

Photostabilization of Polycarbonate by ZnO Coatings

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ABSTRACT: The photostability of bisphenol-A polycarbonate (PC) can be increased by depositing zinc oxide (ZnO) coatings onto PC films by radiofrequency (rf) magnetron sputtering using an Ar–O₂ plasma. The photoprotective efficiency increases with the thickness of the ZnO layer and also depends on the sputtering parameters (rf power, total pressure, plasma composition), which control the properties of coatings. The increasing thickness of the deposits is correlated with variations of the density, grain size, and composition. PC samples with ZnO coatings were submitted to

artificial accelerated ageing ($\lambda > 300$ nm) and the extent of the photodegradation was evaluated by infrared and UV–visible spectroscopies. All the deposition parameters were optimized as a function of the results obtained in photoageing and are described in this article. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 95: 380–385, 2005

Key words: polycarbonates; stabilization; coatings; degradation; photoageing

INTRODUCTION

Bisphenol-A polycarbonate (PC) has excellent physical and mechanical properties such as transparency and rigidity.^{1,2} However, on exposure to sunlight PC suffers from a significant loss of these properties. In particular, the substantial yellowing that appears limits the use of this material if outdoor applications are considered.² The photochemical reactions that occur have been described by a dual photochemistry that involves a direct phototransformation and a photo-induced oxidation. The ratio of both these processes is largely dependent on the spectral distribution of the excitation light source.³ The relative proportion of short and long wavelengths determines the occurrence of direct phototransformation and side-chain photooxidation.^{3,4} Two successive photo-Fries rearrangements are the main processes occurring by absorption of radiations below 330 nm, whereas gem-dimethyl side-chain and phenyl-ring oxidations are induced by radiations above 330 nm. The direct photochemical processes that involve photo-Fries rearrangements of the macromolecular segments cannot be inhibited by antioxidants or quenchers. Moreover, a simple application of the Beer–Lambert law shows that the direct absorption of light in the range 300–330

nm is not reduced if the polymer contains anti-UV stabilization. This can be easily verified by comparing the rate of yellowing of blank samples of PC and samples with anti-UV. The standard methods of photostabilization are not efficient in the case of PC, and thus adapted methods have to be developed. One of the possibilities consists in applying an external UV filter onto the polymer. This external filter is usually composed of a thin layer of an organic polymer with an anti-UV. Another approach of the external stabilization of PC that can be developed is the deposition of a ceramic coating on the polymer. The main role of the ceramic is to absorb the incident photons, but it also offers a severe limitation in terms of oxygen diffusion, thus reducing the rate of formation of the photooxidation products.^{5,6}

Zinc oxide (ZnO) thin films were chosen because of their very interesting characteristics. They present good chemical stability and interesting optical properties because they are transparent in the visible range and absorb UV radiation below 380 nm.^{5,7} These coatings were deposited by the radiofrequency magnetron sputtering technique that allows a low substrate temperature. Moreover, deposits obtained with this method have a better adhesion onto the substrate than those elaborated by other methods such as vacuum evaporation.⁵

The first part of this article describes the chemical changes of PC under UV light. Then the efficiency of ZnO coating to protect the polymer is characterized and the results are discussed on the basis of the structural properties of the ceramic.

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EXPERIMENTAL

PC films (50 μm thick) were supplied by Technifilm (reference Makrofol D.E 6-2; Limburg, Germany). They are amorphous, transparent, and contain no antioxidants. They were ultrasonically cleaned in ethanol before irradiation. The irradiations were carried out in a SEPAP 12.24 unit at a temperature of 60°C with four medium-pressure mercury lamps. This medium-accelerated photoageing device, which allows irradiation at wavelengths above 300 nm, was previously described.⁵ The back of the samples was masked during irradiation to protect them from photooxidation. The formation of the photoproducts was followed by UV-visible and infrared spectroscopies using UV-2101 (Shimadzu, Kyoto, Japan) and Magna-IR 760 FTIR (Nicolet Analytical Instruments, Madison, WI) spectrophotometers, respectively. For both techniques, measurements were performed by transmission mode. ZnO thin films were deposited in a sputtering unit (SCM 450; Alcatel, Annecy, France) from a ZnO target (99.9% purity, 100 mm diameter) fixed on a magnetron-effect cathode and equipped with a radio-frequency generator. The cooled substrate holder was situated in front of the target at a distance of 90 mm. Before deposition, the chamber was evacuated at 10^{-5} Pa, after which the target was presputtered in an argon atmosphere for 30 min to eliminate the surface contamination. The temperature did not exceed 50°C during the deposition, thus preventing damage to the polymer. An X-ray diffractometer (Philips X'Pert; Eindhoven, The Netherlands) was used to determine the crystallographic structure using Cu-K α radiation. The composition of the coatings was analyzed by Rutherford backscattering spectroscopy (RBS) using 2 MeV alpha particles and a 15-nA current intensity. The alpha particles were detected with a silicon surface barrier detector at a 165° angle.

