Improvement of the Surface Properties of Polycarbonate by Organic–Inorganic Hybrid Coatings

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ABSTRACT: Organic–inorganic hybrids (ceramers) were prepared through the sol–gel process with opportune alkoxysilane-terminated polymer chains as the organic phase and tetraethoxysilane as the inorganic network precursor. The consolidation process, used to reach a high degree of crosslinking between the two phases, was carried out with either conventional oven heating or microwave irradiation. High conversion degrees were obtained with both treatments even when microwave postcuring turned out to be much faster than conventional heating (5–10 s vs 40 min). Scratch-test and photooxidation investigations showed a significant improvement in scratch, yellowing, and photodegradation resistance for coated polycarbonate. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 1426–1436, 2008

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INTRODUCTION

Polycarbonates (PCs) represent an extremely useful class of engineering thermoplastics known for their toughness and optical properties. The vast majority of PCs are based on bisphenol A and have glass-transition temperatures in the range of 140–155°C; they are widely regarded for their optical clarity and exceptional impact resistance and ductility at or below room temperature. Other properties, such as the modulus, dielectric strength, and tensile strength, are comparable to those of other amorphous thermoplastics at similar temperatures below their respective glass-transition temperatures. However, although most amorphous polymers are stiff and brittle below their glass-transition temperatures, PCs retain their ductility.[1]

The main limitations are due to their poor scratch, ultraviolet (UV), and solvent resistance. Any improvement of such properties would represent a very important goal from an industrial point of view and a main scientific challenge. These enhancements can be pursued by the physical incorporation of suitable additives even if this approach presents several disadvantages: the specific additive is often required in high loadings to be effective, and this may result in adverse changes in the physical and mechanical properties of the polymer. Additives can also be leached from the polymer through normal service and aging, and this poses an environmental threat in addition to the primary result of the reduction in its effect.

An alternative approach is represented by the application of functional protective coatings directly to the manufactured items. Inorganic protective coatings produced by plasma techniques (chemical vapor deposition (CVD) and plasma enhanced chemical vapor deposition (PE-CVD)) are known to show good abrasion resistance in general,[2] and completely inorganic zinc oxide (ZnO) layers deposited onto PC by sputtering have been recently demonstrated to be effective toward its photodegradation due to solar UV radiation.[3]

However, fully inorganic protective coatings have some problems of poor adhesion due to the difference in the thermal expansion coefficients between the substrate and coating. The use of the aforementioned techniques is also limited by high costs, small item dimensions, and simple geometric form requirements.

The coating of PC surfaces by organic–inorganic hybrids prepared by the sol–gel process could be in most cases an interesting alternative to gas-phase or vacuum-deposition techniques because of the high versatility associated with the application mild conditions.

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The classical sol–gel process[4] consists of a two-step acid- or base-catalyzed reaction of metal alkoxides [$M(OR)_x$] with their partial and/or complete hydrolysis followed by condensation, which leads to the buildup of a three-dimensional inorganic network through the formation of M—O—M linkages. An efficient incorporation of organic chains into this network is also possible, particularly when the organic molecules are characterized by the presence of functional groups reactive in the aforementioned reactions. This approach leads to organic–inorganic hybrid materials,[5] also known as ceramers, in which the intimate mixing favored by the covalent bonding between organic and inorganic moieties can lead to the formation of crosslinked structures composed of nanosized organic and inorganic domains. The resulting material is transparent and macroscopically uniform even if phase-separated.

These materials have already gained much interest because of the remarkable improvement in properties such as the optical, mechanical, thermal, electrical, and magnetic properties in comparison with those of pure organic polymers. Several applications have been developed for this kind of hybrid material,[6–8] particularly in the field of protective coatings of both organic and inorganic substrates.

In this study, organic–inorganic hybrid materials were prepared from triethoxysilane-terminated polymer chains [i.e., poly(ethylene oxide) (PEO) or polycaprolactone (PCL)] as the organic component because of their good thermodynamic miscibility with PC[9–12] and from tetraethoxysilane (TEOS) as the inorganic network precursor; the hybrids were subsequently obtained as self-consistent materials or coated onto PC substrates.

Because one of the major points regarding the application of PC is related to its high sensitivity toward abrasion and an enhancement in this property should be an important goal, the scratch resistance of our coated samples was evaluated with respect to the coating composition (in terms of the organic/inorganic ratio) and the type of postcuring treatment applied, namely, conventional oven heating or microwave irradiation. In fact, coupled to the simplicity of the coating system preparation and application, a fast curing step should also represent an important factor for future industrial applications, and in this view, microwave-assisted curing is particularly interesting and innovative.

In addition to the poor scratch resistance, further limiting aspects for PC applications are related to yellowing and degradation due to the impact of solar light on the material. One can simply consider all the problems related to the outdoor applications of PC or to its use in the automotive industry because of the loss of transparency and brilliance due to the material's photooxidation. The possibility of protecting PC surfaces against photodegradation with an opportune transparent coating should then always attract greater attention. For the aforementioned significant advantages presented by the sol–gel approach, this method should be strongly suggested for the preparation of tailored hybrid coatings ensuring a barrier effect toward UV radiation.

We report the results of photooxidation studies performed on PC coated with hybrids based on the PCL organic phase. PCL was chosen for this part of the study rather than PEO because PEO is known to be very sensitive to UV-light-induced oxidation.[13] In this first investigation on the protective effect of ceramers, the attention has been mainly focused on the barrier effect of the coatings. The oxidative degradation induced by exposure to UV light of PC substrates coated with PCL ceramers was followed by infrared (IR) and ultraviolet–visible (UV–vis) spectroscopy. The effects of the composition and thickness of the coatings are discussed. The screen effect that these coatings can have when formulated with organic or mineral UV absorbers will be reported in a forthcoming article.

EXPERIMENTAL

Materials

α,ω-Hydroxy-terminated PEO (purchased from Fluka (Milan, Italy) and having a number-average molecular weight of 600 g/mol), 3-isocyanatopropyltriethoxysilane (ICPTES; Fluka), TEOS (Aldrich, Milan, Italy), hydrochloric acid at a 37% concentration (Carlo Erba, Milan, Italy), and ethanol (EtOH; Carlo Erba, Milan, Italy) were high-purity reagents and were used without further purification.

