

Improved durability of Bisphenol A polycarbonate by bilayer ceramic nano-coatings alumina-zinc oxide

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Abstract

Polycarbonate exposed to sunlight yellows, degrades and loses its usable properties. In order to increase its lifetime, it can be coated with nano-ceramic thin layers of ZnO and Al₂O₃ deposited by sputtering. The role of the ZnO is to absorb the UV photons that can damageable for the polycarbonate. However, one of the limitations in the use of ZnO is the photocatalytic oxidation that could occur at interface ZnO/PC as a consequence of the photocatalytic activity of this oxide. Insertion of Al₂O₃ between PC and ZnO could be a way to inhibit this interfacial oxidation. The photooxidation of the ceramic/polymer assemblies, in condition of artificial accelerated ageing, was measured by infra-red and UV-vis spectroscopies. The results show that the photocatalytic activity of ZnO occurring in monolayer coated substrates can be significantly reduced by insertion of Al₂O₃ and that, in addition, Al₂O₃ decreases the permeability to oxygen of the coating.

Keywords: photoprotection, photoageing, polycarbonate, thermooxidation, thin films.

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1. Introduction

Bisphenol-A polycarbonate (PC) has an excellent toughness, a high transparency and is lightweight. As a consequence, PC is often used as a lighter and tougher substitute for glass or metals in a wide range of applications, including building and automobiles^[1].

Exposing this polymer to weathering drastically changes their properties. As a consequence of the ability of the polymer to absorb UV radiations of the sunlight, several chemical reactions are induced causing embrittlement and colour changes^[2,3].

The chemical mechanisms which are responsible for the UV light induced degradation of PC^[4,5] are well known. When sunlight falls onto PC, the monomer units absorb energy of short wavelength in the near-UV range: this is particularly so for the ester and the carbonate groups in α position to the aromatic rings. The absorbed energy provokes the rupture of covalent bond triggering photolytic reaction (without oxygen intervention) and photooxydative reaction (with oxygen fixation) reactions. Both mechanisms can take place in the environment and are closely intertwined^[6,7] (Figure 1).

In order to suppress these damages, several methods can be used:

- An effective way of protecting polymers from the effects of photodegradation is to add to the polymers UV-absorbing additives. These non-coloured UV-filters absorb the incident UV light that is damageable for the

polymer and are transparent in the visible domain^[8]. The UV energy absorbed by the stabiliser must be dissipated without producing reactive species. However, the inhibition of the ageing by UV-absorbers is not fully efficient when photodegradation results from direct absorption of sunlight radiations by the intrinsic chromophoric groups of polymer^[9]. This is the case for aromatic polymers. This effect is a direct result of the Beer-Lambert law, and a simple calculation shows that, in the first layers, the competition of absorption between the polymer and the additive is in favour of the polyme^[10]. Consequently, an efficient photoprotection of the sample surface (below 100 μ m) cannot be achieved. Another drawback of the use of UV-absorbers is their fatigue as these compounds are known to also act as anti-oxidant^[11]: their degradation gives rise to the formation of coloured by-products;

- Protecting the surface by coating the substrate with a thick varnish containing UV-absorbers is another solution to achieve photoprotection. This permits solving the problem of the competition of absorption between the polymer and the UV-absorber. However, the photooxidation of the varnish may occur inducing the fatigue of the UV-absorbers^[12,13]. Consequently, the ability of the surface layer to totally absorb the incident near-UV light is reduced and a loss of adhesion of the coating occurs; a significant decrease of the durability of the substrate is then observed^[14];

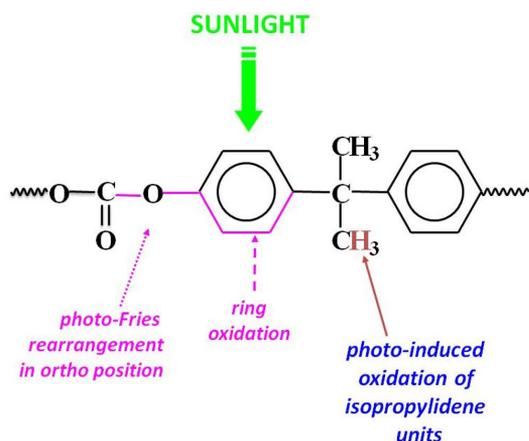


Figure 1. Brief illustration of PC photodegradation mechanism.

