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Flame retarding poly(methyl methacrylate) with nanostructured organic–inorganic hybrids coatings

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Abstract

Organic–inorganic hybrid materials were prepared starting from tetraethoxysilane and α- or α,ω-triethoxysilane terminated poly(ε-caprolactone) (PCL–Si) using the sol–gel process. In all cases the formation of nanocomposites with a high level of interpenetration between organic and inorganic phases was noted. Poly(methyl methacrylate) slabs were dip-coated with PCL–Si/silica hybrids and a very strong increase of the flame resistance (also after UV irradiation) was noted for all coating compositions without marked differences with respect to hybrid compositions. This behavior was attributed to a preferential segregation of silica onto the outer surface, as evidenced by XPS analysis.

Keywords: Flame resistance; Inorganic–organic hybrids; Nanocomposites

1. Introduction

The improvement of flame resistance of transparent polymers such as poly(methyl methacrylate) (PMMA) represents an important industrial goal taking into account its wide use in lighting applications. PMMA is traditionally made flame retardant by physical incorporation of additives, and the use of phosphorous-containing compounds is well established [1]. This approach, however, presents several disadvantages. The additive is often required in high loadings to be effective, which may result in adverse changes to the physical and mechanical properties of the polymer. Additives can also be leached from the polymer through normal service and ageing, which poses an environmental threat and, as a result, reduction in any flame retardant effect. In order to minimize these drawbacks, chemical incorporation of the flame-retardant species through copolymerization of methyl methacrylate with phosphorous-containing monomers or some other chemical modification has been recently proposed [2,3].

An alternative approach is represented by the use of flame retarding coatings, taking into account the thermal degradation mechanism active in PMMA. In fact, during heating, the methyl methacrylate monomer is assumed to arise from the depolymerization of polymer chain by a free radical mechanism, and the evolved combustible gases are responsible for fire ignition and growth [4]. The thermal oxidative decomposition (in the presence of oxygen in the gas phase) is much faster than simple thermal degradation, due to the formation of peroxides and hydroperoxides [5]. From this point of view, the application of a coating with appropriate barrier properties with respect to oxygen and methyl methacrylate monomer is expected to limit flame ignition and growth.

Appropriate coatings can be applied by using plasma techniques [6,7] but there are drawbacks such as cost, poor adhesion with the substrate, loss of transparency, small item dimensions and complex geometrical forms that limits these processes.

In this respect, the coating of polymeric surfaces by wet chemical process can be in most cases an interesting alternative and the sol–gel process, with its associated mild conditions, represents one of the preferred approaches. The classical sol–gel process consists in a two-step acid or base catalyzed reaction, starting with metal alkoxides $M(OR)_4$,

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typically tetraethoxysilane (TEOS) [8]. Even though the reaction mechanism may be quite complex and until now not well understood, several reactions can occur involving metal alkoxides hydrolysis and formation of intermediate species of the metal hydroxide type. These species then undergo a stepwise polycondensation involving both hydroxy and alkoxy groups with the formation of a metal oxide three-dimensional network.

The sol–gel process has proved to be flexible enough for an efficient incorporation of organic oligomers or polymers, in particular this approach is particularly interesting for reactants bearing at least two reactive groups so that when they are involved in the hydrolysis–condensation reactions they can behave as flexible links between silica domains. The resulting materials are known as organic–inorganic hybrids [9,10], also commonly designated as *ceramers* due to the combination of the properties of ceramics (high modulus, thermal stability and low coefficient of thermal expansion) with those of organic polymers (high ductility and low temperature processing). These materials are often also known as phase-interconnected nanocomposites because of the high level of interconnection between the two phases with domain phase sizes approaching the nanometer scale. Ceramers have a huge potential for applications in a variety of advanced technologies [11], both as structural materials, including their use as matrices for high performance composites and functional materials, such as catalyst supports, sensors and active glasses. However, the main commercial applications, at present, are in the field of protective coatings of both organic and inorganic substrates. Ceramers have been already recognized as barrier coating materials to obtain high barrier properties for oxygen, water vapor and volatile organic compounds permeation in the field of polymeric packaging materials [12,13]. In principle, the same barrier properties can be usefully employed to confer the desired flame resistance to PMMA according to the previously discussed thermal degradation mechanism, together with the preservation of the transparency thanks to the nanosizes of organic and inorganic domains.

Of course, the chemical nature of the organic component is of primary importance to obtain adhesion to the polymeric substrate which has to be protected. In this respect, hydroxy terminated poly(ε-caprolactone) (PCL) is a commercially available aliphatic polyester which presents some interesting features because of its miscibility with several polymers [14–16] and because it can be easily prepared in different molecular weights and molecular weight distributions, also with polydispersity close to unity [17]. Furthermore PCL can be synthesized in linear or star-branched structures with a well defined number of functional end-groups suitable for subsequent reactions, thus allowing a deep study of the effects of the molecular structure of the organic oligomer on the characteristics of the final ceramer.