α,ω-Hydroxy-terminated PCL was prepared in bulk by the ring-opening polymerization of caprolactone (CL) monomer (purchased from Aldrich and used after distillation over calcium hydride) in the presence of tin(II) 2-ethylhexanoate ($SnOct_2$) as the initiator and with ethylene glycol (EG; obtained from Aldrich and used as received) as the transfer agent. The reaction was typically carried out in a glass flask under magnetic stirring at 120°C for 24 h. The molar ratio used, 20/1/0.02 CL/EG/$SnOct_2$, led to a nominal degree of polymerization of 20, which corresponded to a molecular weight of about 2300 g/mol.

The PC substrates used for photooxidation studies were commercial, untreated, transparent films (Makrofol DE 6-2), 125 μm thick, from Bayer (Milan, Italy). For the scratch test, PC substrates were commercial, untreated, transparent slabs 3.0 mm thick.

Preparation of α,ω-triethoxysilane-terminated PEO and PCL

α,ω-Triethoxysilane-terminated polymer chains (called PEOSi and PCLSi in the following) were prepared by the bulk reaction of the corresponding α,ω-hydroxy-terminated polymers with ICPTES (molar ratio of 1/2). The reaction was usually carried out in a 50-mL glass flask equipped with a calcium chloride trap and under magnetic stirring at 120°C for 3 h, as already reported in a previous article.[14]

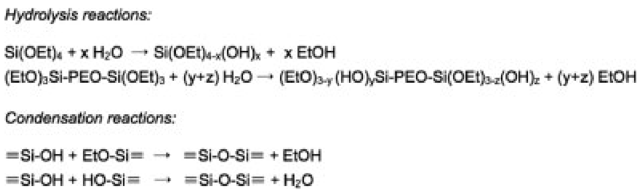
Preparation of the organic–inorganic hybrids

The same procedure was followed for the preparation of PEO- and PCL-based hybrids.

Mixtures of TEOS and the α,ω-triethoxysilane-terminated polymer (PEOSi or PCLSi) were dissolved in EtOH at a concentration of about 10% (w/v), and then water (for the hydrolysis reaction) and hydrochloric acid (as the catalyst) were added in the following molar ratios with respect to the ethoxide groups of both the functionalized polymer and TEOS: EtO—/H_2O/HCl = 1/1/0.05.

A typical preparation for PEOSi/TEOS hybrids was as follows: PEOSi (1.20 g) and TEOS (0.80 g) were added to 20 mL of EtOH in a screw-thread glass vial and mixed until a homogeneous solution was obtained. Then, water and HCl were added under vigorous stirring at room temperature for about 10 min. The closed vial was placed in an air-circulating oven at 70°C for 30 min to allow partial progression of the sol–gel reaction. The clear solution was then cast into a closed polytetrafluoroethylene dish, and the solvent was slowly evaporated at room temperature for about 1 week to get self-consistent samples for further analysis. As an alternative, the solution was deposited onto clean PC films by spin coating with a Laurell WS-400B-NPP-Lite instrument (North Wales, PA) operating at a spin rate of 2000 rpm over 30 s (ACL 15) to obtain a deposited hybrid film having a typical thickness of about 0.3–0.4 μm.

Hybrid materials based on PEO were characterized by final organic/inorganic weight ratios of 7/3 and 3/7, assuming the completion of the sol–gel reactions reported in Scheme 1. PEO-based samples were coded as follows: PEOSi/SiO_2 7/3 indicates a coating with an organic/inorganic ratio of 7/3 (w/w) and a coating thickness of 0.3–0.4 μm, and PEOSi/SiO_2 3/7 indicates a coating with an organic/inorganic ratio of 3/7 (w/w) and a coating thickness of 0.3–0.4 μm.



Scheme 1 Hydrolysis and condensation steps in the sol–gel process.

Hybrid materials based on PCL were characterized by final organic/inorganic weight ratios of 4/6 and 8/2, assuming the completion of the aforementioned sol–gel reactions. The EtOH solutions were roll-coated onto clean PC films, and different coatings thicknesses (0.6–0.75 and 1.3–1.5 μm) were obtained, depending on the solution concentration. Thicker coatings were obtained with more concentrated solutions (ca. 20% w/v). PCL-based samples were coded as follows: PCLSi/SiO_2 4/6 L indicates a coating with an organic/inorganic ratio of 4/6 (w/w) and a coating thickness of 0.6–0.75 μm, PCLSi/SiO_2 4/6 H indicates a coating with an organic/inorganic ratio of 4/6 (w/w) and a coating thickness of 1.3–1.5 μm, PCLSi/SiO_2 8/2 L indicates a coating with an organic/inorganic ratio of 8/2 (w/w) and a coating thickness of 0.6–0.75 μm, and PCLSi/SiO_2 8/2 H indicates a coating with an organic/inorganic ratio of 8/2 (w/w) and a coating thickness of 1.3–1.5 μm.

Curing treatments

PEO-based hybrids were subjected to two different postcuring treatments to allow the completion of the polycondensation reaction, namely, conventional heating in an air-circulating oven (WTB Binder, Tuttlingen, Germany) at 80°C for times ranging from 20 to 60 min or microwave irradiation with an Alter TE10n single-mode applicator (Reggio Emilia, Italy) at 2.45 GHz and 350 W with irradiation times ranging from 3 to 15 s.

PCL based hybrids were postcured by conventional heating in an air-circulating oven at 120°C for 24 h.

Characterization

Differential scanning calorimetry (DSC) was performed with a TA DSC2010 instrument (Vimodrone, Italy) to determine the degree of curing that was reached through the curing treatments. Thermal scans were performed in the temperature range of 0–200°C with a heating rate of 10°C/min. The extent of the residual curing reaction was calculated during the first heating scan by the enthalpy value of the endothermic peak corresponding to the volatilization of EtOH and water that formed during the progression of the sol–gel reaction. At least three independent DSC runs were carried out for each sample (type of hybrid and type and time of postcuring treatment), and an average value was derived from each series of tests. A second heating scan was also performed to evaluate the presence of a residual sol–gel reaction or any other thermal transitions. Just before the measurements, all samples were accurately dried under a dynamic vacuum at 40°C for 1 h to eliminate any possible volatile product.

Scratch tests were carried out on a CSM Micro-Combi tester with a Rockwell C diamond scratch indenter (tip radius (R) = 0.2 mm) with the load progressively increasing from 100 to 2000 mN at a load rate of 494 mN/min for a scratch length of 1.0 mm.

Photooxidation was carried out by the exposure of the samples in a Sepap 12–24 accelerated artificial aging device. This medium-accelerated photoaging device has been described previously.[14] It is equipped with four medium-pressure mercury lamps and allows irradiation at wavelengths longer than 300 nm at 60°C and in the presence of atmospheric oxygen. UV–vis spectra were recorded on a Shimadzu UV-2101 PC equipped with integrating spheres. The IR spectra were recorded on Nicolet Magna-IR 510 (Waltham, MA) and 800 Fourier transform infrared spectrophotometers (resolution of 4 cm^{-1}, summation of 32 scans). Samples were regularly analyzed during irradiation.