- We have developed another method to stabilize polymer materials which consists in depositing onto the surface of the polymer a thin ceramic layer transparent in the visible range. The stabilizing action of the ceramic layer is associated with its ability to physically screen out the incident radiation, reducing therefore the rate of the photochemical processes. In addition, the coating acts as a barrier to oxygen and consequently the rate of photooxidation is decreased. This technique has been successfully employed for PET^[15], PEEK^[16], PEN^[17] and PMMA^[18]. The ceramic used was zinc oxide (ZnO) for good chemical stability and interesting optical properties because it's transparent in the visible range and absorb UV radiation below 380 nm^[19,20]. Coatings were elaborated by Radiofrequency Magnetron Sputtering, which permits working at low temperature (generally lower than 60 °C). Moreover, the deposits obtained with this technique have a higher density and a better adhesion to the substrate than those elaborated by other methods such as vacuum evaporation^[21-23].

This method based on an inert outer filter constitutes an interesting alternative to the more classical methods. However, it is known that ZnO manifest a photocatalytic activity^[24]. The Photoactivity due from the development of active species that can cause photooxidative degradation of the polymer films through reaction with oxygen and/ or water^[25].

Most authors have proposed the HOO• and HO• radicals as the predominant reactive species^[26,27]. The photoactivity of these pigments could then constitute a limitation to their use as coatings on polymeric substrates because they could induce a photocatalytic oxidation of the polymer at the interface.

In this paper, we report the results of a preliminary investigation of the possibility of reducing the photocatalysed oxidation by insertion of an inactive Al₂O₃ layer (no photocatalytic activity at the opposite of ZnO) between the polymer and the upper ceramic coating. The feasibility of achieving bilayer ceramic coatings on the polymeric substrate was carried out on the polymer film of Bisphenol-A polycarbonate PC. PC/Al₂O₃/ZnO and PC/ZnO/Al₂O₃ assemblies were successfully obtained.

The photochemical behaviour of the polymer and ceramic/polymer assemblies was tested by exposing the samples in an artificial accelerated photo-ageing device. The chemical evolution of the polymer was assessed by infra-red and UV-vis analysis.

2. Materials and Methods

PC film (50 μm thick) was supplied by Technifilm (ref. Makrofol D.E. 6-2). This polymer does not contain anti-oxidant. It was ultrasonically cleaned in ethanol before coating.

The ceramic coatings of Al₂O₃ and ZnO were carried out in a sputtering unit (Alcatel SCM 450) equipped with a radiofrequency generator operating at 13.56 MHz. Bulk ZnO and Al₂O₃ targets (purity 99.9%; diameter 100 mm) fixed on cooled magnetron effect cathodes were used as starting materials. The substrates were situated at a distance of 90 mm from the targets. The sputtering chamber was evacuated below a pressure of 10⁻⁴ Pa before admitting the sputtering gas which was either pure argon or argon-oxygen mixtures. The plasma composition was controlled by a mass flow meter. The thickness of the deposits was determined by mean of a Jobin-Yvon ELLISEL single wavelength ellipsometre, using the 632.8 nm wavelength.

PC films irradiations were carried out in SEPAP 12.24 units -Atlas- at a temperature of 60 °C with medium-pressure mercury lamps. This medium-acceleration photoaging device has been described previously^[4]. It allows irradiation at wavelengths above 300 nm so that the ageing is representative of the behaviour under natural exposure. The ceramic coating was deposited on both sides of the films.