In this view, the present study deals with preparation and characterization of hybrid materials based on α- and α,ω-triethoxysilane terminated PCL, their application as protective coatings on PMMA substrates and the evaluation of their effect on flame resistance also after long UV irradiation times.

2. Experimental section

2.1. Materials

High purity tetraethoxysilane (TEOS, Aldrich), 3-isocyanatopropyltriethoxysylane (ICPTES, Fluka), hydrochloric acid at 37% concentration (Carlo Erba), ethanol (EtOH, Carlo Erba), tetrahydrofuran (Carlo Erba) and tin(II) octoate ($SnOct_2$, Aldrich) were used as received without further purification.

ε-Caprolactone (CL), ethylene glycol (EG) and *n*-butanol (BuOH) (all from Aldrich) were dried over calcium hydride and distilled just before use. Slabs of standard grade PMMA (Meglas Italy) were used as substrate without any preliminary treatment.

2.2. Preparation of hydroxy terminated poly(ε-caprolactone)

α- and α,ω-hydroxy terminated poly(ε-caprolactone) (PCL–OH) were prepared in bulk by ring opening polymerization of CL in the presence of BuOH or EG as initiators and $SnOct_2$ as catalyst.

The reaction was carried out in a 50 ml glass flask with magnetic stirring, at 120 °C, for 24 h. For the purpose of this paper, the above structures will be, respectively coded as α-PCL(*n*)OH and α,ω-PCL(*n*)OH, in which *n* indicates the average degree of polymerization (DP). The molar ratios used are reported in Table 1.

The progress of the reaction of CL polymerization was monitored by ^{1}H-NMR analysis which showed the complete monomer conversion was reached after 24 h. All the ^{1}H-NMR spectra showed the expected structures and, in particular, the DP was in good agreement with the theoretical value calculated from the monomer/initiator agent ratio.

Table 1
Relative amounts (moles) of reactants used in the synthesis of hydroxy terminated poly(ε-caprolactone)

Code	CL (mol)	BuOH (mol)	EG (mol)	$SnOct_2$ (mol)
α-PCL(20)OH	20	1	–	0.01
α-PCL(50)OH	50	1	–	0.01
α,ω-PCL(20)OH	20	–	1	0.02
α,ω-PCL(50)OH	50	–	1	0.02

2.3. Preparation of triethoxysilane terminated poly(ε-caprolactone)

At the end of the reaction related to the preparation of α- and α,ω-hydroxy terminated poly(ε-caprolactone) samples, ICPTES was directly added to a OH/ICPTES molar ratio of 1:1. The reaction was carried in the same conditions reported above for 3 h. The final products, respectively coded as α-PCL(20)Si, α-PCL(50)Si, α, ω-PCL(20)Si and α,ω-PCL(50)Si, were dried overnight at room temperature under reduced pressure before use.

The progress of the reaction between hydroxy terminated PCL and ICPTES was monitored using FT-IR spectroscopy. It was found that, under the experimental conditions used in this study, the reaction goes to completion within 3 h. The expected structures were also confirmed by the ^{1}H-NMR analysis of the reactant ICPTES and the final products.

2.4. Preparation of PCL /silica hybrids

PCL–Si/TEOS mixtures were dissolved in tetrahydrofuran, a good solvent for PCL and a typical non-solvent for PMMA (two different concentrations were used of 20 and 40 wt%/vol) and water (for the hydrolysis reaction), EtOH (to make the system homogeneous) and HCl (as catalyst) were added at the following molar ratios with respect to ethoxide groups of PCL–Si and TEOS: EtO–:H_2O :EtOH:HCl = 1:1:1:0.1.

A typical preparation was as follows: 2.0 g of a PCL–Si/TEOS mixture were added to 8 ml of tetrahydrofuran and mixed until a homogeneous solution was obtained. Then EtOH, water and HCl (37 wt% solution) were added in the appropriate amount under vigorous stirring at room temperature for about 10 min. The clear solution was then cast into a closed Petri dish and the solvent was slowly evaporated at room temperature for about one week. The samples were also 'post-cured' at 100 °C for 2 h.

The final hybrids were coded as PCL–Si/SiO_2 x:y wt/wt in which x:y represents the weight ratio of organic and inorganic components assuming the completion of the reaction reported in Scheme 1. The PCL–Si/SiO_2 weight ratio was ranged from 2:1 to 1:2.

