

Surface characterisation of plasma-modified poly(ethylene terephthalate)

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Abstract

This paper reports the modifications produced by nitrogen and helium cold plasmas on the surface of PET. The changes have been studied by diffuse reflectance Fourier transform spectroscopy (DRIFTS), atomic force microscopy (AFM) and inverse gas–solid chromatography (IGSC). Nitrogen and oxygen atoms seem to appear on the surface of PET as a consequence of the exposure to the atmosphere after the treatments with plasmas. AFM shows that both plasmas altered in different extent the surface of PET as they break the polymer chains producing low molecular products which appear as bumps on the surface. The surface area and the porosity of PET does not change by plasma treatments even after 15 min. The dispersive component of the surface free energy, γ_s^d , decreases after long treatments with nitrogen plasma whereas it remains almost unchanged after long treatment with helium plasma.

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1. Introduction

The modification and control of the surface properties of poly(ethylene terephthalate) (PET) is a research topic of current interest in view of its broad application range: adhesion, painting, dyeing, gas permeability or composites [1,2]. The need to control the surface characteristics of this polymer (e.g., its acid–base behaviour, hydrophilicity or biocompatibility) stems from specific requirements for given applications. Currently several approaches are being developed with this aim, including laser and UV radiation exposure, alkaline hydrolysis or plasma treatment [3–12]. Among the reported methods, the technique of gas-discharge low-temperature plasma modification is a particularly attractive way to modify the surface chemistry and morphology not only of PET but of polymeric materials in general [2,11,13]. Plasma treatment can be carried out by using chemically reactive (N₂, O₂, CO₂, etc.) or inert (H₂, Ar, He, etc.) gases. The former

lead to the disruption of the polymer chains by the energetic ions and radiation generated in the plasma as well as to the introduction of chemical functional groups on the polymer surface [7,14,15], whereas the chemical effect is absent when inert gases are employed and only ion bombardment and radiation should in principle play a role [16–18]. It is thus interesting to compare the effect of plasma treatment under these different types of gases.

In the present work, we have investigated and compared the modifications induced on the surface characteristics of PET by reactive (N₂) and inert (He) gas plasma treatments under different exposure times. To this end, several different characterisation techniques have been employed: diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), inverse gas–solid chromatography (IGSC), atomic force microscopy (AFM) and CO₂ adsorption. These techniques provide a variety of complementary information on the physicochemical changes on the polymer surface upon plasma exposure. Thus, DRIFTS allows to follow the evolution of the chemical groups present on polymer surfaces, and IGSC is useful to reveal the surface energy of

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different solids [19–24]. The high resolution capabilities of AFM are very suitable to disclose the nanometer scale structural modifications of plasma-treated polymers [25,26] whereas CO₂ adsorption provides information on the surface area and porosity.

2. Experimental

The characteristics of the used commercial PET are: glass transition temperature $T_g = 350$ K, molecular weight $M = 24,000$ g mol⁻¹, melting temperature $T_m = 523$ K and the degree of crystallinity, $X_c = 24\%$. Squared pieces (1×1 cm²) of commercial PET were used for N₂ and He plasmas treatments. These treatments were carried out in a Technics equipment. Prior to the treatment, the sample was outgassed for 5 min to a pressure of less than 0.02 Kp. Then the gas (nitrogen or helium) was admitted up to a pressure of 1 Torr and flowed for 5 min. The power supplied to the system was 200 W for two periods of time. The samples are labelled PET followed by the gas used and the time of treatment in brackets. For instance, sample PET-N₂(15 min) has been prepared by treatment with nitrogen plasma for 15 min.

The surface area and the porosity of the samples were measured by CO₂ adsorption at 273 K in a conventional volumetric system. DRIFTS spectra of all samples were obtained in a Nicolet Magna IR560 spectrometer using a high sensitivity MCT/A detector. Spectra shown are the result of co-adding 200 interferograms obtained at a resolution of 4 cm⁻¹.

