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Surface modification of poly(ethylene terephthalate) polymeric films for flexible electronics applications

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Abstract

The production of Flexible Electronic Devices (FEDs) by roll-to-roll large-scale manufacturing processes is a rapidly growing sector and the development of functional (inorganic and/or organic) thin layers onto flexible polymeric substrates represents one of the key issues for the low cost production of FEDs. However, the flexible substrates should meet advanced demands, as high optical transparency, high barrier properties and increased adhesion of the subsequent functional layers, which will have a major affect on their performance, efficiency and lifetime. Plasma treatment can be successfully employed for the improvement of the bonding structure and surface properties of flexible polymeric substrates. In this work, we report on the effect of Pulsed DC N^+ ion bombardment using different ion energies, on the bonding structure, electronic and optical properties and surface nanotopography of Poly(Ethylene Terephthalate) (PET) substrates. For the investigation of the optical properties, we have used in-situ and real-time Spectroscopic Ellipsometry from the IR to Vis-farUV spectral region, in combination to advanced modeling procedures, whereas Atomic Force Microscopy has been employed for surface nanotopography investigation. As it has been found, the N^+ bombardment leads to the appearance of new chemical bonds (C–N or C–O bonds in Φ-NH_2, Φ-NHR, C(=O)–NHR, Φ–OH, or (C=O)–OH), as well as partial disappearing of the C–O bond of ester group, on a surface layer of PET.

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1. Introduction

One of the state-of-the-art applications of polymer films is the production of Flexible Electronic Devices (FEDs) such as flexible displays and lighting (OLEDs), flexible photovoltaic cells (OPVs), which is a radically expanding sector of the modern industry. FEDs are expected to be integrated in several applications in our everyday life. The use of polymer materials towards this direction is motivated by the advantages and the conducting, and light emitting properties of organics (polymers, oligomers) and hybrids (organic–inorganic composites), combined with easy processing, low cost and production flexibility, which are necessary in large scale roll-to-roll (r2r) configurations [1–5]. The deposition of functional layers (barrier layers, electrodes, Transparent Conductive Oxides — TCO, organic emitters) onto bendable and flexible polymer substrates in new and intelligent production techniques, open up the possibility of cost-effective, roll-to-roll processing in high volumes [5–9]. A major factor for the achievement of the desirable performance, efficiency and lifetime of FEDs is the properties of the polymer substrates in which the multilayered film structure of the device will be encapsulated. The flexible substrate materials should meet specific and advanced demands, in order to be integrated in the production of FEDs, such as high optical transparency and high barrier–low permeability response in atmospheric gases such as oxygen and water vapour [3,10,11]. These properties are determined and controlled by the bonding structure of the polymer substrates, the surface nanostructure and chemistry, which controls the functionality of the subsequent functional layers that are developed onto the polymer substrates, and finally on the film-substrate adhesion [3,10,11]. Therefore, the detailed knowledge of the bonding structure, mechanical response and surface nanotopography of the polymer substrates are of significant importance and affect all the production steps. Among the most suitable polymer materials, Poly(Ethylene Terephthalate) (PET) is an excellent candidate material to be used in the production of FEDs, since it exhibits a combination of important properties, as easy processing, good mechanical

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properties and reasonably high resistance to oxygen and water vapour penetration [6,10,11]. The study of the surface modification of the flexible polymeric substrates and their functionality for the adherence of the deposited oxide barriers, the mechanical response and the surface nanotopography of the final system are of considerable significance. In this work, we study the effect of the plasma treatment by using N_2 atoms on to the optical properties of PET by the use of Spectroscopic Ellipsometry, in an extended spectral region from the IR (900–3500 cm^{-1}) to the Vis-fUV (1.5–6.5 eV) covering all the different light absorption mechanisms. In this way, we report on the changes of their optical and vibrational properties resulted by the implementation of plasma treatment using Pulsed DC N_2 plasma on their surface.

