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Studies of amine treatments influence on poly(ethyleneterepthalate) films

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By applying ammonia plasma treatment and chemical ethylenediamine treatment, amine functionalities were observed in the poly(ethylene terephthalate) (PET) films surfaces. The modified surfaces were characterized by FTIR, fluorescence, wide-angle X-ray diffraction (WAXD) and atomic force microscopy (AFM). Ethylenediamine treatment yielded fewer surface amino groups, and in addition a change in crystallinity as well as degradation of PET. Treatment time dependency of amine concentration is depicted, more amines were incorporated after exposure to a higher energetic plasma resulted by the higher ionisation in the plasma. At higher energies at longer treatment, an increase of the amine concentration was observed. For surface activation, plasma treatment was more efficient than chemical treatment.

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1. Introduction

The use of synthetic materials or special modified natural materials for medical applications and for bioengineering purposes is widespread. A biomaterial has been defined as a "non-viable material used in a biomedical device intended to interact with biological systems" [1]. There are two main requirements biomaterials have to fulfil, namely they have to successfully perform the intended function and secondly they must not induce adverse responses i.e. have to be compatible with the living system and should not provoke dysfunction of the metabolism. It is relatively easy to meet requirements of functionality because design criteria are mostly well defined and many engineering materials are suitable. The biological responses of biomaterials and devices on the other hand are mainly controlled by their surface chemistry and structure, which have to be tailored according to special needs [2,3].

From polyesters class, polyethyleneterephthalate (PET) is the polymer with the most important practical applications because of its physical, chemical, dielectrical, and mechanical unique proprieties [4].

Because of its aromatic-aliphatic structure responsible for hydrophobic behaviour, many studies have been made in order to increase the hydrophility, to find new applications. Such application is the biocompatibilization of PET films by amine functionality. Nitrogen containing PET films can be considered as a potential biomaterial substrate for the proteins attachment and other biologically active molecules. The advantage of attaching nitrogenous functional groups to the film surface is the fact that they may allow direct attachment of bioactive molecules. Plasma treatment can be used to modify a polymer surface in a non-specific manner by changing the wettability or in a more specific manner by introducing a variety of functions groups depending on the type of gas used.

The introduction of amine functionalities on PET surfaces has been achieved by use of ethylenediamine. An alternative to plasma treatment for introduction of amino groups on a polyester surface is chemical etching in the form of aminolysis using diamines. It has been found that the rate of reaction depends on the type of amine used [5] and the percentage crystallinity of the polymer. The degree of amine functionalization was found to be dependent on the treatment time, concentration, and temperature [6].

In the present study, amine functionalities were introduced into the surface of PET films by treatment with ethylenediamine plasma and wet ethylenediamine aminolysis. The surface modified materials were characterized by wide-angle X-ray diffraction (WAXD) for comparing crystallinity. In order to identify the chemical species amino groups on the PET surface, FTIR-ATR (Attenuated Total Reflectance Fourier Transform Infrared) spectroscopy and fluorescence measurements were used. Among these techniques, plasma treatment is particularly versatile because the modification restricted to the top surface of the material, leaving the bulk unaltered

2. Experimental results and discussion

PET film samples (25 × 25 mm, 30 µm thickness), biaxially oriented before the aminolysis reactions, were washed to remove surface contaminants. The strips were cleaned with absolute toluene, acetone and water sequentially bidistilled for 5 min in an ultrasonic water bath. Washed samples were dried at room temperature.

2. 1. Plasma treatments

PET films (25 × 25 mm) were mounted in a metal sample holder where the film was positioned vertically to allow treatment on both sides of the sample. This sample holder was placed on top of a glass slide, which was inserted inside a plasma reactor downstream from coil (~10cm). The plasma reactor is described in Fig. 1.

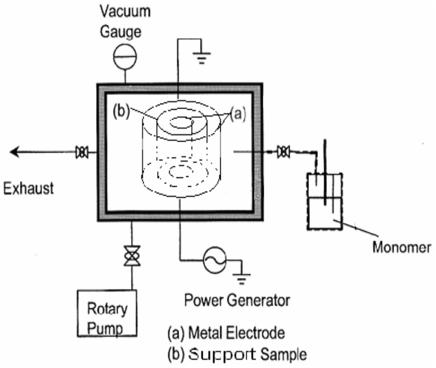

Fig. 1. Plasma reactor

When the pressure inside the reactor reached a base pressure (0.1 Torr), the reactor was filled with ethylenediamine vapors, after which the RF generator was activated at plasma power (2.5 — 20W) and several reaction times.

