nowadays for surface treatment of polymers. Surface properties like morphology, roughness, wettability and crystallinity can be modified by plasma treatments and can be optimized for different purposes. These properties are important in many applications, such as adhesion, printing and coatings. Also, in the field of biomaterials, an especial attention is devoted to the polymer surface properties, since these properties control the reactions mechanism at polymer – biological medium interface [1].

In comparison with other surface modification techniques, such as chemical treatments or irradiation with photons, plasma treatments affects only few monolayers at polymer surface, the bulk properties being preserved. Effects like, functionalization, crosslinking, etching, cleaning, give to the polymer surface new features after plasma treatments and open a broad range of applications in industrial polymer processing.

From the classical RF discharge at low pressure to the atmospheric pressure discharges, almost all types of cold plasma sources were applied to the polymer surface treatment, each one with specific advantages [2-5]. The atmospheric pressure cold plasma sources are distinguished by their rapid kinetic of modification and the possibility to be applied for continuous processes. On the other hand, in case of the low pressure cold plasma sources high plasma volumes can be obtained and an accurate control of the gas phase can be achieved.

In this study we selected the PET films, a polymer from the polyester family. Function of synthesis procedure the PET can be an amorphous or a semi crystalline material. While almost 90% of world PET production is used for synthetic fibers and bottles fabrication, only the 10% covers different industrial applications such as insulators, packing solutions or medical devices. In the medical domain, the PET is used as material for the fabrication of heart valves, test tubes, synthetic mesh or by-passes. Nevertheless from the medical point of view some associated problems are occurring, like the chronic rejection reactions, the infections and the activation of the coagulation cascade. All these problems are related to PET surface properties and in the research laboratories efforts are made to modify

the PET surface properties in order to minimize the mentioned adverse reactions [6-8].

We present results concerning the modification of the PET by plasma treatments in helium at low and atmospheric pressure. A comparison between the two plasma sources concerns the effects induced on specific surface properties like surface energy and surface chemistry, respectively.

Experimental part

PET films (GoodFellow Co.), 125 μm thick were cleaned with ethanol and dried in air before modification by plasma treatment.

The polymer samples were modified using two helium plasma sources at low and respectively at atmospheric pressure. The low pressure discharge (LPD) is produced in a capacitively coupled reactor at 0.4 mbar, being driven by an alternative voltage with 1.2 kV amplitude and 40 kHz frequency. The dissipated power in the discharge volume was maintained at 20 W. The atmospheric pressure discharge (APD) is produced using a dielectric barrier reactor, being sustained by high voltage monopolar pulses, with 3 kV amplitude and 2 kHz frequency. The mean power dissipated in the discharge over the voltage pulse was 30 W.

In both treatment techniques the polymer sample is placed on the ground electrode and the treatment duration was variable in the range from 5 s to 20 min.

The polymer samples were analyzed using the contact angle technique and the measurements were made immediately after the treatments. Drops of test liquids (pure water and formamide) were placed with a random distribution on the PET films and photos were taken using an optical arrangement. Then, the drop photos are processed individually following a snake-based approach for recognition of the drop edge [9]. The error in the contact angle determination is maximum $\pm 1^\circ$.

The surface energy components of PET films were calculated using the Owens and Wendt model [10].

The FTIR spectra were collected using a Fourier Transform Infra-Red spectrometer (Nicolet Impact 4000) with an ATR accessory having a diamond internal reflection

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element. Spectra were collected in the 4000 – 600 cm^{-1} range with 4 cm^{-1} resolution, the final spectrum being the average of 32 acquisitions. To avoid experimental artifacts such as the irreproducible sample – ATR crystal contact, the internal normalization of spectra was used. The reference band is located at 1410 cm^{-1} and is associated with in plane ring deformations [11].

The UV-Vis spectra of the PET films were recorded using a Jasco V-570 spectrophotometer with an integrating sphere, in the range 200 – 400 nm with 0.5 nm resolution.

Results and discussions

It is known that the APD treatments are very efficient for surface functionalization [5,11]. The low ion energy, around 0.01 eV, minimize the etching processes, while the presence of free radicals and reactive species based on nitrogen and oxygen functionalities assures chemical reactions at the plasma polymer interface. In case of LPD treatment the energy of ions accelerated in the front of instantaneous cathode is sufficient to remove oligomers from the polymer surface and to redeposit them. Chemical processes implies reactions with degradation products based on oxygen (e.g. CO_2 , CO , H_2O) that result during polymer bonds breaking, followed by the incorporation of these products into the surface. In both treatment techniques bond breaking occurs also under the incidence of UV photons, the helium plasmas being known for production of UV and VUV photons [12].