Step 1. Hydrolysis

$Si(OEt)_4 + x\ H_2O \rightarrow Si(OEt)_{4-x}(OH)_x + x\ EtOH$

$(EtO)_3Si\text{-}PCL\text{-}Si(OEt)_3 + (x+y)\ H_2O \rightarrow (EtO)_{3-x}(HO)_xSi\text{-}PCL\text{-}Si(OEt)_{3-y}(OH)_y + (x+y)\ EtOH$

Step 2a. Condensation with formation of ethanol

~Si-OH + EtO-Si~ → ~Si-O-Si~ + EtOH

Step 2b. Condensation with formation of water

~Si-OH + HO-Si~ → ~Si-O-Si~ + H_2O

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

2.5. Deposition of PCL/silica hybrids onto PMMA substrate

PCL–Si/TEOS sol–gel solutions were prepared according to the procedure above described. The sol–gel reactions were carried out for different times ranging from 0 to 240 min (at room temperature or at the refluxing temperature). PCL–Si/silica hybrids were deposited onto PMMA slabs ($15 \times 15 \times 3\ mm^3$) by dip-coating from homogeneous sol–gel solutions. The samples, after a period of 30 min at room temperature, were subjected to a thermal post-treatment at 100 °C for 2 h.

2.6. Characterization

FT-IR analysis was performed with a Brucker IFS48 spectrometer. A minimum of 64 scans with a resolution of 2 cm^{-1} was used. Samples were analyzed as thin films cast on sodium chloride window.

^{1}H-NMR analysis was performed with a Varian Gemini System 300 MHz instrument by using $CDCl_3$ as solvent and tetramethylsilane as internal reference.

Differential scanning calorimetry (DSC) was performed with a TA DSC2010 instrument in the range from −100 to +120 °C with a heating rate of 20 °C min^{-1}; thermograms of the crude samples were recorded immediately after a heating scan followed by a quick cooling.

Thermogravimetric analysis (TGA) was performed with a Perkin Elmer TGA 7 instrument in air in the range 30–700 °C with a heating rate of 20 °C min^{-1}.

Organic soluble fractions were extracted from hybrids with tetrahydrofuran, in a Soxhlet apparatus, for at least 50 h, until no further weight loss was detected.

Transmission electron microscopy (TEM) analysis was carried out with a Philips JEM 2010 microscope in which the contrast between organic and inorganic phases permitted to avoid any specific staining.

Fracture surfaces of coated specimens were gold-coated and examined by scanning electron microscopy (SEM) using a Philips XL-40 instrument.

XPS measurements were carried out on the vacuum-side surface using a V.G. ADES 400 hemispherical analyzer and a single-channel detector system. The Mg K$\alpha_{1,2}$ line from a V.G. XR3 dual anode X-ray tube was used as the source, operated at 210 W (14 kV and 15 mA). High resolution spectra of carbon 1s (C_{1s}), silicon 2p (Si_{2p}) and oxygen 1s (O_{1s}) core level for each sample were acquired. Data were collected at 20° takeoff angle between the sample and the analyzer corresponding to a sampling depths of approximately 10–20 Å. Binding energies were referenced to the C–H level at 285.0 eV. Overlapping peaks in C_{1s} region were resolved into their individual components by using a curve-fitting program. The deconvolutions were based on the knowledge of the XPS spectrum of the PCL homopolymer. A correction for hydrocarbon contamination at 285.0 eV has been carried out taking into account the theoretical ratio of 5:1 between peaks of PCL methylene groups and the carbonyl groups (288.9 eV).

In order to evaluate the flame resistance, a Glow Wire Test apparatus (IEC 695-2-1) was used; the time to the flame ignition from the contact between the specimen and the glow wire was measured (temperature of the wire 730 °C).

UV radiation exposure tests were carried out by using Osram Ultravitalux UV 300W lamp. The distance between specimens and lamps was of about 50 cm.

3. Results and discussion

PCL–silica hybrids have been extensively studied by Jerome and co-workers [18–21] who prepared transparent hybrid materials starting from tetraethoxysilane and α,ω-hydroxy or α,ω-triethoxysilane terminated PCL by the sol–gel process. The use of α,ω-triethoxysilane terminated PCL was recommended to obtain a shorter gelation time and a better phase interconnection, probably due to the higher reactivity of triethoxysilane end groups with respect to the hydroxyl counterpart. Furthermore, it was observed that the amount of polymeric fraction incorporated into the silica network was limited by the early vitrification of the reactive system; this drawback was limited by curing the sample at a high enough temperature (100 °C) [19]. It was also observed that the thermal stability of PCL was improved by incorporation into the inorganic network. The phase morphology of these materials was found to be co-continuous, particularly for contents of both components close to 50 wt%, with surface to surface distance between PCL and silica domains in the region of about 5 nm [20,21].

The characterization of the hybrids obtained in this paper gave results very similar to those previously reported, even though the preparation of the triethoxysilane terminated PCL was carried out in bulk contrary to the solution synthesis proposed by Jerome and co-workers [18].