2. Experimental details

The examined polymeric films were industrially supplied biaxially oriented PET films of thickness ~50 μm, treated with mechanical stretching. The surface modification of the polymeric films has been performed by Pulsed DC plasma treatment with N_2 gas, in an ultra high vacuum chamber with a base pressure of $P_b = 1.2 \times 10^{-7}$ Torr. The partial pressure of the working gas was $P(N_2) = 30$ mTorr and constant flow at 40 sccm. The treatment process has been performed at RT using different values of a pulsed negative voltage (V_P) from 200 to 700 V, with a frequency of 100 Hz. The investigation of the optical properties of the polymeric films has been studied in detail by Spectroscopic Ellipsometry (SE) technique in a wide spectral region from the IR (vibrational properties) to the Vis-fUV (electronic properties). The IR measurements (900–3500 cm^{-1}) were performed by a Fourier Transform IR phase modulated Spectroscopic Ellipsometer (FTIRSE) adapted to the ultra high vacuum chamber using BaF_2 windows. The Vis-fUV SE spectra measurements were performed using a Phase Modulated Spectroscopic Ellipsometer (PMSE) (1.5–6.5 eV). A detailed description of the FTIRSE and PMSE units has been given elsewhere [2,4,12]. In order to eliminate the multiple reflections of the incident light at the top and bottom interfaces of PET that introduces interference fringes to the measured pseudo-dielectric function $<\varepsilon(\omega)> = <\varepsilon_1(\omega)> + i<\varepsilon_2(\omega)>$, their back side has been sandpapered in order to scatter and diffuse the transmitted light. Finally, the investigation of the surface nanotopography of the PET has been performed by Atomic Force Microscopy (AFM) using a commercial system. The AFM images of the surface were taken in non-contact mode to avoid the polymer surface deformation, simultaneously with the phase images, using a rectangular Si cantilever with less than 10 nm nominal tip radius.

3. Results and discussion

The unit cell of PET is characterized by a triclinic symmetry with a density of 1.455 gr/cm^3 and it has a C_{2h} point symmetry [13]. It is consisted by an aromatic ring and an ester function (terephthalate group), and by a short aliphatic chain that constitutes the ethylene segment [11,13,14]. The aliphatic moiety $-[OCH_2CH_2O]-$ can be found in two conformations, *gauche* (exists in the amorphous regions) and *trans* (exists in both crystalline and amorphous regions). During the large scale production of PET films with thicknesses in the order of μm, by large scale r2r techniques, the applied mechanical stretching leads to the preferential orientation of the macromolecular chains towards the stretching direction (or Machine Direction — MD) [3,11]. As a result, the bonding structure of PET resembles a "composite-like" material that consists of oriented (crystalline-like) and non-oriented (amorphous with randomly complex macromolecular chains). Therefore, the optical response of PET films includes the contribution of both (oriented and non-oriented) regions leading to an anisotropic optical behavior.

The electronic and optical properties of PET have been studied by Spectroscopic Ellipsometry through the analysis of the measured pseudo-dielectric function $<\varepsilon(\omega)> = <\varepsilon_1(\omega)> + i<\varepsilon_2(\omega)>$ that includes information from both the optical properties and the thickness of the PET films [2,11]. The $<\varepsilon(\omega)>$ is a function of the complex ratio of the Fresnel reflection coefficient parallel and perpendicular ($\tilde{r}_p$) and ($\tilde{r}_s$) to the plane of incidence, described by the equation [11]:

$$\tilde{\rho} = \frac{\tilde{r}_p}{\tilde{r}_s} = \tan\Psi \; e^{i\Delta} \qquad (1)$$

where Ψ and Δ are the ellipsometric angles that correspond to the amplitude ratio and the relative phase change, respectively, and they are directly related to the electronic and optical properties. In this work, all optical investigations have been performed with the plane of incidence parallel to the MD.

The pseudodielectric function $<\varepsilon(\omega)> = <\varepsilon_1(\omega)> + i<\varepsilon_2(\omega)>$ of PET in the IR spectral region, measured by FTIRSE, has been discussed in detail elsewhere [5]. Most of the characteristic absorption bands corresponding to the bonding vibrational modes of the IR-active chemical bonds of PET appear at the wavenumber region 900–1800 cm^{-1}, whereas above 1800 cm^{-1} the $<\varepsilon(\omega)>$ spectra is dominated by interference fringes due to the multiple reflections of light at the polymeric film interfaces. Among the more intense characteristic vibration bands, we observe the vibration modes at ~940 and ~971 cm^{-1} (*trans*) that could be attributed to the C–O stretching mode, the aromatic CH_2 stretching mode at ~1125 cm^{-1}, the ester mode at ~1255 cm^{-1}, the in-plane deformation of the C–H bond of the para-substituted benzene rings at ~1025 and ~1410 cm^{-1} and furthermore, the characteristic vibration band at 1720 cm^{-1} corresponding to the stretching vibration of the carbonyl C=O groups [11,15,16]. The band at 1342 cm^{-1} is attributed to the wagging mode of the ethylene glycol CH_2 groups of the *trans* conformations, whereas the characteristic peak at 1470 cm^{-1} corresponds to the CH_2 bending mode, and the C–H in plane deformation mode appears at ~1505 cm^{-1} [11,15,16].

Fig. 1 shows the measured $<\varepsilon(\omega)>$ of PET in the IR spectral region, before and after the Pulsed DC N_2 plasma treatment using various V_P values. The main absorption bands observed in the FTIRSE spectra of PET seems almost unchanged, due to small modification depth and the large penetration depth of IR

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