Spectrometer fluorescence Perkin Elmer has been used to determine p-amine concentration.

2. 2. Chemical treatments

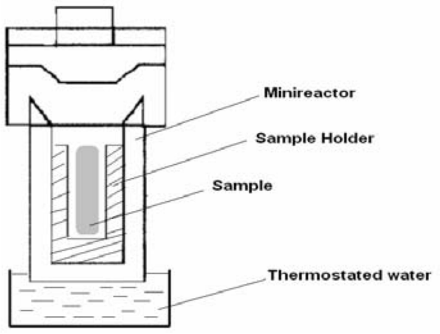

Fig. 2. Chemical minireactor

The films were treated with aqueous ethylenediamine (ED) (99%, Merck, Germany) films in inoxidable minireactor steel (Fig. 2), at 80 °C at different times. After treatment, samples were subjected to extensive washing with water bidistilled and dried at room temperature. ATR-FTIR spectra (64 scans, 2 cm^{-1} resolution, wavenumber range 4000 — 650 cm^{-1}) were acquired on VERTEX 70 BRUKER diamond ATR accessory. Peak height measurements were performed with the spectral analysis software (Opus 5).

WAXD was used to study the changes in cristallinity of the nitrogen containing poly(ethylenetherepthalate) film induced by chemical and plasma treatments. WAXD patterns were recorded with a D8 Advance Bruker AXS diffractometer. X rays were generated using a CuKα source with an emission current of 36mA and a voltage of 30kV. A 0.6 mm divergence slit was used for all samples to improve the signal-to-noise ratio. Scans were collected over the range 2θ = 4- 45° using a step size of 0.01° and a count time of 0.5s/step.

3. Results and discussion

The surface of the PET films was functionalized by different methods: amine plasma treatment and chemical aminolysis, in order to introduce amino groups. The general reaction scheme for the aminolysis of PET is presented in Fig. 3 [3].

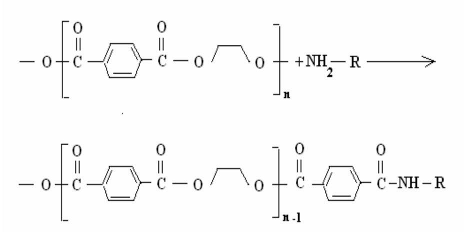

Fig. 3. General reaction scheme for the aminolysis of PET

3.1. FTIR-ATR measurements

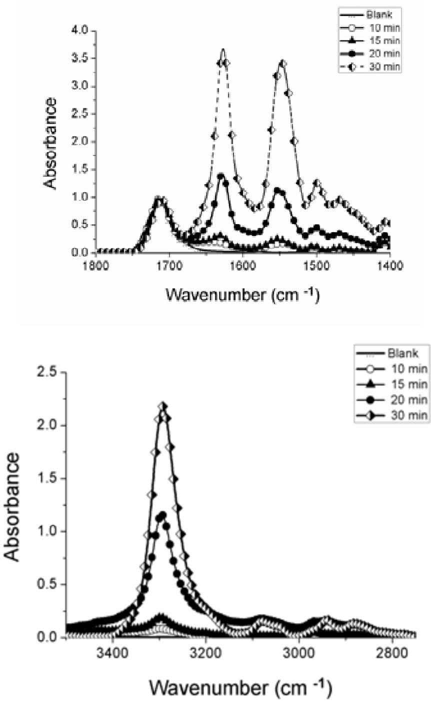

Fig. 4. FTIR-ATR spectra

The polyester film undergoes chemical aminolysis. There is a nucleophilic attack of the nitrogen on the carbon centre of the carbonyl ester. This would normally be a rapid reaction. The randomly attacks the carbonyl groups of the polymer molecular present on the surface groups of the film and removes them as short chains. Treatments of our PET films with ethylenediamine vapors at 80° C and different time reaction it was noticed with FTIR-ATR in Fig. 4.

Due to aminolysis process with ethylenediamine, the appearance of one peak at 1630 cm^{-1} corresponding to amide II stretching vibration of carbonyl groups can be observed. Also, the FTIR-ATR spectrum measured at ambient pressure spectrum presents the signals corresponding to CH-N group stretching at 1551 cm^{-1}, as well as NH strain vibration with CO ester stretching, in which NH group has the biggest share. The amide II mode (3295 cm^{-1}) includes NH in plane bending and can be amplified with the increase of the treating time. At a time, the spectrum contains the conformation sensitive NH band from ethylenediamine at 3400 cm^{-1}.