Table 2
DSC analysis for α- and α,ω-triethoxysilane terminated PCL (heating rate 20 °C min^{-1}, second scan)

Code	Average molecular weight (g mol^{-1})	T_g (°C)	T_m (°C)	ΔH_m (J/g)
α-PCL(20)Si	2600	−64.8	33.2	60.3
α-PCL(50)Si	6020	−67.3	51.9	76.6
α,ω-PCL(20)Si	2840	−67.6	37.4	64.1
α,ω-PCL(50)Si	6260	−65.6	54.7	81.4

The progress of the reaction between hydroxy terminated PCL and ICPTES was monitored using FT-IR spectroscopy by comparing the broad absorption band of the hydroxyl groups of PCL–OH (at about 3500 cm^{-1}) to the absorption band of the urethane groups (at about 3380 cm^{-1}) and following the disappearing of the absorption band related to isocyanate groups (at 2270 cm^{-1}). Typical FT-IR spectra recorded at different reaction times are reported in Fig. 1.

The expected structures were also confirmed by the ^{1}H-NMR analysis of the reactant ICPTES and triethoxysilane terminated PCL oligomer (PCL–Si) whose spectra and signal assignments are reported in Figs. 2 and 3, respectively.

The spectrum of PCL–Si (Fig. 3) showed the presence of signals attributable to both reactants and the absence of the signal at 3.65 ppm, related to the methylene groups adjacent to hydroxyl end groups of PCL–OH, indicating that the reaction between terminal groups of PCL and isocyanate groups was complete.

In Table 2 results obtained from DSC analysis are reported for PCL–Si. In all cases a glass transition temperature (T_g values ranging from −64.8 to −67.6 °C) and a melting transition temperature (T_m values ranging from 33.2 to 54.7 °C) were clearly observed, increasing with the molecular weight of PCL segment, and approaching the value typical of high molecular weight PCL ($T_g \sim -60$ °C and $T_m \sim +60$ °C). As a general trend, the higher values of both melting temperature and enthalpy were noted for α,ω-triethoxysilane terminated PCL with respect to mono-functional PCL, for the same DP.

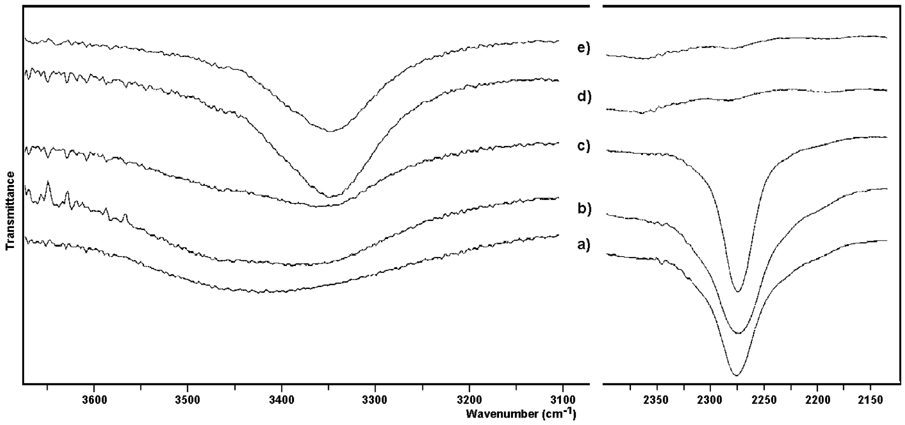

Fig. 1. Synthesis of triethoxysilane terminated poly(ε-caprolactone): FT-IR spectra recorded at different reaction times, (a) 0 h, (b) 0.5 h, (c) 1.5 h, (d) 2.5 h, (e) 3 h.

Table 3
Maximum organic soluble fractions extracted with tetrahydrofuran from different hybrids as a function of PCL/SiO_2 ratio (sol–gel solution concentration: 20 wt%/vol; reaction temperature: room temperature; PCL/SiO_2 ratio calculated assuming the completion of the sol–gel reaction reported in Scheme 1)

Code	PCL/SiO_2 ratio (wt/wt)		
	1/2	1/1	2/1
α-PCL(20)Si/SiO_2	7.3%	17.7%	23.6%
α-PCL(50)Si/SiO_2	6.7%	19.4%	24.2%
α,ω-PCL(20)Si/SiO_2	6.2%	13.5%	18.7%
α,ω-PCL(50)Si/SiO_2	10.3%	19.7%	28.1%

On the contrary to PCL–Si samples, all the prepared PCL–Si/SiO_2 hybrids were fully transparent and DSC analysis showed no melting transitions. Both evidences are preliminary indications for the formation of a morphology in which PCL and silica phases have dimensions less than the wavelength of visible light and that PCL chains bonded to silica domains are not able to organize themselves into crystalline domains.