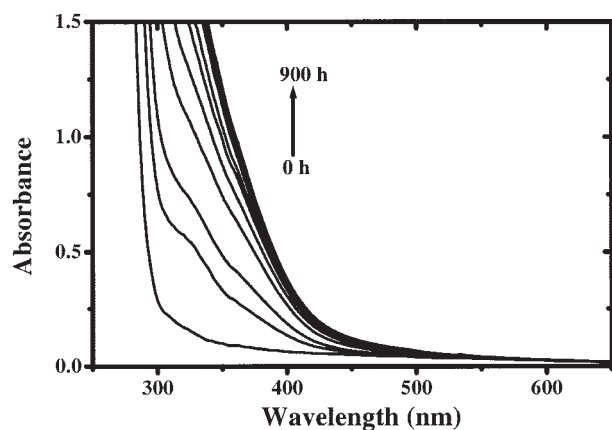


Figure 1 UV-visible spectra of PC irradiated between 0 and 900 h.

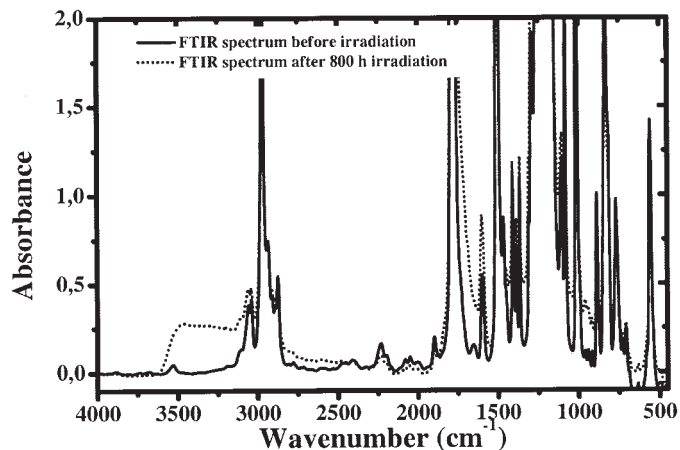


Figure 2 FTIR spectra of PC films.

RESULTS AND DISCUSSION

Chemical changes in the PC exposed to $\lambda > 300$ nm

The rate of phototransformation of the polymer can be characterized by measuring the concentration of the photoproducts that accumulate in the polymer during irradiation.⁸⁻¹¹ As shown in Figures 1 and 2, the photooxidation of PC at $\lambda > 300$ nm leads to noticeable modifications of the UV-visible and IR spectra. Figure 1 shows an increase of absorbance between 300 and 500 nm with a shoulder at 320 nm. This shoulder results from the formation of the primary photo-Fries product, which largely contributes to the yellowing of PC during photoageing.¹² In the IR domain (Fig. 2), two regions are of particular interest in the analysis of the photooxidation of PC. The first is related to the hydroxyl region (3800–3200 cm^{-1}) [Fig. 3(a)] and the second concerns the carbonyl region (1900–1500 cm^{-1}) [Fig. 3(b)]. As photooxidation proceeds, the hydroxyl and carbonyl absorption bands broaden and several bands with definite maxima are observed to develop at 1690, 1713, 1840, and 1860 cm^{-1} . In the hydroxyl region, the formation of a broad absorption band occurs, with maxima around 3470 and 3330 cm^{-1} . These maxima are more easily observed after a subtraction of the initial spectrum to the spectra of the irradiated film. The photoproducts responsible for the observed absorption bands have been identified^{2,3} as the following: aromatic-chain ketones (1690 cm^{-1}), aliphatic-chain acids (1713 cm^{-1}), and cyclic anhydrides (1860–1840 cm^{-1}). The absorptions at 3470 and 3330 cm^{-1} correspond, respectively, to the formation of bonded alcohols and carboxylic acids. A detailed analysis of the formation of the products is described in Rivaton et al.^{2,3}