RESULTS AND DISCUSSION

Microwave and oven-heating postcuring of the PEOSi/SiO$_2$ hybrids

To evaluate the degree of conversion of the sol–gel process, dynamic DSC analysis was carried out on self-standing PEO-based hybrids before and after the two different types of postcuring treatments, namely, conventional heating and microwave irradiation. The residual degree of conversion was evaluated by the measurement of the enthalpy corresponding to the endothermic peak attributable to the vaporization of volatile products during the first heating scan; this means evaluating the advancement of the crosslinking reaction in the hybrid by the monitoring of the formation of its volatile byproducts.

Typical DSC thermograms of PEOSi/SiO$_2$ 3/7 before and after microwave irradiation and for different times of irradiation are reported in Figure 1. Similar curves were recorded also for PEOSi/SiO$_2$ 7/3 and for the other samples postcured by conventional oven heating. The endothermic peak from about 30 to 150°C can be correlated to the vaporizing of volatile products (H_2O and EtOH) that formed during the first heating scan according to the aforementioned reaction scheme. This endothermic peak can be considered an indirect indication of the residual degree of cure remaining in the hybrid after the partial progression of the sol–gel reaction between PEOSi and TEOS that occurred in solution at 70°C for 30 min; as expected, the peak decreases with increasing irradiation time. The second heating scan evidenced in all cases the absence of any peak, indicating that the sol–gel process was completed during the first heating scan and that no other reversible transitions (crystallization and/or melting of PEO segments) were present.

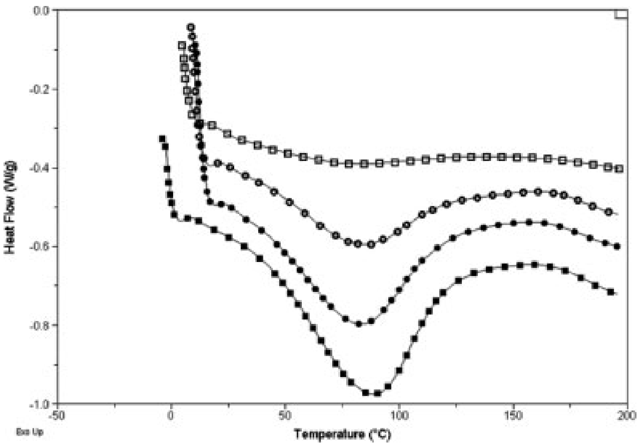


Figure 1 DSC traces of PEOSi/SiO$_2$ 3/7: (■) first scan before postcuring, (●) first scan after 5 s of microwave irradiation, (○) first scan after 15 s of microwave irradiation, and (□) second scan after 15 s of microwave irradiation.

A quantitative evaluation of the conversion degree reached at different curing times can be calculated by integration of that endothermic peak. The corresponding enthalpy values are reported in Table I.

In all cases, the enthalpy peak area was significantly lower than the corresponding value before postcuring, indicating that both microwave and thermal postcuring treatments were effective in promoting the conversion of —Si—OH and —Si—OEt groups in —Si—O—Si— linkages.

The highest conversion degrees (proportional to the inverse of the enthalpy peak area) were obtained by oven heating for both hybrid compositions. In this respect, microwave irradiation could be considered a less efficient postcuring treatment. On the other hand, microwave irradiation resulted in an enormously faster curing method if we compare the time necessary to obtain similar values of the enthalpy peak area. For example, enthalpy values of 130–150 J/g were recorded after 10 s in the case of microwave irradiation and after 2400 s in the case of oven heating for PCLSi/SiO$_2$ 3/7 samples. In other words, microwave irradiation represents a very fast curing method for organic–inorganic hybrids and seems particularly interesting for industrial applications when the process time is a strictly restrictive parameter.

Furthermore, a different trend of the enthalpy peak area as a function of the treatment time was noted for the two postcuring methods. In particular, samples postcured by oven heating showed a monotonic decrease of the enthalpy with a corresponding increase of the degree of crosslinking. Contrary to this behavior, enthalpy values recorded for microwave-irradiated hybrids showed a minimum for intermediate treatment times (5 s for PEOSi/SiO$_2$ 7/3

TABLE I
DSC Analysis: Enthalpy of the PEOSi/SiO$_2$ Samples at Different Curing Times and Treatments

Hybrid	Type of postcuring treatment	Treatment time (s)	Enthalpy peak area (J/g)
PEOSi/SiO$_2$ 7/3	None	—	109.6
	Microwave	3	80.8
		5	61.9
		10	65.9
		15	91.0
	Oven (80°C)	1200	53.7
		2400	23.4
		3600	18.9
PEOSi/SiO$_2$ 3/7	None	—	408.7
	Microwave	3	304.4
		5	200.2
		10	137.9
		15	224.6
	Oven (80°C)	1200	303.4
		2400	147.8
		3600	69.0

and 10 s for PEOSi/SiO2 3/7). To explain this unexpected result, the occurrence of some degradation reaction, which in turn leads to the formation of volatile byproducts, could be supposed. In this case, the volatilization of byproducts during the first heating scan of DSC analysis can cause an overestimation of the enthalpy value attributed to the completion of the sol–gel process alone. Of course, this interpretation needs to be supported by a specific analysis of the volatile products that formed during heating, but numerical modeling and in-site instrumental measurement of the sample temperature during microwave irradiation can be of great interest for estimating the occurrence of localized overheating during the cure. For this, both numerical modeling and instrumental measurements were performed. Numerical modeling of the microwave heating in the single-mode applicator was performed with the commercial software Concerto 4.0 (Vector Fields, UK). The software allows the calculation of the specific absorption rate (W/kg) in a lossy medium exposed to microwaves of a given frequency, thus providing an input to thermal calculations. In the case of 600 W of incident microwave power at 2.45 GHz, equivalent to an effective power of 350 W because of impedance mismatching, for a 20 mm × 20 mm polymeric PC substrate coated with 300 nm of PEO, assuming a residual content of 0.3% EtOH after the partial progression of the reaction, it was possible to calculate the temperature rise in the coating, provided that all the solvent was completely evaporated. For this simple model, assuming the PC substrate to be a nondissipative medium with respect to the more lossy coating, only heat generation in the sample was considered, conduction, convection, and irradiation being neglected. As far as instrumental measurements are concerned, temperature evolution during the curing treatment was monitored without the samples being contacted by means of a Sitel IKST14-09 optical pyrometer (Milan, Italy) precalibrated on the sample emissivity, and the heat distribution was recorded with an Irisys 1011 thermal camera, which was pointed at the sample during the microwave exposure. The pyrometer was able to measure only the surface temperature, which was cooled by the surrounding environment, and it provided an average temperature value on a relatively large area of the sample (spot diameter = 10 mm).