The surface energy of PET films is increased after both types of plasma treatment (fig. 1). The increase of the surface energy is due to the increase of the polar component, the dispersive component remaining almost unaffected by the plasma treatments. In case of the APD treatments few seconds of modification are sufficient to increase the surface energy of the polymer film. No further modifications are found for longer treatment durations (fig. 1.a.). In case of the LPD treatment the surface energy value depends on treatment duration (fig. 1.b.). It is observed that after the 4 min of treatment the surface energy attains a maximum value which it is kept despite of the increase of the treat duration up to 10 min.

Both the plasma treatments do not induce major modifications in the FTIR spectra of PET films (fig. 2). The treated polymer spectrum presents the same shape in comparison with the untreated sample. Still, there are some variations in the absorbance of specific chemical groups like the CH_2 , $\text{C}=\text{O}$ or $\text{C}-\text{O}$.

In the PET structure the rotational isomerism in ethylene glycol residue give rise to *gauche* and *trans* conformers. The *gauche* conformers can be found only in the amorphous regions of the polymer, while the *trans* conformers are present in both, amorphous and crystalline regions. This gives the possibility to separate the contributions of different chemical groups located in the amorphous or the crystalline regions. For example, in the amorphous regions some characteristic absorption bands are associated with CH_2 wagging vibrations located around 1370 cm^{-1} , $\text{C}=\text{O}$ stretching vibrations around 1722 cm^{-1} and $\text{C}-\text{O}$ stretching vibrations around 1040 cm^{-1} . In the crystalline regions the same vibrations are shifted to lower wavenumbers, respectively at 1340 cm^{-1} , 1712 cm^{-1} and 970 cm^{-1} .

As can be seen in the figure 3, the APD treatment induces an increase of CH_2 and $\text{C}-\text{O}$ absorbance in both, amorphous and crystalline regions, while the $\text{C}=\text{O}$ absorbance is increased in the amorphous domains and decreased in the crystalline domains. In case of the LPD treatment the CH_2 and $\text{C}-\text{O}$ absorbance is increased in the amorphous

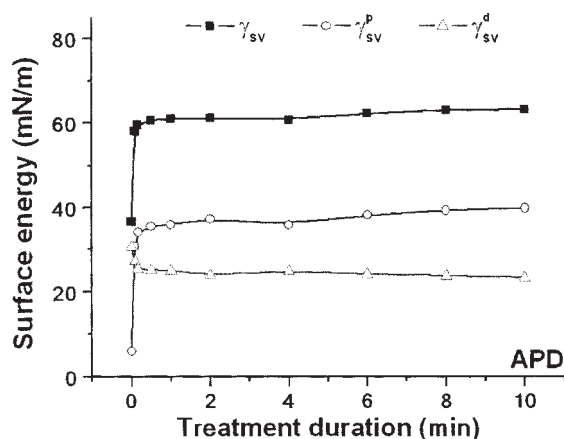


Fig. 1.a. Values of surface energy components for plasma modified PET films with APD (a) and LPD (b)

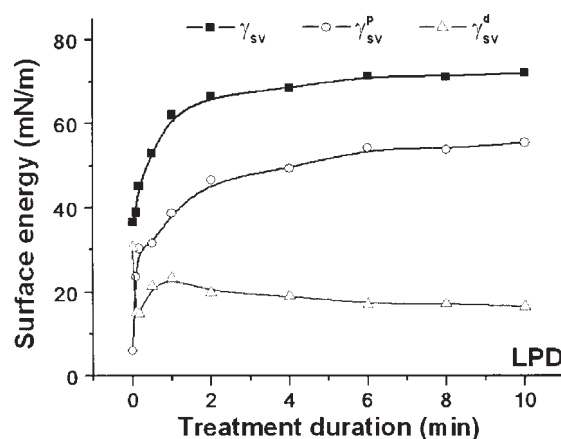


Fig. 1.b. Values of surface energy components for plasma modified PET films with APD (a) and LPD (b)

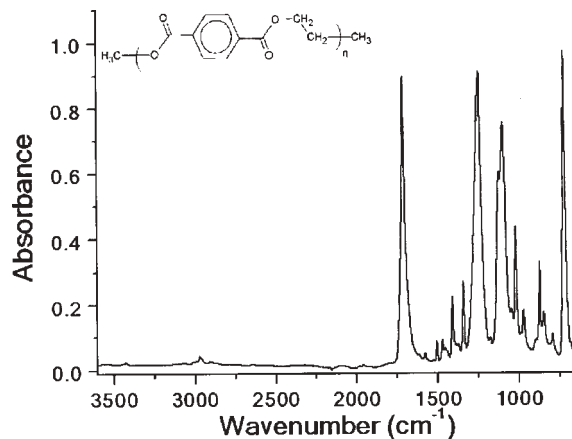


Fig. 2. Typical FTIR spectrum of the PET film

regions while in the crystalline regions the absorbance decreases. The $\text{C}=\text{O}$ absorbance decrease in both regions.