PC photoprotection by ZnO

To optimize the photoprotection of the polymer by a ceramic deposit, one can act on both the thickness of

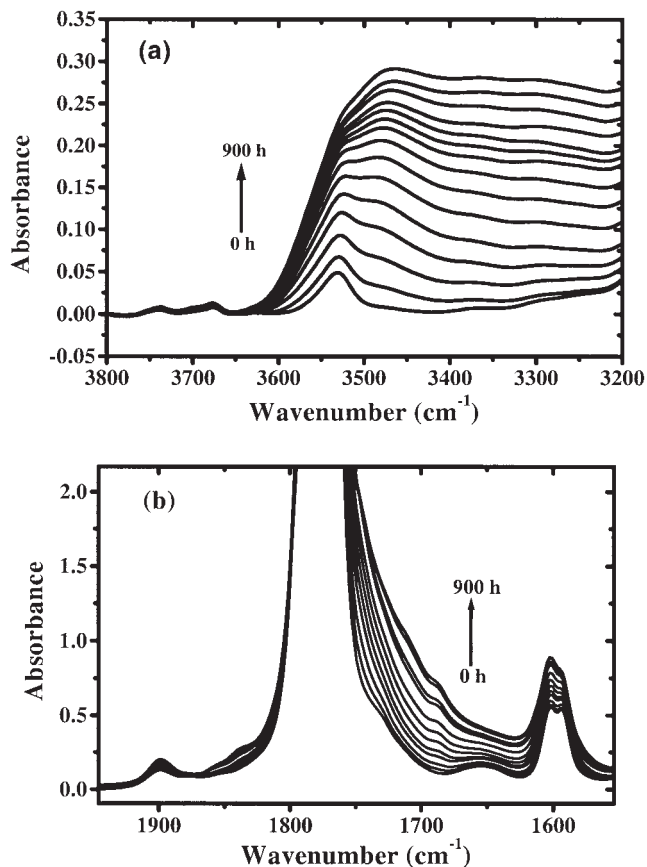


Figure 3 FTIR spectra of PC films obtained at different irradiation times: (a) hydroxyl region; (b) carbonyl region.

the coating and its optical properties. However, other properties have also to be considered, for example, adhesion of the ceramic on the polymer, stresses in the deposit, and barrier effect of the layer to oxygen. The variation of the sputtering parameters modifies all the properties of the coating.^{7,13-15} As a consequence, most of them must be taken into account to obtain a polymer/ceramic assembly of good quality.

We have chosen for this study to operate in conditions that previously gave good results.^{5,8} The sputtering parameters were fixed to 0.89 W/cm² for the power density, 1 Pa for the total pressure, and 5% O₂ in the plasma Ar-O₂. Figure 4 presents the absorbance at 3470 cm⁻¹ versus the irradiation time for PC films covered by ZnO layers of different thicknesses. This absorbance regularly decreases versus the increase of the coating thickness. The same result is obtained concerning the variation of the IR absorbance in the carbonyl region and the variation of the UV-visible absorbance. These results clearly indicate an increase of the photoprotection with the coating thickness. To quantify this effect, the initial slopes of the curves plotted in Figure 4 were calculated, results of which are given in Figure 5. An important photoprotection is obtained when the ZnO thickness is ≥ 200 nm.

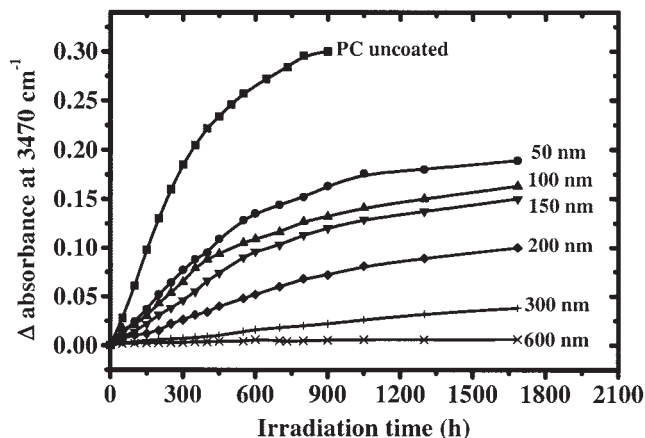


Figure 4 Variation of absorbance at 3470 cm⁻¹ versus irradiation time for PC film coated with ZnO deposits of various thickness [deposition parameters: 0.89 W/cm² power density, 1 Pa total pressure, Ar-O₂ (5%) plasma].