Thermooxidation experiments were carried out in a ventilated oven at temperatures of 170 °C.

The evolutions of UV-vis and infrared spectra were recorded respectively on a Shimadzu UV-2101 PC equipped with an integrating sphere and on a Nicolet Magna-IR 760 FTIR spectrophotometer.

3. Results and Discussions

3.1 Photooxidation of PC

Since polycarbonate light absorption is up to 330 nm, this polymer is directly reachable to UV light that is present in terrestrial solar radiation.

The resulting photodegradation of PC at λ > 300 nm leads to noticeable modifications of the UV-vis and infrared spectra of irradiated films that are worthy to be recalled.

Figure 2 shows the effect of irradiation on the UV-vis absorption spectrum of PC. For short exposure time, the maxima observed to develop around 320 and 355 nm are related to photo-Fries rearrangement of the carbonate units^[4]. As irradiation proceeds, these bands are rapidly overlapped by an unstructured absorption at wavelengths below 500 nm. This absorption, attributed to a mixture of colored species formed in ring oxidation^[4-6], produces the yellowing of the irradiated film.

Photooxidation of PC leads in parallel to notable modifications of the IR spectra of the samples. In the hydroxyl absorption region (3800-3000 cm⁻¹), a broad

increase of absorbance centred around 3400 cm^{-1} is observed (Figure 3) and attributed to the formation of alcohols, acids and hydroperoxides^[4-6].

The rates of photooxidation and photolysis can be characterised by determining the concentration of the stable

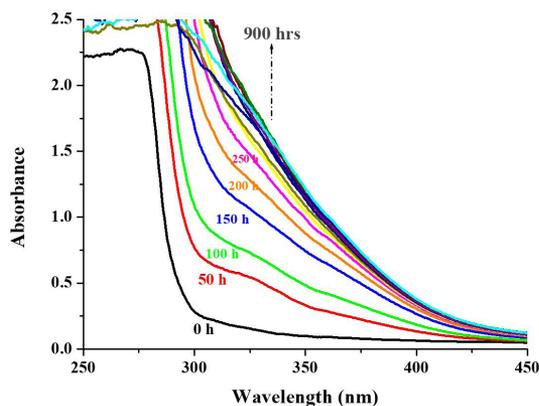


Figure 2. Evolution of the UV-visible spectrum of PC films subjected to irradiation.

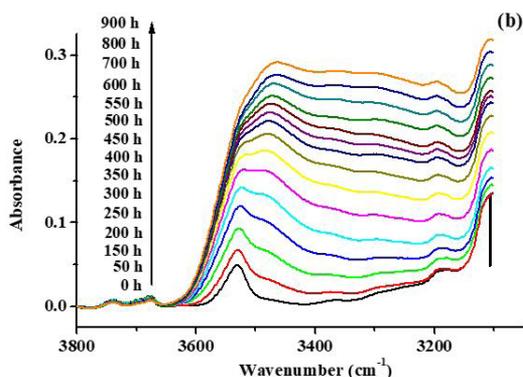
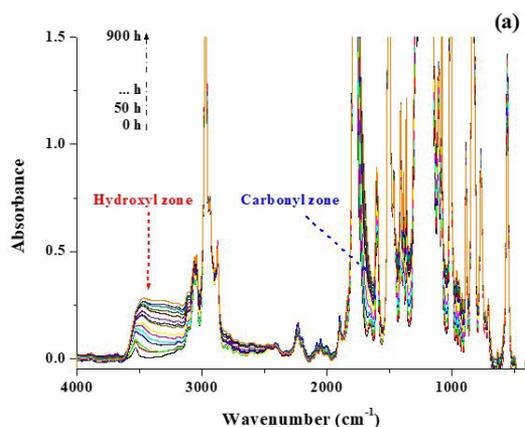


Figure 3. Evolution of the IR spectrum of PC (a) in the $4000\text{--}400\text{ cm}^{-1}$ and (b) in the $3800\text{--}3000\text{ cm}^{-1}$ –hydroxyl region–, during irradiation.

photoproducts detected by UV-vis and infrared analysis, and that accumulates during irradiation:

- The photo-yellowing of polycarbonate can be assessed by measuring the absorption increase at a wavelength of 400 nm ;
- Measuring the increase of absorbance in the hydroxyl region can be used to characterise accurately the progress of the photodegradation reactions in PC.

