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Lifetime improvement of poly(ethylene naphthalate) by ZnO adhesive coatings

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Abstract

Zinc oxide (ZnO) coatings were deposited by RF magnetron sputtering on the surface of poly(ethylene naphthalate) (PEN) films to protect the polymer against ultraviolet (UV) radiation. To increase the adhesion of the coating, PEN films were submitted to cold plasma treatments before deposition. Wettability measurements showed that the adhesion strength of the coatings was increased by a CO_2 plasma treatment of PEN and varied with the oxygen partial pressure in the sputtering gas. The photodegradation of the ceramic/polymer assemblies, in conditions of artificial accelerated ageing, was monitored by infra-red and UV-vis spectroscopies. Results showed that photoprotection increases with ZnO thickness up to 200 nm. In addition, the sputtering parameters, which act on the composition, the structure and the optical properties of ZnO, were optimised to obtain the best coating in terms of UV and oxygen barrier.

Keywords: Poly(ethylene naphthalate); Photo-oxidation; Zinc oxide; Photoprotection; Sputtering; Plasma treatment; Adhesion

1. Introduction

Poly(ethylene naphthalate) (PEN) is a transparent aromatic polymer which exhibits remarkable thermal and mechanical properties. Consequently PEN could be used in many domains like bottle fabrication, flexible printed circuits and electrical applications [1,2]. Because the light absorption by PEN extends up to 380 nm, this polymer absorbs the ultraviolet (UV)-light present in the terrestrial solar radiation, which produces photodegradation of the polymer causing embrittlement and photoyellowing. PEN photodegradation has received little attention in the literature [3,4]. A comprehensive study on the photolysis and photooxidation of PEN has been more recently published by Scheirs et al. [5]. It was shown that the photodegradation was limited to a 10 μm superficial layer. In photooxidative conditions, acidic end-groups are formed. In addition, the conversion of the naphthalene units results in an intense photoyellowing of the polymer accompanied by gel formation.

It is very difficult to protect aromatic polymers from the photodegradation which results from direct absorption of sunlight radiation by the intrinsic chromophoric groups. We have developed a photostabilisation method which was successfully employed for PET [6,7], PEEK [8] and PC [9]. The technique consists in covering the surface of the polymer with a thin ceramic layer (ZnO or TiO_2) transparent in the visible range. The deposition was carried out by sputtering from a ZnO or TiO_2 target fixed on a magnetron cathode. Compared to other methods, such as vacuum evaporation, this technique presents interesting advantages such as lower substrate temperature (usually lower than 60 °C), a better adhesion of the ceramic on the polymer and a higher ceramic density. The stabilising action of the deposit is

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associated with its ability to absorb the photons that are damaging for the polymer and to create a barrier to oxygen diffusion.

We have chosen ZnO to protect PEN against photoageing, as this oxide offers a higher absorption than TiO_2 for near-UV photons.

To enhance the adhesion of coatings, most polymers need preliminary treatments to increase the reactivity of their surface. Various treatments can be used such as chemical, photochemical and plasma types [10–13]. In this study, we have used cold plasma treatment because it presents several advantages: the action is limited to the outermost surface, the bulk properties of the film are maintained, and this treatment can be carried out in a sputtering chamber, which eliminates any possibility of contamination.

In this paper, we report our investigations to increase the photostability of PEN films in conditions of artificial accelerated ageing. At first, the effects of plasma treatments, using inert or reactive gases, on PEN surface were investigated by wettability measurements. The adhesion strength of the zinc oxide coatings on PEN was evaluated by peeling tests. Afterwards the barrier properties of the coating were examined versus its thickness. Finally, the photoprotective effect of zinc oxide coatings was investigated. The photochemical behaviour of the ceramic/polymer assemblies was tested by exposing the samples in an artificial accelerated photo-ageing device. The chemical evolution of PEN was assessed by infra-red and UV-vis analysis. We focused also our investigation on the improvement of the photoprotective effect of ZnO by varying the thickness of deposits and the sputtering parameters: RF power, total pressure, oxygen partial pressure.

2. Experimental

PEN films are commercial grade of ICI Kaladex 2000 having a thickness of 25 μm for most of the studies. They were ultrasonically cleaned in ethanol. Irradiations were carried out in a SEPAP 12.24 unit at a temperature of 60 °C with medium-pressure mercury lamps. This medium-accelerated photoageing device has been described previously [5]. It allows irradiation at wavelengths longer than 300 nm.

UV-visible spectra were recorded on a Shimadzu UV-2101 PC and a Perkin Elmer (Lambda 3), both equipped with integrating spheres. The infrared spectra were recorded on Nicolet Magna-IR 510 and 800 FTIR spectrophotometers (nominal resolution of 4 cm^{-1}, 32 scans summation). Samples were regularly analysed during irradiation.

Plasma treatments of the films and the coating depositions were achieved in a sputtering unit (Alcatel SCM 450) equipped with a radiofrequency generator. A ZnO target (100 mm diameter, 99.9% purity) fastened on a magnetron effect cathode was used as the starting material for deposition. PEN film was fixed on a cooled substrate holder situated at 90 mm from the target. The oxygen partial pressure in the argon-oxygen plasma was adjusted by means of mass flow controllers.

The surface free energy of PEN was determined by wettability using the two-liquid method which consists in measuring the contact angle of a polar liquid (water) on the polymer in presence of second non-miscible liquid (hydrocarbon) [14].

The adhesion of the coating on the polymer was characterised by the 180° peeling test [15]. This test permits calculating the adhesion strength per unit interfacial area W from the following relationship: $W = 2F/\lambda$, where F is the force necessary for the rupture of the assembly, and λ the width of the separation front. To achieve the measurements, a film of ethylene acrylic acid (EAA) was first thermally bonded on the coating according to the conditions previously described [16]. Then the peeling test is carried out at room temperature by pulling the EAA film at a 180° peeling angle and at a rate of 50 mm/min. The nature of the rupture was characterised by X-ray energy dispersion spectrometry (EDX) which allows the analysis of the composition of the two de-bonded surfaces.

The gas permeation measurements were performed on a Lyssy apparatus (GPM 5000 model) using helium as a carrier gas and separation of the gases by chromatography. The test area was 50 cm^2 and the PEN films have a thickness of 12 μm in order to get a sufficient sensitivity.

3. Results and discussion

3.1. Properties of the PEN surface and ZnO coating

3.1.1. PEN surface treatments

The surface free energy of solids (γ_S) has two components: the polar one γ_S^P due to specific interactions, such as Debye and Keesom or acid-base interactions, and the dispersive component γ_S^D corresponding to London interactions. The surface free energies (γ_H) of various hydrocarbons, their interfacial energies with water (γ_{HW}) and the measured contact angles ($\theta_{SW/H}$) on the surface of PEN are given in Table 1. From the representation of $\left[\gamma_W - \gamma_H + \gamma_{HW}\cos\theta_{SW/H}\right]$ versus $[(\gamma_W^D)^{1/2} - (\gamma_H)^{1/2}]$

Table 1
Energy data of hydrocarbons and contact angles for water on PEN in presence of hydrocarbon

Hydrocarbon	γ_H (mJ/m^2)	γ_{HW} (mJ/m^2)	$\theta_{SW/H}$ (°)
Hexane	18.4	51.1	107.75
Octane	21.3	51.0	108
Decane	23.4	51.0	109
Dodecane	25.4	51.1	109.25