In the visible spectral range the PET films are transparent. The plasma treatment preserves this property, no new absorption bands being detected in the PET spectra. In the UV spectral range we found several absorption bands (fig. 4). The untreated polymer presents a broad band around 300 nm which corresponds to $n \rightarrow \pi^*$ transition of oxygen atoms from $\text{C}=\text{O}$ groups. The band centered at 225 nm is associated with the $\pi \rightarrow \pi^*$ transitions in orbitals of $\text{C}=\text{C}$ bond.

The APD treatment induces variation in the $\text{C}=\text{C}$ bond absorbance, while the LPD treatment seems to reduce the absorbance of $\text{C}=\text{O}$ bonds and to modify strongly the

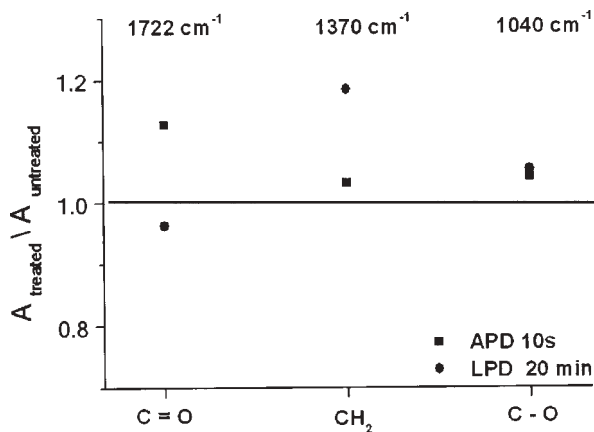


Fig. 3.a. Variation of absorbance for selected chemical groups in the both regions, amorphous (a) and crystalline (b)

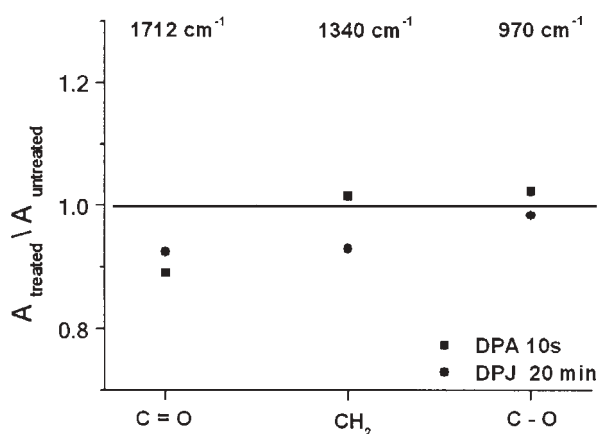


Fig. 3.b. Variation of absorbance for selected chemical groups in the both regions, amorphous (a) and crystalline (b)

position of the C=C absorption band, this band being shifted to 250 nm.

Conclusions

Plasma surface treatment is a suitable solution to modify the surface properties of commercial PET films. Both, the APD and the LPD treatments are efficient to increase the PET surface energy with different kinetics. The increase of the surface energy is due to the increase of its polar component, the dispersive component remaining unaffected by the plasma treatments. The surface chemistry analyzed by AFTR-FTIR and UV-Vis is preserved, certain variations in the absorbance of the existing chemical groups being found.

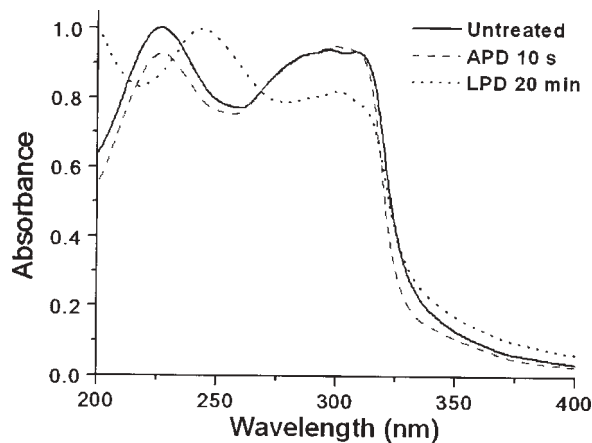


Fig. 4. UV-Vis normalized spectra of modified polymer samples

Taking into account the treatment duration it may emphasize the better efficiency of APD, 10 s of treatment being sufficient to induce the value of the surface energy comparable with the one obtained after 4 min of LPD treatment.

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