Because light absorption by PC extends up to 330 nm, this polymer absorbs the UV light in terrestrial solar radiation (Fig. 6). This figure also shows the dependency of the absorption of the ZnO deposit with the thickness of the layer. Thus, as previously evidenced, the efficiency of the coating is correlated to its thickness. For example, at 340 nm, if the layer thickness is 200 nm, the percentage of incident light absorbed by the ceramic is about 95%. However, it is also important to take into account the parameters that act on the optical properties of a deposited material, mainly its composition and structure. Figure 7 shows that the O/Zn atomic ratio depends on the thickness of the deposit. The oxygen concentration decreases when the thickness increases. This decrease can be produced by the continuous bombardment of argon atoms backscattered by the target during the film deposition. An increasing in the deposition time can provoke the scission of ZnO bonds, thus lowering the

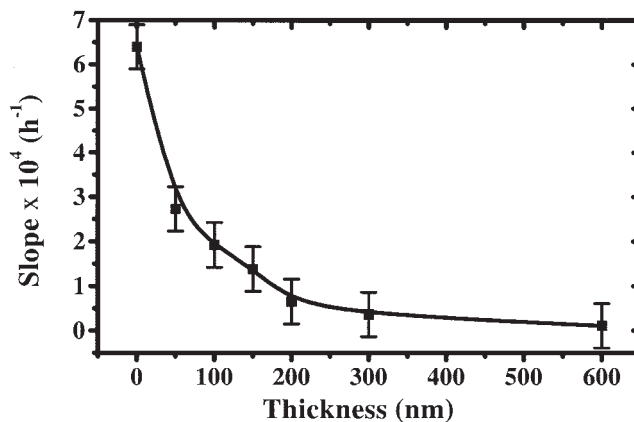


Figure 5 Slope of the curves "Δ absorbance versus irradiation time" at the beginning of the irradiation.

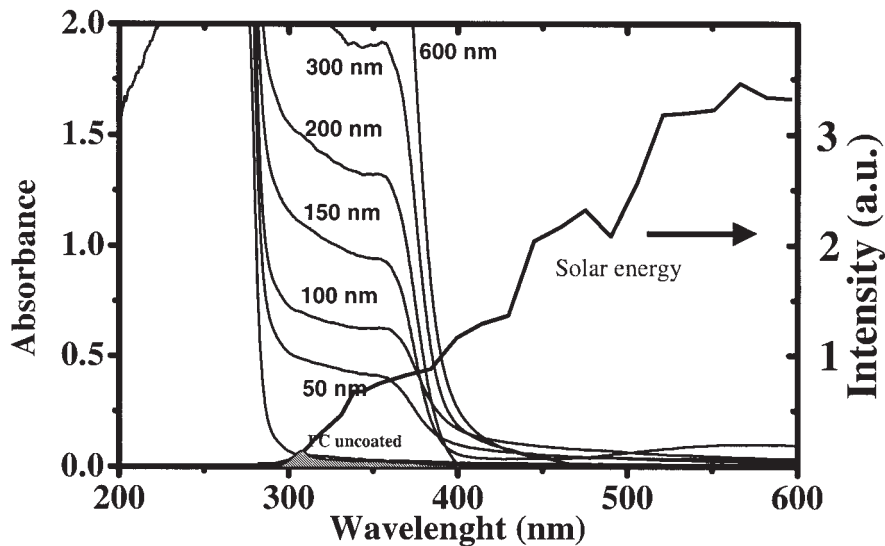


Figure 6 UV-visible spectra of PC samples with ZnO coatings of various thickness. Comparison with the solar spectrum.

oxygen concentration. Previous experiments have shown that a decrease in the O/Zn ratio leads to a decrease of the optical band gap, which is about 3.2 eV.^{7,8} This decrease of the optical band gap enhances the near-UV absorption of the protective coating and therefore improves the photoprotection of the polycarbonate.

ZnO thin films deposited by sputtering are dense but highly textured.⁷ There are partly crystallized with the *c*-axis perpendicular to the substrate surface. The grain size was calculated from the (002) lines of the hexagonal ZnO würtzite phase determined by X-ray diffraction. For each deposit, the density was calculated from the measurement of the thickness and the composition per surface unit obtained from RBS analysis. As can be observed in Figure 8, the grain size and

the density of the ZnO coating increase with its thickness. The deposits of low thickness have more grain boundaries and microvoids, probably as a result of a short deposition time. At the beginning of growth of the layer, the substrate temperature is low and the deposit consists mainly of separated islands. Because of their low mobility, the sputtered particles diffuse too slowly at the surface of the substrate to fill all the voids.¹⁶ Afterward, the coalescence of the crystallites and the growth of grains are favored by a higher mobility of the surface particles. It is very important to note that the greater dense coating gives the best barrier effect to the diffusion of oxygen when the PC film is exposed to the daylight in air.