3.2 Nano-ceramic coating on PC

Spectra reported on Figure 4 show the absorption properties of ZnO and Al_2O_3 mono or bilayer coatings in the UV-vis region. ZnO presents a high absorption in the area from $300\text{ to }400\text{ nm}$. This absorption clearly depends on the thickness of the coated layer. On the opposite, Al_2O_3 is totally transparent in this region. The bilayer $\text{Al}_2\text{O}_3/\text{ZnO}$ coating absorbs more than $\text{ZnO}/\text{Al}_2\text{O}_3$ in this region.

In a former paper^[19], we have shown that ZnO coating is efficient in protecting PC against photodegradation. The photostability of coated PC increases with the thickness of the layer. As an example, Figure 5 shows the increase of absorbance at 400 nm and in the hydroxyl domain versus the irradiation time of unprotected PC and of three different polymer/ceramic assemblies: 50 nm ZnO , 100 nm ZnO and 600 nm ZnO . One can note that the rate of photooxidation decreases when the thickness of the coating increases and that the photoprotective effect is fully efficient when the thickness is 600 nm .

This photostabilising effect can be easily explained. An increase of the thickness of ZnO coating not only increases the screening effect of the ceramic for the photons damageable for the polymer, but also gives ZnO grain with higher size and density^[19]. Therefore, the permeability to oxygen of the ceramic coating is decreased and consequently the rate of oxidation of the polymer is also reduced.

Then the feasibility of Al_2O_3 deposit on PC was experimented. In a first time, Al_2O_3 coatings of 100 nm and 600 nm have been deposited on PC. The rate of yellowing and the rate of formation of hydroxyl products are shown in Figure 5. Analysis of the curves given in this figure provides the following comment: at low conversion degree (below 100 h), the photodegradation of PC is not inhibited by Al_2O_3 whatever

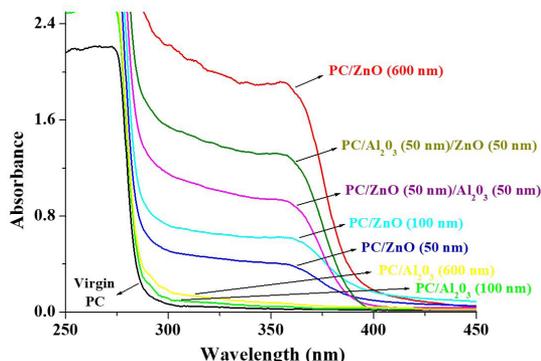


Figure 4. UV-visible spectra of reference and ceramic(s) coated PC films before irradiation versus different thicknesses.

its thickness; but for longer exposure duration, Al₂O₃ causes a decrease in the rate of oxidation of PC.

These results can be interpreted through simultaneous intervention of photooxidative and photolytic reactions^[28]. The UV-visible spectrum in Figure 4 obviously indicates that the polycarbonate cannot be protected against solar radiation by alumina coatings. As a consequence, photo-Fries rearrangement of PC, which does not implicate oxygen, is not inhibited by the presence of the alumina thin film. However, the ulterior oxidative reactions induced by the photo-Fries products, are prevented because Al₂O₃ behaves and acts as an oxygen inhibitor. To put it differently, alumina does not inhibit photolytic processes (without oxygen intervention) but decreases the degree of oxidative reactions as this covering is impermeable to oxygen.