Weight loss data obtained by TGA in air showed the presence of a residue whose amount was in good agreement with the theoretical content of silica, as calculated from the initial composition and according to the reactions proposed in Scheme 1.

As previously reported [18], a fraction of organic phase may result extractable in tetrahydrofuran after curing being not chemically bonded to the silica domains; for this reason selective extraction of unreacted PCL was carried out on all the samples prepared in this work using tetrahydrofuran as solvent. The Soxhlet extraction data are reported in Table 3. A linear increase of the extracted fraction with the PCL content was noted in all cases. The extraction of PCL segments may derive from both the incomplete formation of covalent bonding between organic and inorganic phases during sol–gel reaction and/or from the hydrolysis of PCL chains notwithstanding their bonding to silica, remembering that sol–gel reactions were carried out under strong acidic conditions. ^{1}H-NMR analysis of the extracted fraction showed the absence of triethoxysilane groups and the presence of carboxylic acid terminal groups, and therefore seems to support the above reported hypothesis.

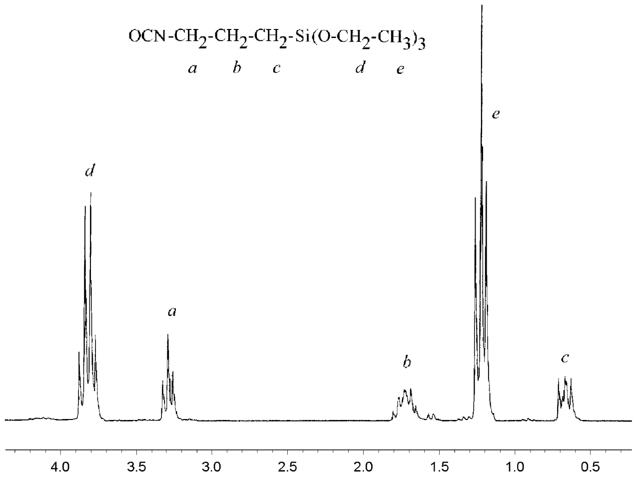

Fig. 2. ^{1}H-NMR spectra of ICPTES with the corresponding signal assignments.

TEM micrographs of a thin film of ceramer cast onto a copper grid showed (Fig. 4) the presence of two different phases having domain size less than 5 nm, clearly indicating the formation of a nanosized morphology, that can explain transparency and the disappearing of any PCL melting transition.

3.1. Coating of PMMA

In order to investigate the effect of different experimental conditions on the final properties of the coating, several samples were prepared using different reaction times and concentrations of the sol–gel solution.

Preliminary tests were carried out by coating PMMA slabs with TEOS sol–gel solutions, without any organic polymer co-reactant. Unfortunately, the resulting films were too brittle and presented very poor adhesion with the PMMA substrate. On the basis of these indications, we decided to use a reactive organic phase, such as PCL, with the purpose to improve the flexibility and the adhesion properties of the hybrids.

A typical SEM micrograph of fracture surface of coated PMMA slabs is reported in Fig. 5. As it appears it is quite easy to measure the coating thickness which values are reported in Fig. 6 for all samples.

From the reported data an almost linear increasing of the coating thickness was noted by increasing both the concentration solution and the time of the sol–gel reaction before dipping. This behavior can be explained taking into account the increase of solution viscosity, due to either the higher initial concentration or the higher extent of the network formation with reaction time, that in turn increases the amount of coating onto the substrate. Furthermore, it is interesting to note the slight effect due to organic–inorganic

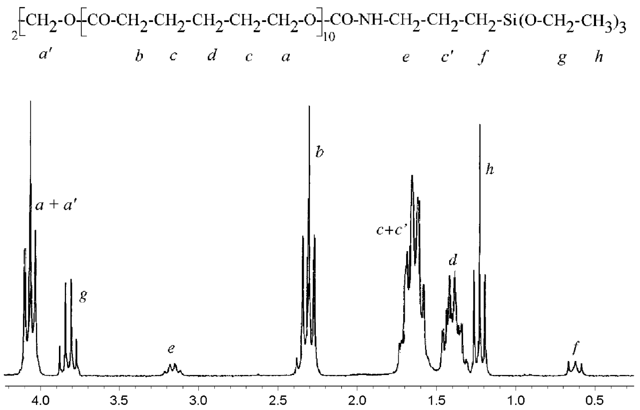

Fig. 3. ^{1}H-NMR spectra of PCL–Si with the corresponding signal assignments.