3.2 Fluorescence measurements

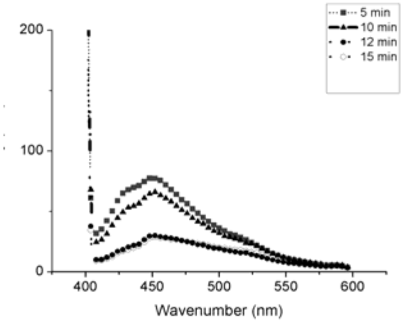

Fig. 5. Fluorescence spectra

During plasma treatment, a variety of reactive species are produced to the atmosphere of amine and they can all interact with the exposed material surface. The samples modified in plasma treatment were by exposure to amine atmosphere, radicals generated during the plasma treatment to produce hydrophilic groups on surface of PET films.

A very sensitive semi-quantitative method to determine p-amine concentration is the fluorescent labeling with Fluram. Samples with a diameter of 13 mm were immersed into a solution of 10 mg Fluram (Fluorescamine, Fluka 47614) in 20 ml dry acetone. After shaking for 5 min at room temperature the samples were washed twice with water and once in absolute ethanol. The samples were dried for 15 min in air and placed into the solid sample holder of a fluorescence spectrometer. Measurements were performed with excitation at 335 nm and emission at 467 nm.

To investigate the distribution groups on PET surface, spectra from the fluorescence were assessed for presence of amino functional groups (Fig. 5).

3.3 WAXD measurements

Changes in the surface cristallinity, as a result of aminolysis, were measured using WAXD. Because of the low electron density of PET film, the CuKα beam penetrates the entire sample, and the changes observed by XRD relate more to the bulk crystallinity.

Fig. 6 shows the diffraction pattern obtained for a film aminated in plasma, for 10 min over the range 2θ = 20-35°.

Gaussian fit of all data demonstrates the presence of two peaks in the diffraction pattern, occurring at 2θ = 23 and 26°. These refer to the (110) and (100) atomic planes of PET [7], respectively. As Table 1 shows, the cristallinity is affected by the amination conditions (time of exposure, type of amination: chemical or plasma treatments). The intensities of these peaks are related to the degree of crystallinity of the film.

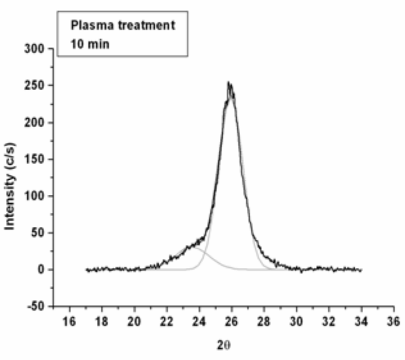

Fig. 6. Gaussian fit of WAXD pattern

The intensity of the (100) peak is the highest for the film aminated for 15 min, in plasma, indicating that the sample is mostly crystalline.

Table 1. Intensity of the (100) atomic plane for aminated PET.

Treatment time (min)	Intensity (plasma)	Intensity (chemical)
10	252	143
15	363	334
20	231	561
30	246	100
45	380	-

Considering the sample morphology, the interpretation of these data is possible. At treatment of 5 min ethylenediamine etches the amorphous regions between the crystallites forming very fine parallel lines in the surfaces of PET film. These parallel lines are also present in the sample aminated for 10 min. At treatment times beyond 30 min, the degradation is sufficient to cause the lamellae to be stripped away from the film surface. WAXD analysis suggests that the removal of a layer of lamellae occurred at 30 min, with the intensity of the (100) peak reaching the minimum value of the sample. This is evident also from weight-loss measurements. At 45 min, the intensity of the (100) peak increases again. This is probably due to the formation of a new crystalline surface underneath the first row of lamellae. The etching of the amorphous regions between the rows of lamellae and between the individual lamellae is more severe. Therefore, it would be expected that this film would exhibit a higher degree of surface cristallinity because there are fewer amorphous regions.

Referring to chemical treatment of PET, the intensity of the (100) peak is the highest for the film aminated for 20 min, indicating that the sample is most crystalline. At 10 min, the aminolysis reaction of PET drew in Fig. 3 takes place at the surface of the sample. The presence of amide groups has been reported by several researchers studying the surface modification of PET [8] and is most likely due to the amide functionality. With the increasing of time, N will be present in regions deeper and deeper in PET film, so an increasing in the surface N content cannot be achieved trough longer reaction times, which is in concordance with other researcher's work [8]. In fact, several researchers have suggested that the mechanism of polymer aminolysis is via diffusion [9]. At 30 min, the degradation of PET film is evidenced by the low intensity.