A comparison of the calculated and measured temperature profiles is reported in Figure 2, and they show good agreement. The small difference in the temperature distribution between the model and the real samples can be ascribed to the variation of the substrate material permittivity with temperature (i.e., the material tends to couple better with microwaves as the temperature increases), which has been omitted in the simplified model. The results show that there is a pronounced temperature mismatch between those regions of the sample that are located in an inner position inside the applicator and the outer regions; this can be ascribed to the nonhomogeneous electromagnetic field distribution. The values of the temperature increase obtained by the simulation are affected by a slight underestimation due to the imperfect impedance matching in the model between the microwave source and the load, which in the experimental tests was partially compensated by the use of a movable plunger. Further uncertainties in this calculated temperature values can be ascribed to the spectrum of the real microwave source (magnetron), which is centered around 2.45 GHz but can have a 0.01-GHz broad band. Nevertheless, both the simulation and measurements confirm the existence of a localized overheating of the sample that, if prolonged in time, can lead to its

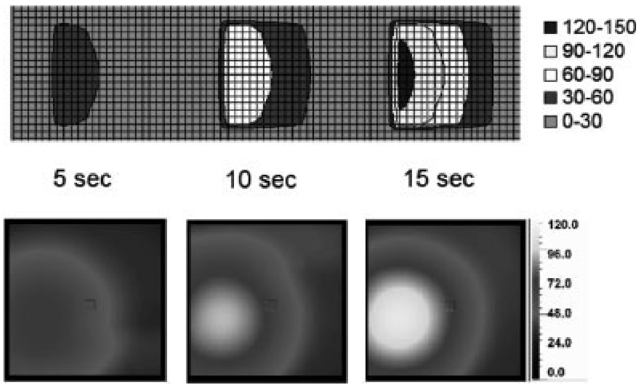


Figure 2 (Top) Calculated and (bottom) measured temperature profiles after 5, 10, and 15 s of microwave irradiation.

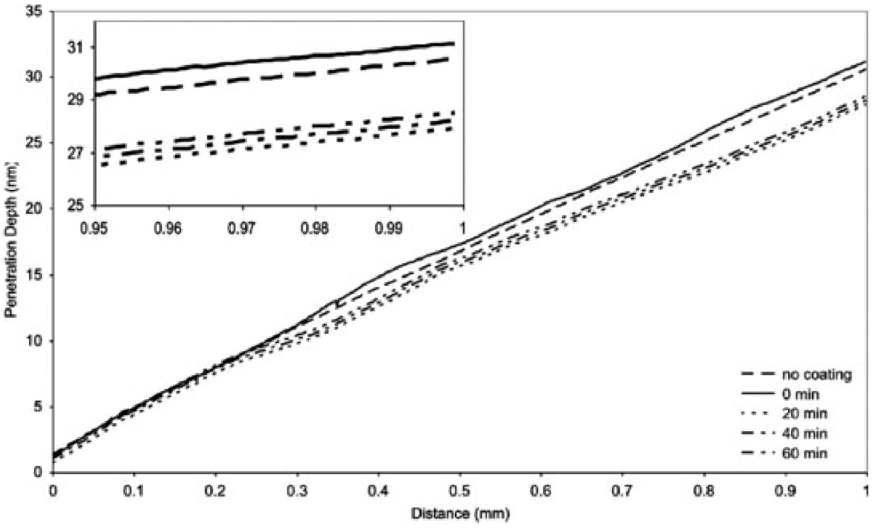


Figure 3 Scratch test: PD as a function of the scratch length of uncoated PC and PC coated with PEOSi/SiO$_2$ 7/3 before and after the postcuring treatment (oven heating).

partial degradation, thus explaining what was observed in the DSC measurements.

Scratch resistance of PC coated with the PEOSi/SiO$_2$ hybrids

To evaluate the enhancement in the scratch resistance of PC slabs coated with PEOSi/SiO$_2$ hybrids, samples were prepared as follows: hybrid solutions in EtOH were deposited by spin coating onto 3.0-mm-thick PC slabs, and the systems were subjected to the previously discussed postcuring treatments. Scratch tests were carried out by a scratch being formed by a progressively increasing load (from 100 to 2000 mN) for a final scratch length of 1 mm. A typical output of the scratch test is reported in Figure 3, in which the trend of the penetration depth (PD) is shown as a function of the scratch length of uncoated PC and PC coated with PEOSi/SiO$_2$ 7/3 before and after the thermal postcuring treatment (oven heating) lasting for 20, 40, or 60 min. Similar trends were also seen for the other samples. As expected, all the samples showed a progressive increase of PD due to the increasing applied load.

The slope of the PD curves was systematically higher in the case of uncoated PC or PC coated with hybrids that were not subjected to any postcuring treatment with respect to coated samples subjected to a postcuring treatment (either microwave irradiation or oven heating). The results of scratch tests for all samples are reported in Table II, in which the final PD values (i.e., at a scratch length of 1.0 mm) of uncoated PC and PC coated with different hybrids and subjected to different postcuring treatments (type and time) are reported.

According to the lower slope of the previously discussed PD–distance curves, the final PD values were lower when hybrids coated onto PC were postcured by oven heating or by microwave irradiation.

These data indicate that organic–inorganic hybrids are effective coatings for the improvement of the scratch resistance of polymeric substrates such as PC.