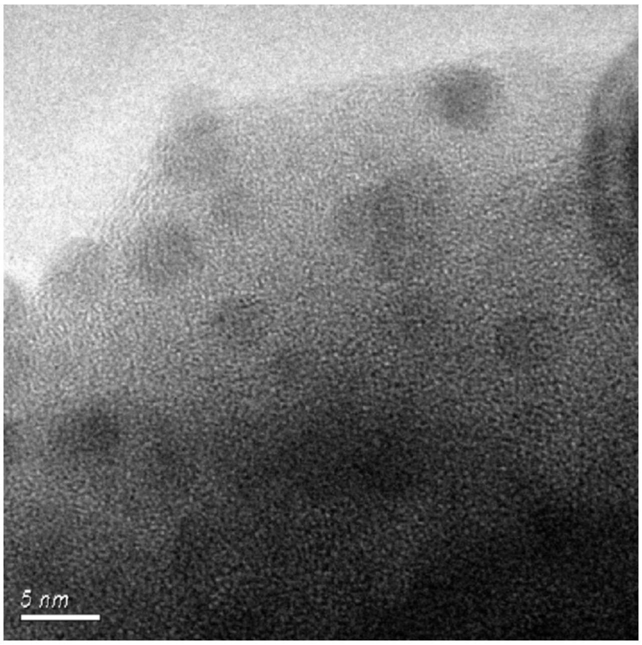

Fig. 4. TEM micrograph of α,ω-PCL(20)Si/SiO_2 2/1 wt/wt (sol–gel solution concentration 5 wt%/vol, sample obtained by casting of PCL–Si/TEOS mixtures on copper grid).

ratio: the systems richer in SiO_2 lead to slightly higher coating thickness, probably due to a higher concentration of reactive functional groups when TEOS/PCL–Si ratio increases, thus leading to more viscous solutions in the same reaction time.

Information about the surface chemical composition of coated PMMA slabs were obtained by XPS analysis. From the surface composition data reported in Table 4, a strong silica surface enrichment compared to the correspondent bulk composition was noted for the investigated samples indicating a preferential segregation of silica domains onto the air-coating interface.

In all samples, the preferential segregation of SiO_2 onto the outer surface, makes the very surface of the coating almost completely inorganic. On the other hand, an enrichment of the organic phase at the coating-PMMA interface can be tentatively supposed taking into account the observed good adhesion between the coating and the substrate as a result of the greater chemical affinity of PCL and PMMA. Some preliminary results of TEM analysis and scratch resistance tests seem to support this hypothesis [22]; in fact, as it can be observed in Fig. 7, the interface between coating and PMMA is not well defined, confirming that at least in the 10–20 nm scale there is a good interconnection between coating and PMMA.

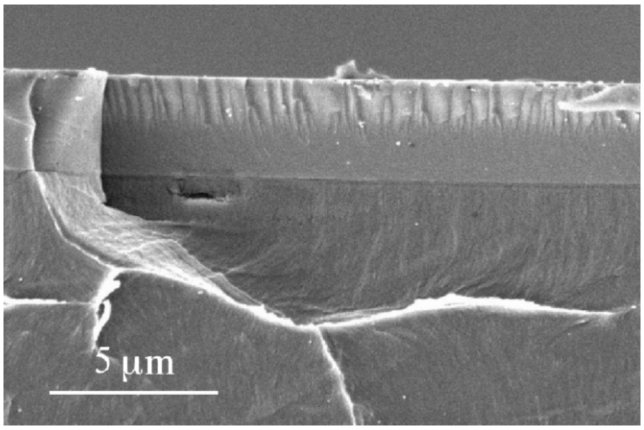

Fig. 5. SEM micrographs of the edge view of fracture surface of PMMA slabs coated with α,ω-PCL(20)Si/SiO_2 1/2 wt/wt (sol–gel solution concentration 40 wt%/vol, reaction time before dipping: 30 min).

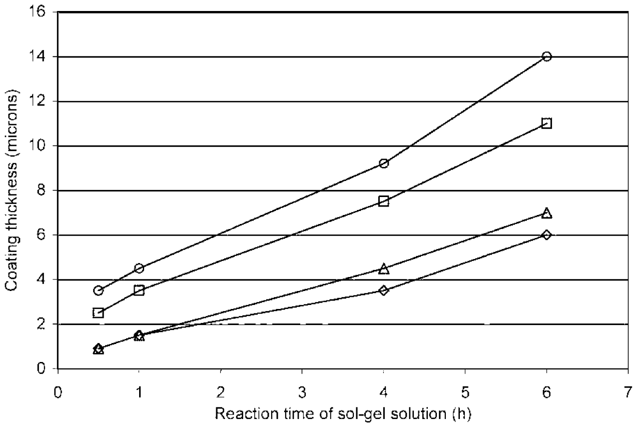

Fig. 6. Thickness of coatings based on α,ω-PCL(20)Si/SiO_2 hybrid as a function of sol–gel solution concentration and reaction time at room temperature before dipping ((◇) PCL/SiO_2 1/1 wt/wt, 20 wt%/vol; (□) PCL/SiO_2 1/1 wt/wt, 40 wt%/vol; (△) PCL/SiO_2 1/2 wt/wt, 20 wt%/vol; (○) PCL/SiO_2 1/2 wt/wt, 40 wt%/vol).