3.4 AFM measurements

Atomic force microscopy measurements were performed on SOLVER PRO-M, NT-MDT Rusia with NOVA software, on semi-contact mode.

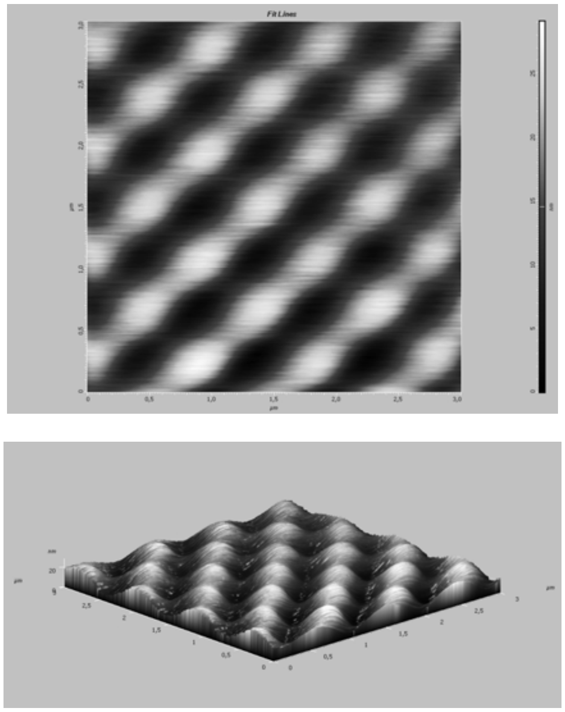

Fig. 7. Untreated PET.

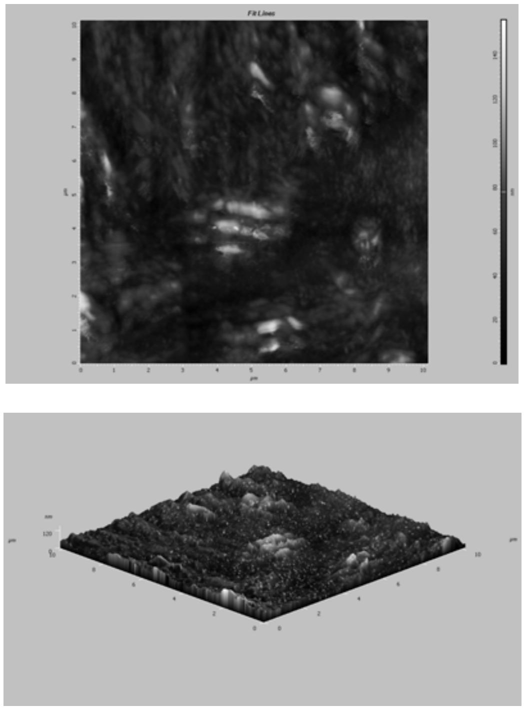

Fig. 8. Chemical treatments, 10 min.

In Fig. 7 the untreated PET is presented. Fig. 8 and 9, AFM for PET chemical, respectively plasma treatments demonstrates that plasma treatments are more efficient in surface activation than chemical treatments.

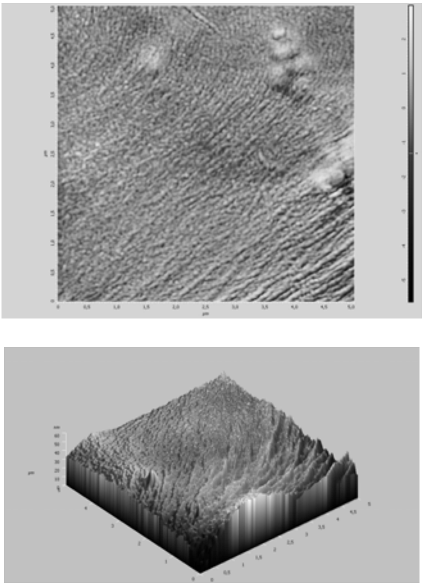

Fig. 9. Plasma treatments, 10 min

4. Conclusions

The surface of the PET films was functionalized by different methods, amine plasma treatment and chemical aminolysis, in order to introduce amino groups.

Treatment time dependency of amine concentration is depicted, more amines were incorporated after exposure to a higher energetic plasma resulted by the higher ionization in the plasma. After a short treatment amine groups were incorporated in PET. At higher energies at longer treatment, an increase of the amine concentration was observed. Our results indicate that after a longer time treatment degradation of surfaces was predominant, while in the initial phase implantation reactions were determinant.

For surface activation, plasma treatment was more efficient than chemical treatment.

Further work is optimal conditions of PET surface functionalization study for biocompatibility with proteins.

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