To optimize the deposition conditions of ZnO coating for the PC photoprotection, we varied the main sputtering parameters. For this purpose, we chose a coating thickness of 200 nm that presents an accurate value of

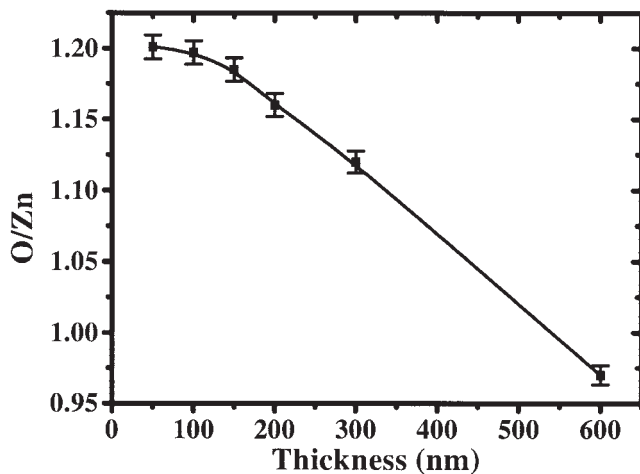


Figure 7 O/Zn atomic ratio versus the thickness of ZnO deposits.

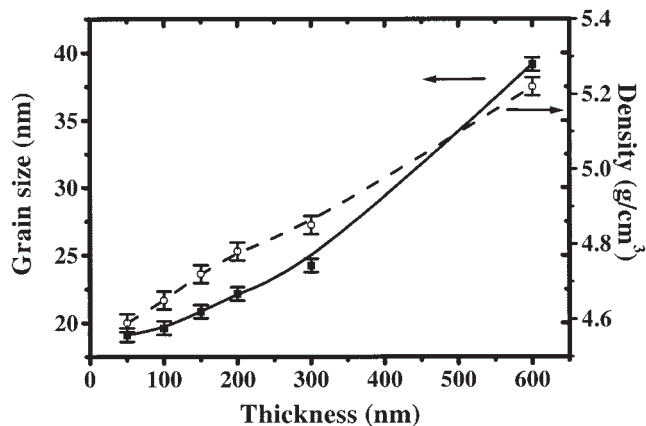


Figure 8 Grain size and density of ZnO coating versus thickness.

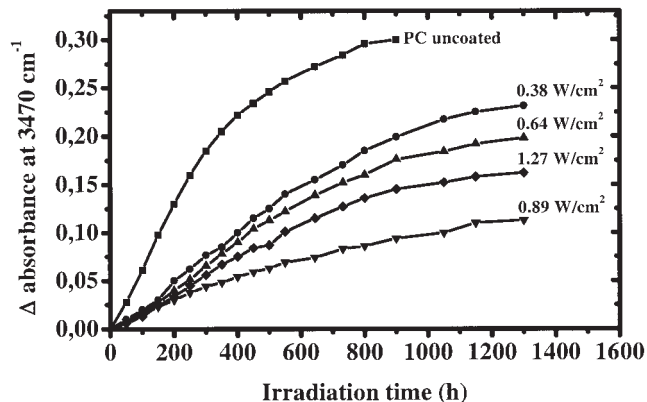


Figure 9 Variation of absorbance at 3470 cm^{-1} versus the irradiation time for PC films coated with ZnO deposits [200 nm thick, 1 Pa total pressure, Ar–O₂ (5%) plasma] obtained at various power densities.

absorbance for the kinetic measurements. The absorbance of the ZnO/PC assemblies was measured at 3470 cm^{-1} versus the irradiation time for about 1300 h.