To obtain the desired protective effect, a postcuring step is necessary to improve the degree of the sol–gel reaction, thus providing a high crosslinking density and hence a harder surface. Both oven heating and microwave irradiation were effective post-

TABLE II
Scratch Test: Final PD (Scratch Length = 1 mm) of Uncoated PC and PC Coated with Different Hybrids Subjected to Different Postcuring Treatments (Type and Time)

	Postcuring treatment		
Coating	Type	Time (s)	Final PD (nm)
None	—	—	30.5
PEOSi/SiO$_2$ 7/3	None	—	31.1
	Microwave	3	25.5
		5	24.9
		10	24.9
		15	24.9
	Oven (80°C)	1200	27.9
		2400	28.2
		3600	28.5
PEOSi/SiO$_2$ 3/7	None	—	29.8
	Microwave	3	23.1
		5	23.3
		10	23.8
		15	23.3
	Oven (80°C)	1200	23.5
		2400	23.2
		3600	23.6

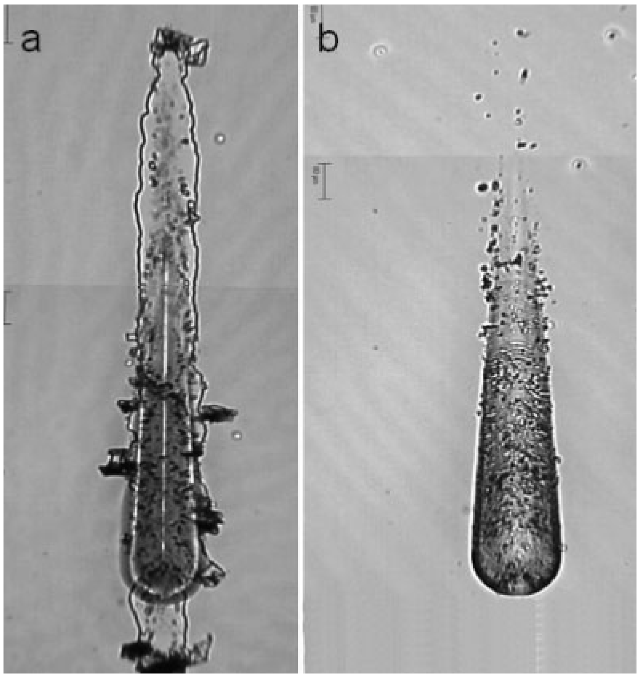


Figure 4 Optical micrographs of scratches performed on PC coated with (a) PEOSi/SiO_2 7/3 and (b) PEOSi/SiO_2 3/7 hybrids postcured by microwave irradiation (irradiation time = 5 s).

curing methods, and the scratch resistance (in terms of the final PD) was almost independent of the type and duration of the treatment. On the other hand, the hybrid composition (organic–inorganic final ratio) also seems to have an effect on the scratch resistance; in fact, substrates coated with postcured hybrids having a higher inorganic content (PEOSi/SiO_2 3/7) showed an average value of the final PD (independently of the time of treatment) of 23.4 nm for both oven heating and microwave irradiation, whereas postcured samples based on PEOSi/SiO_2 7/3 hybrids showed average values of 25.0 (microwave irradiation) and 28.2 nm (oven heating). For these samples, a harder surface was obtained through the microwave-irradiation curing treatment, and this result is a further factor supporting the effectiveness of this method versus the traditional thermal one.

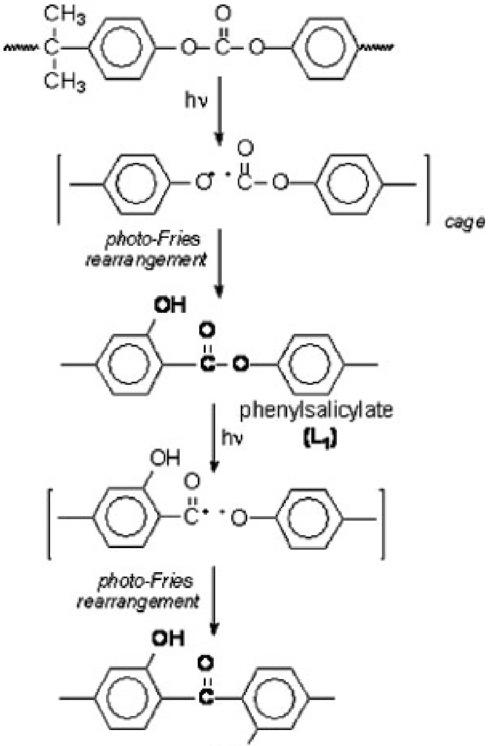
These considerations were further supported by the optical micrographs of the scratches present on the surface after the test. Some examples are reported in Figure 4, in which the higher scratch resistance related to coatings with the higher inorganic content is quite evident. From Figure 4(b), it is clearly evident that no detachment of the silica-rich coating from the substrate occurred in the region around the scratch profile, and this also means that the coating has good adhesion to the PC substrate and that the sol–gel approach leads to a hard, resistant, and effective surface coating.

As expected, scratch resistance tends to improve with the inorganic phase content increasing. However, the differences between coatings with markedly different organic–inorganic contents were not so high, and this behavior could be attributed to a preferential surface segregation of silica domains independent of the bulk composition, a phenomenon already observed, reported, and discussed for this kind of material.[14]

Photooxidation of PC coated with the PCLSi/SiO_2 hybrids

Reactions that result from the exposure of PC to UV light under conditions representative of solar light can be described by a dual photochemistry,[15,16] which involves direct phototransformation and induced photooxidation. These reactions provoke a dramatic yellowing of the polymer and a degradation of the mechanical and physical properties of the material, thus representing one of the outmost limiting aspects for PC applications. Direct absorption of radiation below 330 nm provokes indeed two successive photo-Fries rearrangements, as shown in Scheme 2.

UV radiation above 330 nm is likely to induce *gem*-dimethyl side-chain photooxidation and phenyl ring oxidation. Both processes produce various oxidized species with chain scissions and crosslinking.



Scheme 2 Direct phototransformation of PC.

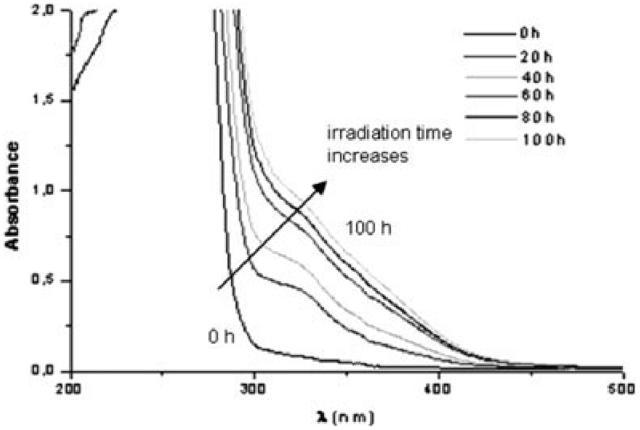


Figure 5 UV–vis spectra of uncoated PC film during photooxidation.

These photochemical reactions can be evidenced by the modifications of the UV and IR spectra of the exposed samples. Yellowing can be easily quantified by the measurement of the increase of absorbance at 400 nm (Fig. 5), which mainly reveals the contribution of the photoinduced oxidation of PC, whereas the variations at 325 nm can be used to monitor the direct phototransformation that generates the photo-Fries products L1 and L2.