In a second time, polycarbonate coated with bilayers ZnO and Al₂O₃ samples were experienced. To find out some degradation and yellowing after an adapted exposure time, we reduced the thickness of ZnO and Al₂O₃ coatings to 50 nm. To obtain a precise proof of ZnO photocatalytic activity action at the polycarbonate interface, another test was

carried out in which Al₂O₃ was deposited above ZnO. The rate of photo-yellowing and the rate of formation of hydroxyl products are shown in Figure 5. Analysis of the curves presented in this figure indicates that Al₂O₃/ZnO coatings have a greater photostabilisation efficacy than ZnO alone.

This effect can be explained by the Al₂O₃ coating which eliminates the photocatalytic activity of ZnO, which in turn promotes PC degradation at the interface between PC and ZnO. Whereas the photooxidation and photo-yellowing of bilayer PC/ZnO/Al₂O₃ coating is well noted and thus less photostabilizing and so less photoprotective than PC/Al₂O₃/ZnO coatings.

The scanning electron microscopy was used to evaluate the superficial changes of PC coated with ZnO (50 nm and 600 nm) and those coated with bilayer ZnO (50 nm) and Al₂O₃ (50 nm). Figure 6 shows the micrographs of the layer surface obtained. The sputtered thin films have a granular microstructure. The grain size is about 40 to 130 nm diameter. The growth of the deposit is columnar type. The size of the columns, whose ends appear at the surface of the deposit, increases with the thickness. The ceramic coating PC/Al₂O₃-ZnO exhibits an increase in the size of columns which corresponds to a coalescence of grains forming a homogeneous surface. Therefore, PC / Al₂O₃-ZnO nano-coatings are dense and exhibit the best barrier properties against the diffusion of gases, especially oxygen.

In conclusion, PC/Al₂O₃/ZnO coatings exhibit the best photoprotective efficiency as this assemblage integrates ZnO capacity to absorb in the UV-vis band with Al₂O₃ oxygen barrier property without the photocatalytic effect. Table 1 summarizes the photoprotection of polycarbonate by zinc oxide and/or alumina ceramic nano-coatings.

3.3 Thermooxidative ageing

In order to determine whether ceramic deposits could inhibit PC thermooxidation because of their barrier effect to oxygen diffusion. PC uncoated and PC covered with ceramic coatings were placed at a temperature of 170 °C in a ventilated oven for a period of approximately 400 days. Thermooxidation kinetics of the samples was followed to observe the appearance and development of thermooxidized photoproducts.

Figure 7 shows the evolution of the UV-visible absorption spectra of virgin PC and PC coated with bilayer ceramic Al₂O₃/ZnO during the thermooxidation. The absorbance increases without a specific maximum, in contrast to photooxidation where the formation of photo-Fries products resulted in the appearance of an absorption band at 320 nm. The yellowing that develops in thermooxidation is approximately equivalent for coated PC films as for virgin PC.

Figures 8 and 9 represent the IR spectra of these thermooxidized samples in the domain of carbonylated and hydroxylated products. The bands at 1724 and 1690 cm⁻¹ are