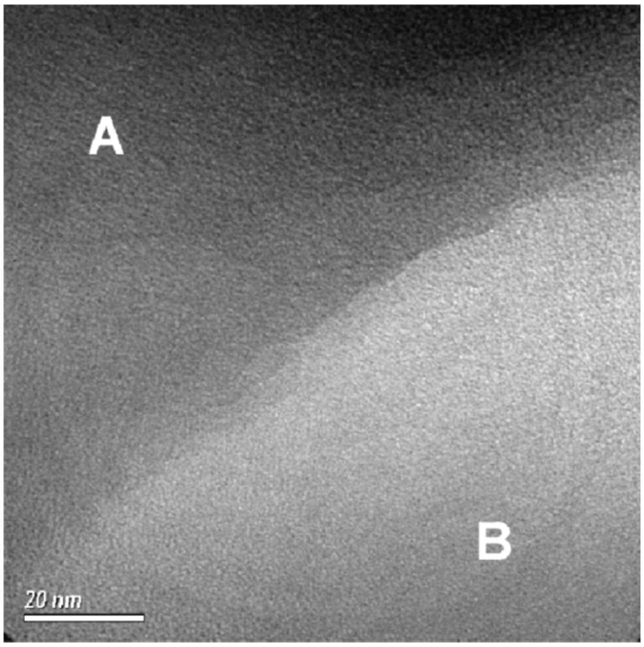

Fig. 7. TEM micrograph of the edge view of ultramicrotomed surface of PMMA slabs coated with α,ω-PCL(20)Si/SiO_2 1/1 wt/wt (sol–gel solution concentration 20 wt%/vol, reaction time before dipping: 30 min; A: coating zone, B: PMMA zone).

Table 4

XPS analysis of outer surface of PMMA coated with α,ω-PCL(20)Si/SiO_2 (PCL/SiO_2 ratio calculated assuming the completion of the sol–gel reaction reported in Scheme 1)

PCL/SiO_2 ratio (wt/wt)	SiO_2 bulk content (wt%)[a]	Si/C atomic ratio[b]	SiO_2 surface content (wt%)[b]
2/1	33	0.74	70
1/2	67	1.42	82

[a] From initial composition.
[b] From XPS analysis.

Some preliminary tests of flame resistance of coated and uncoated samples were performed by using a Glow Wire Test apparatus, in which the time necessary to have flame ignition after the contact between the specimen and the hot glow wire (730 °C) was measured. Operative conditions for the preparation and application of these hybrids were chosen to lead to a coating thickness of about 4 μm for all samples; the results are reported in Table 5.

In all cases, a very strong increase of flame resistance (ranging from 70 to 120%) was noted with respect to uncoated PMMA. However, a straightforward correlation of molecular structure (i.e. molecular weight and/or functionality) and composition with time to flame is not clearly evident. Quite similar results, observed for samples with different PCL/SiO_2 ratios, can be explained taking into account the preferential surface segregation of silica phase which was found in all cases high enough to ensure an efficient barrier against diffusion of oxygen and low molecular weight by-products (methyl methacrylate monomer) which are responsible for flame ignition. These results are in line with current thinking about the flame retardant mechanism operating in nanocomposites obtained by dispersion of an inorganic nanophase into a polymer matrix. However, in this latter case the inorganic component is dispersed throughout the polymer bulk and can hardly reach concentration as high as 80% onto the surface, as observed in the present study.

In addition, flame resistance data obtained after UV radiation exposure showed that this treatment was very detrimental for uncoated PMMA, in fact it was observed a decrease of the time to flame of 24% probably due to the photo-oxidation and the formation of low molecular weight products onto the surface. On the contrary, the time to flame for coated PMMA subjected to the same UV radiation exposure time was almost unchanged as reported in Table 5 indicating that the hybrid coating is also able to improve UV resistance of PMMA.

4. Conclusions

α- and α,ω-triethoxysilane terminated PCL (PCL–Si) were prepared and used to obtain organic–inorganic hybrid coatings with different organic/inorganic ratios by the sol–gel approach. TEM analysis, as well as visual transparency and DSC data, were in agreement with the formation of a nanocomposite structure with a high level of interpenetration between PCL and SiO_2 phases. The coating thickness (from 1 to 15 μm) were found to be dependant by both sol–gel reaction time, the concentration of the coating solution and the PCL/SiO_2 ratio. Surface chemical composition, investigated by XPS, showed a preferential segregation of silica onto the outer surface. For all coated samples, a very

Table 5

Flame resistance of PMMA uncoated and coated with different hybrids as a function of PCL/SiO_2 ratio before and after 50 days exposure to UV radiation (sol–gel solution concentration: 20 wt%/vol; reaction temperature: refluxing; reaction time before dipping: 4 h; PCL/SiO_2 ratio calculated assuming the completion of the sol–gel reaction reported in Scheme 1)