The degrading effects induced by the exposure of polymers to outdoors conditions can be limited by stabilizers. Stabilizers include several types of additives: UV absorbers used to protect PC from the UV radiation by competitive absorption, quenchers used to deactivate the excited states, antioxidants with chain-breaking antioxidants, hydroperoxide decomposing antioxidants, and hindered amine stabilizers.[17] The various processes that provoke the oxidation of polymeric materials can be generally efficiently limited by the addition of combinations of these various stabilizers to oxidizing polymers. Complementary antioxidants and protection of stabilizers (e.g., UV absorbers and phenolic antioxidants) are responsible for excellent results.

As recalled previously, the photoyellowing of PC induced by UV light results from both photoinduced oxidation and a photo-Fries rearrangement. Inhibition of the photoyellowing can be indeed obtained by a reduction of the absorption of the UV radiation with UV absorbers and/or by the limitation of the propagation of the oxidation with antioxidants. However, total absorption by a UV absorber of the radiation impinging the material cannot be achieved as far as the surface of the polymer is concerned. This is especially true in the case of those polymers that strongly absorb in the UV range, such as PC. This direct result of the Beer–Lambert law, which shows that the layers at the surface of the sample cannot be protected by the UV absorber, is supported by many experimental results.[18,19] For this reason, an efficient stabilization of PC against photoyellowing cannot be achieved so simply. To suppress the surface yellowing, an elegant solution is to prevent the radiation from reaching the surface of the polymer. A coating containing a UV absorber capable of absorbing the incident radiation is generally deposited onto the substrate to absorb the UV radiation before it impacts on the PC substrate. This coating also acts as a physical barrier to oxygen, which decreases the rate of oxidation of the polymeric substrate by limiting the oxygen flux at the surface of the polymer.

Two different approaches can achieve this goal. Aliphatic polymeric coatings are used with UV absorbers. According to the absorber concentration and the thickness of the coating, complete photoprotection of the substrate can be obtained. However, because the coating is an organic polymer, the lifetime of the multilayer part systems depends on the photostability of this coating under irradiation, which necessitates complementary stabilization of the coating against photooxidation.

Another approach consists of depositing a ceramic coating such as ZnO on the surface of PC. ZnO strongly absorbs in the UV range and constitutes a physical barrier to oxygen. As a result of these properties, ZnO coatings decrease the rate of oxidation and the rate of photoyellowing of PC, the efficiency depending on the thickness and the structural properties.[20] Surface properties of the ZnO/polymer assembly can be improved by a hard upper layer such as Al_2O_3, which confers to the polymer antiscratch properties and also acts as an excellent barrier for oxygen.[21]

Ceramers represent an interesting alternative approach because besides their valuable mechanical properties, these materials can act as protective layers in terms of a screen effect when mixed with UV absorbers and also as a barrier to oxygen.

In this study, we investigated the effect of PCLSi/SiO_2 hybrids with various compositions on the oxidation and yellowing of PC induced by exposure to UV light in the presence of air. PCL was chosen rather than PEO because PEO is known to be very sensitive to UV-light-induced oxidation.[13]

Accelerated artificial aging was performed on uncoated PC films and PC coated with different PCL-based hybrids under irradiation at long wavelengths (>300 nm) at 60°C in the presence of atmospheric oxygen. The effects of both the hybrid composition and coating thickness were taken into account. The oxidative degradation of the samples induced by UV light was followed by IR and UV–vis spectroscopy. The kinetics of oxidation of PC were compared to those of coated PC through the plotting of the variation of the absorbance of some specific

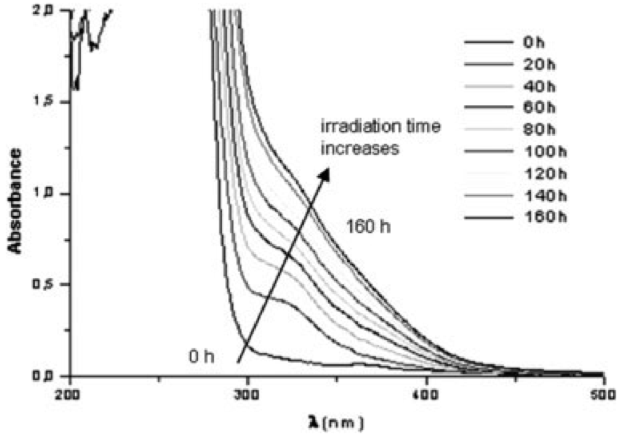


Figure 6 UV–vis spectra of PC film coated with PCLSi/SiO_2 4/6 L during photooxidation.

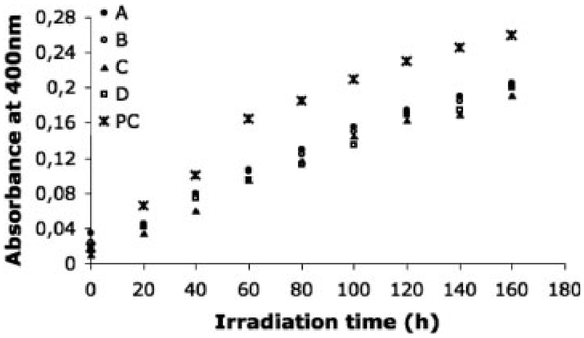


Figure 8 Evolution of the absorption band at 400 nm for PC films that were uncoated and coated with ceramers: (A) PCLSi/SiO_2 4/6 L, (B) PCLSi/SiO_2 4/6 H, (C) PCLSi/SiO_2 8/2 L, (D) PCLSi/SiO_2 8/2 H, and (PC) uncoated film.

wave numbers or wavelengths against the irradiation time:

- The variation of the absorbance at 3490 and 1687 cm^{-1} measured on the IR spectra.
- The evolution of the absorbance at 325 and 400 nm measured on the UV–vis spectra.