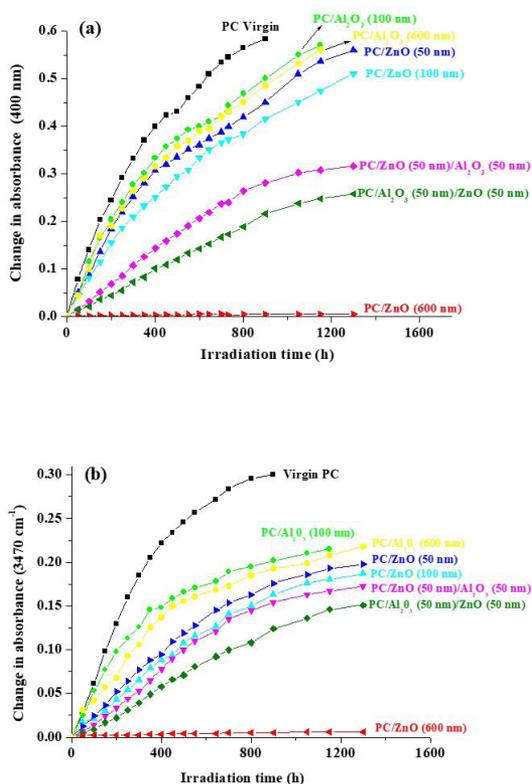


Figure 5. Increase of the absorbance at (a) 400 nm and (b) 3470 cm⁻¹ versus irradiation time.

Table 1. Photoprotective ceramic coatings on PC.

Sample	Protection against:		Interfacial photocatalytic activity
	Photon	Oxygen	
PC/ZnO	yes	yes	yes
PC/Al ₂ O ₃	no	yes	no
PC/Al ₂ O ₃ -ZnO	yes	yes	no

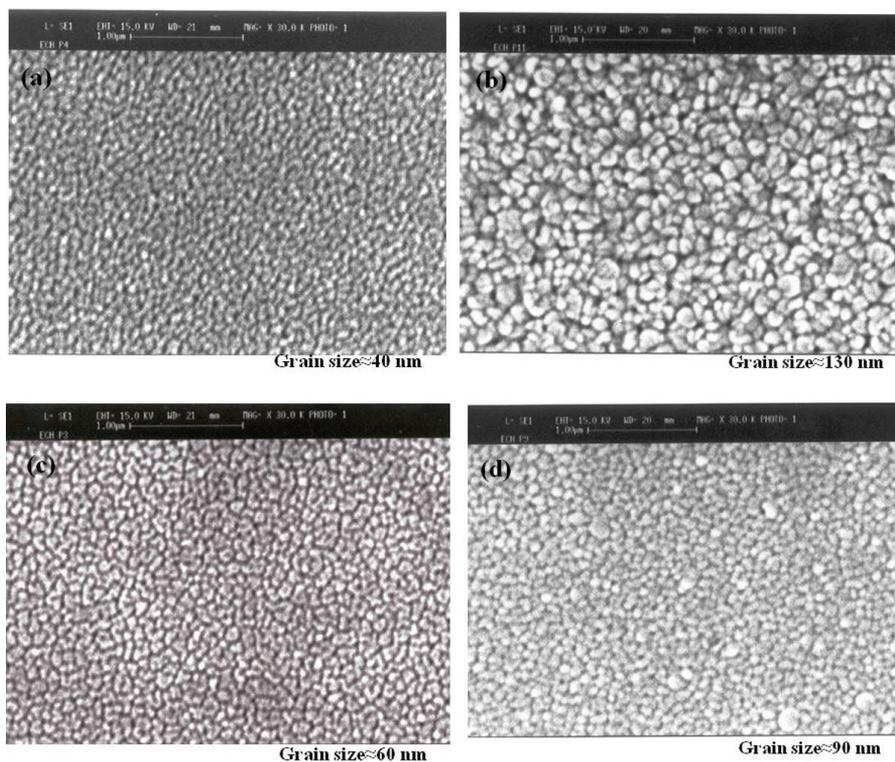


Figure 6. Scanning Electron Micrographs of polycarbonate film surfaces coated by (a) ZnO-50 nm, (b) ZnO-600 nm (c) ZnO-50 nm/ Al_2O_3 -50 nm and (d) Al_2O_3 -50 nm/ZnO-50 nm.