For the plasma composition previously used (5% O₂ in the Ar–O₂ gas mixture), the effects of the sputtering power and the total pressure can be seen in Figures 9 and 10 respectively. The best photoprotection is obtained if the ZnO coating is deposited with a power density of 0.89 W/cm^2 and under a pressure of 1 Pa (i.e., under the sputtering conditions used for the study versus the thickness). The power and the pressure are related parameters that act on the composition, structure, microstructure, and optical properties of the deposit. In particular, they play a role in the value of the optical band gap, which determines the absorption in the UV domain.⁸ Consequently, the degree of photodegradation of PC is influenced by the deposition conditions of the ZnO protective coating. From a macroscopic perspective, if the power de-

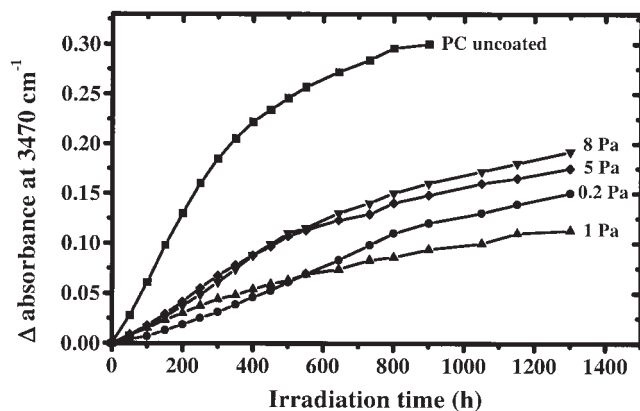


Figure 10 Variation of absorbance at 3470 cm^{-1} versus the irradiation time for PC films coated with ZnO deposits [200 nm thick, 0.89 W/cm^2 power density, Ar–O₂ (5%) plasma] obtained at various total pressures.

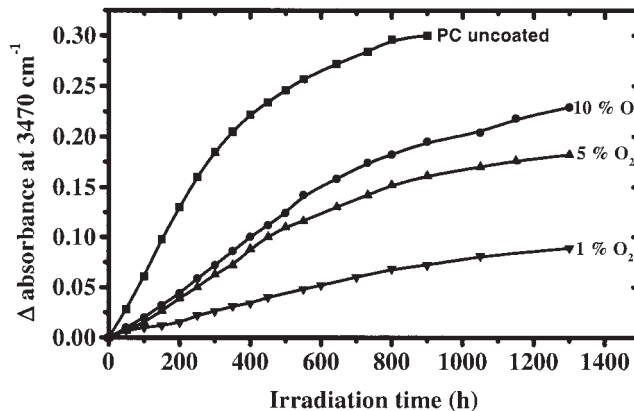


Figure 11 Variation of absorbance at 3470 cm^{-1} versus the irradiation time for PC films coated with ZnO deposits (200 nm thick, 1 Pa total pressure, 0.89 W/cm^2 power density) obtained with Ar–O₂ at various plasma compositions.

creases or the pressure increases, the mobility of the sputtered particles decreases and the deposits are less dense, resulting in a less-efficient filtering effect of the light by the ZnO coating. On the contrary, for higher power and/or lower pressures, the sputtered particles are highly energetic and their continuous bombardment on the growing layer provokes a high level of stresses and generates ZnO coatings of low optical quality.

The study of the plasma composition was carried out with the previously optimized sputtering power and total pressure. Figure 11 shows that the composition with 1% oxygen in the Ar–O₂ plasma gives the best photoprotection to the polycarbonate. This result is interesting for the elaboration of the ZnO coating having the smallest thickness for a given photoprotection. Meanwhile, deposits obtained at low oxygen concentration are less homogeneous and present greater stresses.

The deposition of ZnO coatings can be implemented on large substrates using appropriate sputtering devices. The photoprotective efficiency of thin deposits of about 200 nm can be optimized by additional alumina coatings. A future report will describe the feasibility and the additional properties obtained by multilayer coatings on polycarbonate.

CONCLUSIONS

The infrared and UV–visible analyses are crucial in characterizing the important modifications that occur when polycarbonate is submitted to UV-light irradiation. ZnO coatings, deposited by sputtering on PC films, readily improve the photostability. The efficiency of the coating can be characterized in terms of yellowing and oxidation of the PC substrate. The efficiency increases as evidenced with the thickness of the deposit, which verifies the Beer–Lambert law. The

growth in thickness is closely related to a decrease in the O/Zn atomic ratio and increases in the density and grain size. Moreover, the efficiency depends on the sputtering parameters because these parameters control the permeability of the coating. A good photoprotection of PC is observed for deposits obtained from a sputtering power of 0.89 W/cm^2 and a total pressure of 1 Pa if argon plasma containing 5% oxygen is used. The best photoprotection is obtained with an oxygen concentration of 1%. In conclusion, ZnO coatings of about 200 nm thickness can significantly improve the long-term behavior of PC for outdoor applications.

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