Measurements were performed for all the samples every 20 h over 160 h of exposure, and spectra were compared for the same sample at different times and also for different samples; examples are shown in Figure 5 (for uncoated PC film) and Figure 6 (for PC coated with PCLSi/SiO_2 4/6 L, 600–750-nm thickness). A protective effect can be immediately deduced from the data plotted in Figures 7 and 8, in which the absorbance at 325 and 400 nm is plotted against the irradiation time for all samples and for uncoated PC; the increase in the absorbance at 400 nm (related to yellowing) is lower for PC samples coated with ceramers than for the uncoated PC. Moreover, Figure 8 shows that the ceramers applied to samples PCLSi/SiO_2 8/2 L and PCLSi/SiO_2 8/2 H have a slightly higher protective effect than PCLSi/SiO_2 4/6 L and PCLSi/SiO_2 4/6 H. On the other hand, no significant effect of the coatings thickness was observed. A comparison of the increase of the absorbance at 325 nm on the one hand and at 400 nm on the other hand shows that the coating used here offers protection as a barrier to oxygen. As expected, no important decrease of the rate of formation of L1 and L2 (characterized by the increase of absorbance at 325 nm) can be observed. The effect of the coating on the oxygen diffusion is confirmed by the IR analysis. The kinetics of oxidation of PC were compared to those of protected PC films through the plotting of the variations of the absorbance at 3490 and 1687 cm^{-1} measured on the IR spectra after subtraction of the initial IR spectrum as a function of the irradiation time; as examples, Figures 9 and 10 are shown for sample PCLSi/SiO_2 4/6 L in the two different

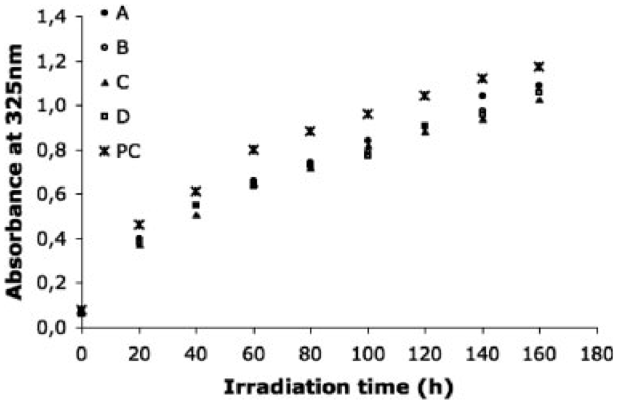


Figure 7 Evolution of the absorption band at 325 nm for PC films that were uncoated and coated with ceramers: (A) PCLSi/SiO_2 4/6 L, (B) PCLSi/SiO_2 4/6 H, (C) PCLSi/SiO_2 8/2 L, (D) PCLSi/SiO_2 8/2 H, and (PC) uncoated film.

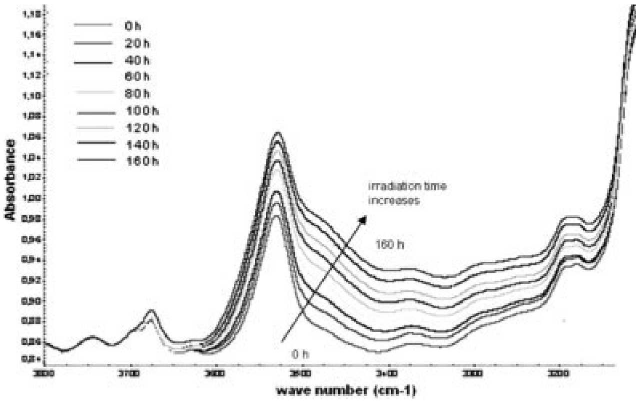


Figure 9 IR spectra of the PC film coated with PCLSi/SiO_2 4/6 L during photooxidation in the hydroxyl domain of 3800–3100 cm^{-1}.

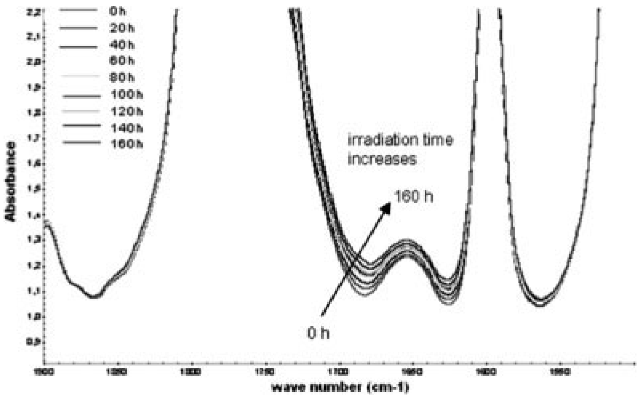


Figure 10 IR spectra of the PC film coated with PCLSi/SiO_2 4/6 L during photooxidation in the carbonyl domain of 1900–1500 cm^{-1}.

spectral regions. The IR spectroscopy results were similar for all samples coated with different hybrids. However, the comparisons of the kinetic rates of oxidation for the different samples reported in Figures 11 and 12 show that hybrid-coated PC samples were less degraded than uncoated PC, even though it appeared difficult to establish which kind of coating was the most protective. However, a long irradiation time (>100 h) permitted discrimination of the various samples, and it seems that (see Fig. 12) samples PCLSi/SiO_2 8/2 L and PCLSi/SiO_2 8/2 H might have given better results, confirming what already was observed by UV–vis measurements.

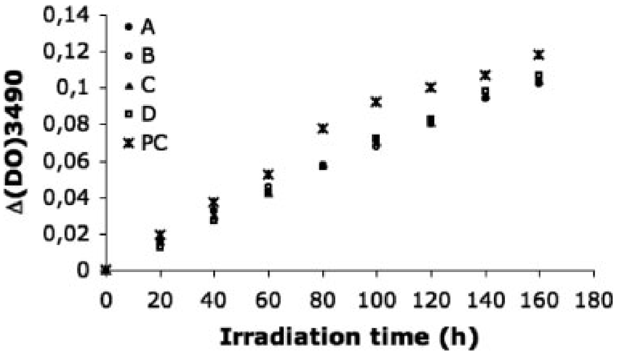


Figure 11 Variation of the absorbance at 3490 cm^{-1} [Δ(DO)3490] during photooxidation for PC films that were uncoated and coated with ceramers: (A) PCLSi/SiO_2 4/6 L, (B) PCLSi/SiO_2 4/6 H, (C) PCLSi/SiO_2 8/2 L, (D) PCLSi/SiO_2 8/2 H, and (PC) uncoated film.