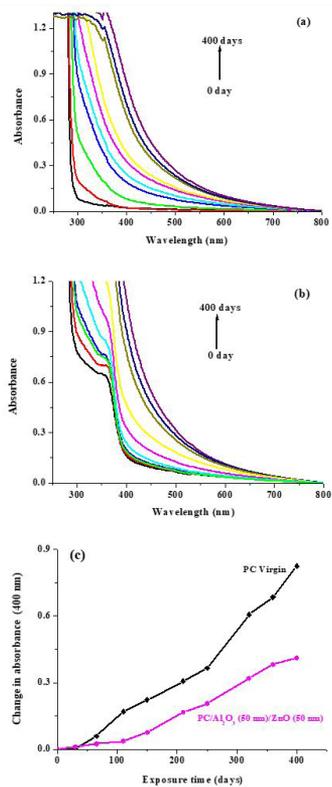


Figure 7. Evolution of the UV-visible spectra of (a) virgin PC and (b) PC coated with $\text{Al}_2\text{O}_3/\text{ZnO}$ bilayer during thermooxidation at 170 °C; (c) Change in absorbance determined from UV-vis (400 nm) spectra vs exposure time.

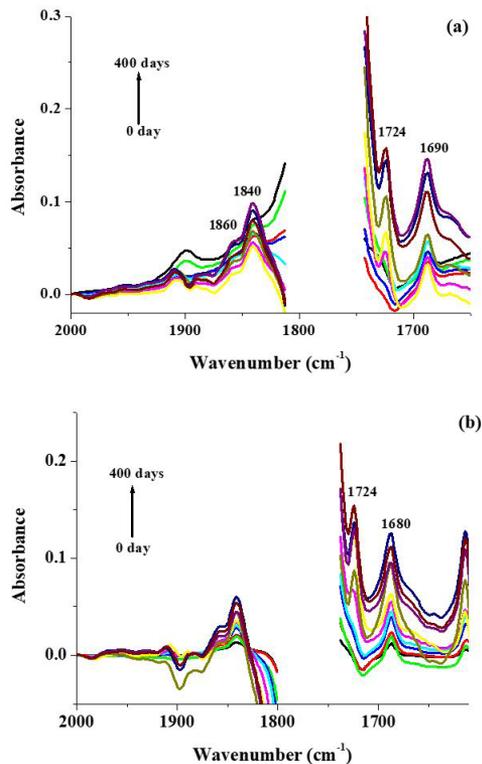


Figure 8. Evolution of the spectra in the region of carbonylated product of (a) virgin PC and (b) PC coated with $\text{Al}_2\text{O}_3/\text{ZnO}$ bilayer during thermooxidation at 170 °C.

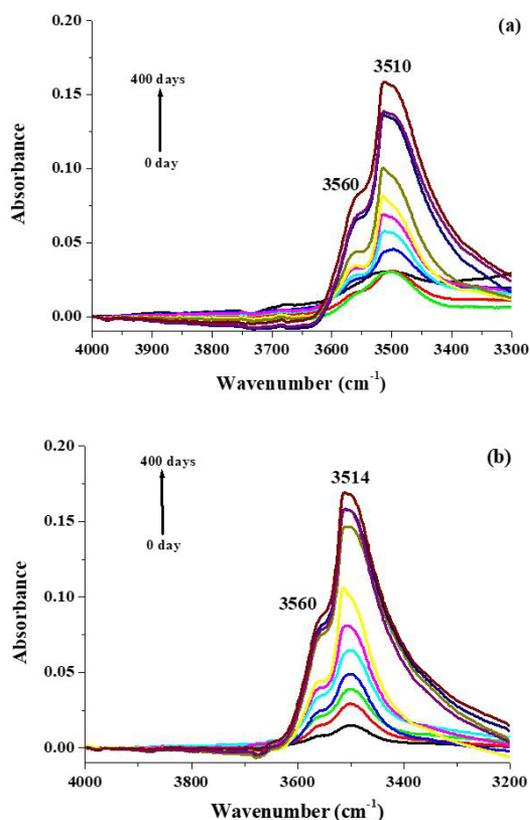


Figure 9. Evolution of the spectra in the region of hydroxylated products of (a) virgin PC and (b) PC coated with $\text{Al}_2\text{O}_3/\text{ZnO}$ bilayer during thermooxidation at 170°C .