Atomic force microscopy (AFM) analyses were carried out in the tapping mode of operation under ambient conditions with a Nanoscope Multimode IIIa, from Digital Instruments. Rectangular Si cantilevers with spring constants of ~ 40 N m⁻¹ and resonance frequencies around 250 kHz were employed. The nominal tip radius of curvature of these probes was 5–10 nm. To reduce sample disturbance to a minimum and track the sample surface topography accurately, scanning was performed under light tapping conditions, i.e., with a set-point to free amplitude ratio of about 0.9 [27].

The IGSC measurements were carried out in a Carlo Erba gas chromatograph equipped with a flame ionisation detector. A 125 cm \times 5 mm i.d. glass column, which was packed with ~ 11 g of PET, was used. For this the squared pieces of PET were cut in small pieces of <0.5 mm in size. Before the measurements the column was conditioned for 24 h at 373 K in nitrogen flow. The experiments were carried out using nitrogen as carrier gas and at several temperatures in the range 303 and 363 K. The molecular probes were *n*-alkanes from *n*-C₁₀ up to *n*-C₁₄. To inject the vapour of these probes several amounts in the range 0.1–5.0 μ L were withdrawn from the headspace of liquid samples. At least three different amounts of each probe were injected at each temperature. The highly symmetrical shape of the chromatographic peaks and the fact that the peak maxima did not depend on the amount injected are evidences of the equilibrium nature of

the adsorption experiments and of the process is produced in the region of the Henry's law [28]. Under these conditions the specific retention volume V_s is the equilibrium constant which can be obtained from the experimental retention volume, V_R :

$$V_s = \frac{V_R}{SW}, \quad (1)$$

where S is the surface area obtained by CO₂ adsorption, W is the weight of PET inside the column and V_R is the retention volume:

$$V_R = F_{\text{corr}}(t_R - t_0), \quad (2)$$

where F_{corr} is the flow of the carrier gas, corrected for the temperature of the experiment and the pressure drop, t_R is the retention time and t_0 is the hold-up time [28].

From the retention data of the *n*-alkanes measured as a function of the temperature the thermodynamic parameters of adsorption can be determined. For this it is necessary to take into account that the adsorption takes place in the Henry's law region and that the concentration in both vapour and adsorbent phases is very low. Under these conditions the standard enthalpy of adsorption, ΔH_A^0 , can be obtained [29] from the slope of the plot of $\ln V_s$ versus $1/T$ as:

$$\ln V_s = -\frac{\Delta H_A^0}{RT} + C. \quad (3)$$

The variation of the standard free energy of adsorption, ΔG_A^0 , can be determined from [28,29]:

$$\Delta G_A^0 = -RT \ln \left(V_s \frac{p_{s,g}}{\pi_s} \right), \quad (4)$$

where $p_{s,g}$ is a reference pressure having a value of 1 atm (101 kN m⁻²) and π is the two-dimensional pressure of the adsorbed state, 0.338 mN m⁻¹ [24,29]. The values of ΔG_A^0 are useful because they allow to obtain the dispersive component, γ_s^d , of the surface free energy by using the semi-empirical relationship proposed by Dorris and Gray [30] which is based on the incremental change in ΔG_A^0 per methylene group for a series of *n*-alkanes:

$$\gamma_s^d = \frac{1}{\gamma_{\text{CH}_2}} \left[\frac{-\Delta G_{\text{CH}_2}}{N a_{\text{CH}_2}} \right]^2, \quad (5)$$

where ΔG_{CH_2} is the adsorption free energy of one methylene group, N is the Avogadro number, a_{CH_2} is the area of an adsorbed methylene group (0.06 nm²) and γ_{CH_2} is the surface free energy of a surface made of $-\text{CH}_2-$ groups, that is [28]:

$$\gamma_{\text{CH}_2} = 35.6 - 0.058(t - 30), \quad (6)$$

where γ_{CH_2} is given in mJ m⁻² and t , the temperature, is in degrees Celsius. It is interesting to note that because γ_s^d in Eq. (5) depends on the differential quantity ΔG_{CH_2} , it is independent of the surface area of the solid and therefore is a fundamental parameter which gives information about the surface free energy of the solid.

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