Coating code	PCL/SiO_2 ratio (wt/wt)	Time to flame (s)	Std. dev. (s)	Time to flame (s) after UV exposure	Std. dev. (s)
None	–	6.3	0.6	4.8	0.9
α-PCL(20)Si/SiO_2	1/2	12.7	1.1	11.0	0.8
α-PCL(20)Si/SiO_2	1/1	12.3	1.5	–	–
α-PCL(20)Si/SiO_2	2/1	11.7	0.6	–	–
α-PCL(50)Si/SiO_2	1/2	11.3	0.6	–	–
α-PCL(50)Si/SiO_2	1/1	10.7	0.6	–	–
α-PCL(50)Si/SiO_2	2/1	11.3	0.6	–	–
α,ω-PCL(20)Si/SiO_2	1/2	10.7	1.5	–	–
α,ω-PCL(20)Si/SiO_2	1/1	14.0	0.1	13.9	0.8
α,ω-PCL(20)Si/SiO_2	2/1	12.0	1.0	–	–
α,ω-PCL(50)Si/SiO_2	1/2	12.3	1.5	–	–
α,ω-PCL(50)Si/SiO_2	1/1	11.7	2.1	–	–
α,ω-PCL(50)Si/SiO_2	2/1	11.7	0.6	–	–

strong increase of flame resistance (ranging from 70 to 120%) was put in evidence with respect to uncoated PMMA without the loss of transparency. For similar coating thickness, the flame resistance properties were almost independent of molecular weight and/or functionality of the organic component and from PCL–Si/silica ratio. It can be supposed that the preferential surface segregation of silica phase was in all cases enough to ensure sufficient barrier properties toward oxygen and low molecular weight degradation products (methyl methacrylate monomer). Finally, it was also observed that the hybrid coating was able to improve UV resistance of PMMA.

References

[1] For a review of this area, see, for example.Ebdon JR, Jones MS. In: Salamone JC, editor. Polymeric materials encyclopedia. Boca Raton: CRC Press; 1996. p. 2301–411. and references cited therein.

[2] Price D, Pyrah K, Hull TR, Milnes GJ, Ebdon JR, Hunt BJ, Joseph P, Konkel CS. Polym Degrad Stab 2001;74(3):441–7.

[3] Price D, Pyrah K, Hull TR, Milnes GJ, Ebdon JR, Hunt BJ, Joseph P, Konkel CS. Polym Degrad Stab 2002;77(2):227–233.

[4] Kashiwagi T, Hirata T, Brown JE. Macromolecules 1985;18(2): 131–8.

[5] Brown JE, Kashiwagi T. Polym Degrad Stab 1996;52(1):1–10.

[6] Vanlandeghem A, Greger R, Palmers J. WO Patent 01/89721.

[7] Yanagihara K, Kimura M, Shinkai M. JP Patent 61200134.

[8] Brinker CJ, Scherer GW. Sol–gel science. The physics and chemistry of sol–gel processing. New York: Academic Press; 1990.

[9] Schmidt H. Macromol Symp 2000;159:43–55.

[10] Novak BM. Adv Mater 1993;5:422–33.

[11] Taylor A. Paper 29. In Conference Papers of ‘Organic–Inorganic Hybrids’, UK:Guilford, June 2000. p. 12–14.

[12] Amberg-Schwab S, Katschorek H, Weber U, Hoffmann M, Burger A. J Sol–Gel Sci Technol 2000;19(1–3):125–9.

[13] Amberg-Schwab S, Hoffmann S, Bader S, Gessler M. J Sol–Gel Sci Technol 1998;13(1–3):141–6.

[14] Krause S. Polymer–polymer compatibility. In: Paul DR, Newman S, editors. Polymer blends. New York: Academic Press; 1978.

[15] Utracki LA. Commercial polymer blends. London: Chapman and Hall; 1998.

[16] Porter RS, Wang LH. Polymer 1992;33:2019–30.

[17] Pitt CG. Drugs and the pharmaceutical sciences. Biodegrad Polym Drug Delivery Syst 1990;45:71–120.

[18] Tian D, Dubois Ph, Jerome R. Polymer 1996;37:3983–7.

[19] Tian D, Dubois Ph, Jerome R. J Polym Sci, Polym Chem 1997;35: 2295–309.

[20] Tian D, Blancher S, Dubois Ph, Jerome R. Polymer 1998;39: 855–64.

[21] Tian D, Blancher S, Jerome R. Polymer 1999;40:951–7.

[22] Messori M, Toselli M, Pilati F, Fabbri E, Fabbri P, Busoli S. Surf Coat Int Part B, Coat Trans 2003; in press.