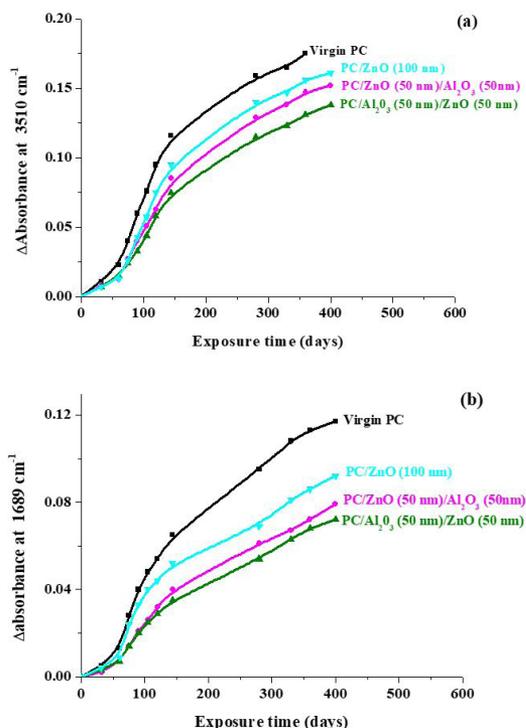


Figure 10. Kinetics of appearance of thermooxidation products in (a) hydroxyl region (b) carbonyl region.

attributed respectively to aliphatic and aromatic ketones^[2]; as for the doublet at $1840/1860\text{ cm}^{-1}$, also observed in photooxidation (Figure 3a), indicates the oxidation of the aromatic ring^[2]. One of the differences between thermo- and photo-oxidation is the non-accumulation in thermooxidized films of saturated aliphatic acids detected at 1713 cm^{-1} in photooxidation.

In the hydroxyl domain, the formation of hydroxylated products (alcohols and phenols) characterized by absorption bands at 3560 and 3514 cm^{-1} is observed. On the other hand, there is no appearance of a wide absorption band between $3200\text{--}3300\text{ cm}^{-1}$ corresponding to carboxylic acids. This observation is in good agreement with the analysis of the carbonyl domain.

The advancement state of polycarbonate thermooxidation included in the different systems can be characterized by the formation of the hydroxylated and carbonyl products. Figure 10 shows that the rate of thermooxidation is slowed down by the presence of a ceramic coating. The most effective coating is the one with bilayer $\text{Al}_2\text{O}_3/\text{ZnO}$: the role of the ceramic is to limit the diffusion of oxygen responsible for the thermal ageing of the PC, and the barrier effect increases with the thickness of the surface deposit.

4. Conclusions

Coating polycarbonate with ZnO thin layers reduces the rate of photodegradation of the polymer as a result of the screen effect role of the ceramic. Meanwhile, our results show that these coatings have some photocatalytic activity. The light excitation of the thin ZnO layers generates the formation of activated species (mainly $\text{OH}\cdot$, $\text{HO}_2\cdot$ radicals) which are susceptible to initiate photooxidative reactions at the surface of the coated polymer. The insertion of an Al_2O_3 thin layer between the ceramic and the polymer provides a higher photoprotective efficiency which can be attributed to the suppression of the photocatalysed degradation of the polymer at the interface PC/ZnO. In addition, the Al_2O_3 deposit acts as a barrier to oxygen limiting therefore oxidative degradation involved in the mechanism of photodegradation of the coated polymer. The results show that it is also possible to deposit Al_2O_3 above ZnO obtaining therefore a hard upper layer. In term of photostabilisation, this bilayer is also more efficient than ZnO alone as both the screening effect of ZnO and the impermeability of Al_2O_3 are involved.

As a conclusion, the durability of PC can be drastically improved by a bilayer $\text{Al}_2\text{O}_3\text{-ZnO}$ ceramic nano-coatings which ensures a good photoprotection and significant thermooxidative inhibition.

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