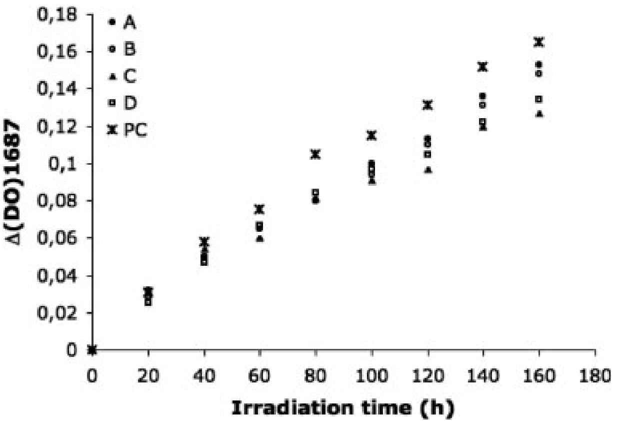


Figure 12 Variation of the absorbance at 1687 cm^{-1} [Δ(DO)1687] during photooxidation for PC films that were uncoated and coated with ceramers: (A) PCLSi/SiO_2 4/6 L, (B) PCLSi/SiO_2 4/6 H, (C) PCLSi/SiO_2 8/2 L, (D) PCLSi/SiO_2 8/2 H, and (PC) uncoated film.

These preliminary investigations give a first approach to the role played by hybrid coatings based on PCL against photooxidation when deposited onto PC films. The experimental results revealed a limited but significant improvement with respect to uncoated PC, which was due to the fact that they constituted a barrier only to O_2 and not to the UV radiation that impinged on the PC substrate. It is necessary to investigate in more detail the effect of the coating composition to maximize the protection efficiency. The possibility of applying this kind of protective coating even to objects of complex shapes could draw widespread attention for several industrial applications.

CONCLUSIONS

PEO/silica and PCL/silica hybrids, to be applied onto PC substrates, were easily prepared by a sol–gel process. To increase the degree of reaction and thus to crosslink the thermoset system, different postcuring treatments were carried out by conventional oven heating and microwave irradiation. The extent of the postcuring reaction was investigated by DSC analysis, which showed that both postcuring treatments were efficient enough to almost complete the sol–gel reaction. However, microwave irradiation led to crosslinked coatings with a process time of some seconds (5–10 s), whereas the same level of conversion degree was reached in about 40 min in the case of oven heating. Moreover, microwave heating selectivity, because of the mismatch of dielectric properties between the coating and the candidate substrates to be used, offers interesting possibilities of scale-up of the process to many low-loss dielectrics.

Scratch tests carried out on PC substrates coated with PEO/silica hybrids evidenced a significant increase of scratch resistance with respect to uncoated PC. Postcuring treatment (both microwave irradiation and oven heating) was absolutely necessary to achieve a sufficiently high conversion degree of the sol–gel reaction (crosslinking degree) and thus the desired antiscratch effect of the coating.

Photooxidation tests carried out on uncoated PC thin films and the same films coated with PCL/silica hybrids demonstrated a protective effect of the hybrid coatings against photooxidation. This effect can be easily improved by the variation of the composition and formulation of the hybrids. This will be the object of further studies undertaken by two research groups that collaborate in this area. The main objective of the upcoming experiments is to focus on the screen effect of the coatings to limit the UV radiation at the surface of the polymer. A screen effect will be obtained by the development of proper formulations with organic and mineral UV absorbers.

As a general conclusion, from an industrial point of view, great advantages can be obtained by the application of PCL- or PEO-based hybrid coatings onto PC substrates: although transparency and clarity are maintained, enhanced resistance can be obtained toward different environmental factors, such as oxidative UV irradiation, scratching, and abrasion. As a second point, the possibility of performing fast curing processes through microwave irradiation represents an attractive possibility for scaling up this application.

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References

1. Brunelle, D. J. In Technical Information Series; Center, G. E. R. D., Ed.; General Electric: New York, 2002; p 32.
2. (a) Vanlandeghem, A.; Greger, R.; Palmers, J. WO Pat. 01/89721 (2001); (b) Yanagihara, K.; Kimura, M.; Shinkai, M. Jpn. Pat. 61200134 (1986).
3. Moustaghfir, A.; Tomasella, E.; Rivaton, A.; Mailhot, B.; Jacquet, M.; Gardette, J. L.; Cellier, J. Surf Coat Technol 2004, 180–181, 642.
4. Brinker, C.; Scherer, G. Sol–Gel Science: The Physics and Chemistry of Sol–Gel Processing; Academic: Boston, 1990.
5. Kickelbick, G. Prog Polym Sci 2002, 28, 83.
6. Haas, K. H.; Wolter, H. Curr Opin Solid State Mater Sci 1999, 4, 571.
7. Messori, M.; Toselli, M.; Pilati, F.; Fabbri, E.; Fabbri, P.; Busoli, S. Surf Coat Int Part B: Coat Trans 2003, 86, 181.
8. Messori, M.; Toselli, M.; Pilati, F.; Fabbri, E.; Fabbri, P.; Busoli, S.; Pasquali, L.; Nannarone, S. Polymer 2003, 44, 4463.
9. Cruz, C. A.; Paul, D. R.; Barlow, J. W. J Appl Polym Sci 1979, 23, 589.
10. Jonza, J. M.; Porter, R. S. Macromolecules 1986, 19, 1946.
11. Chaoxu, L.; Qingshan, K.; Qingrong, F.; Yanzhi, X. Mater Lett 2005, 59, 773.
12. Balsamo, V.; Calzadilla, N.; Mora, G. A.; Müller, J. J Polym Sci Part B: Polym Phys 2001, 39, 771.
13. Morlat, S.; Gardette, J. L. Polymer 2001, 42, 6071.
14. Messori, M.; Toselli, M.; Pilati, F.; Fabbri, E.; Fabbri, P.; Pasquali, L.; Nannarone, S. Polymer 2004, 45, 805.
15. Scheirs, J.; Gardette, J. L. Polym Degrad Stab 1997, 56, 339.
16. Rivaton, A.; Mailhot, B.; Soulestin, J.; Varghese, H.; Gardette, J. L. Polym Degrad Stab 2002, 75, 17.
17. Pospisil, J.; Nespurek, S. In Handbook of Polymer Degradation, 2nd ed.; Halim Hamid, S., Ed.; Marcel Dekker: New York, Chapter 6, p 191.
18. Mailhot, B.; Rivaton, A.; Gardette, J. L.; Moustaghfir, A.; Tomasella, E.; Jacquet, M.; Ma, X.-G.; Komvopoulos, K. e-Polymer [online] 68, 2005.
19. Claudé, B.; Gonon, L.; Verney, V.; Gardette, J. L. Polym Test 2001, 20, 771.
20. Moustaghfir, A.; Rivaton, A.; Tomasella, E.; Mailhot, B.; Cellier, J.; Jacquet, M.; Gardette, J. L. J Appl Polym Sci 2005, 95, 380.
21. Moustaghfir, A.; Tomasella, E.; Jacquet, M.; Rivaton, A.; Mailhot, B.; Gardette, J. L.; Bêche, E. Thin Solid films 2006, 515, 662.