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Synthesis and characterisation of silica hybrids based on poly(ε-caprolactone-b-perfluoropolyether-b-ε-caprolactone)

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Abstract

Poly(ε-caprolactone-b-perfluoropolyether-b-ε-caprolactone) (PCL–PFPE–PCL) triblock copolymers having hydroxy end groups were readily functionalised with triethoxysilane end groups by reactions with 3-isocyanatopropyltriethoxysilane. Organic–inorganic hybrids were prepared by using the sol–gel process in the presence of tetraethoxysilane and hydroxy or triethoxysilane terminated PCL–PFPE–PCL. Fully transparent hybrid materials with high content of organic matter were obtained only in the case of alkoxysilane functionalised copolymers. For such systems the PCL–PFPE–PCL copolymer was so intimately mixed with the inorganic network to prevent crystallisation of the PCL segments. The progress of the sol–gel reaction was limited by the early vetrification of the reactive system, while the interpenetration of the organic phase was enhanced by curing the samples at 100 °C. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Perfluoropolyether; Poly(ε-caprolactone); Inorganic–organic hybrids; Ceramers

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1. Introduction

Over the last decade increasingly more attention has been given to organic–inorganic hybrid materials [1] owing to the unique opportunity that these systems provide to combine the attractive properties of inorganic glasses, such as high modulus, thermal stability and low coefficient of thermal expansion, with the high ductility and low temperature processing characteristics of organic polymers. As the two phases are interconnected and the domain sizes of these phases approach those of supramolecular entities, these materials are often known as nanostructured materials or “phase-interconnected” nanocomposites.

Hybrids materials have an immense potential for applications in a variety of advanced technologies, both as structural materials [1,2], including their use as matrices for high performance composites [3] and functional materials [4], such as catalyst supports [5], sensors [6] and active glasses [7]. The main commercial applications, at present, are in the field of protective coatings of both organic and inorganic substrates [8].

The sol–gel process represents the preferred way for the synthesis of these nanostructured materials. The classical sol–gel process consists in a two step hydrolysis–condensation reaction, starting with metal alkoxides $M(OR)_4$, typically tetraethoxisilane $Si(OCH_2CH_3)_4$ or titanium isopropoxide $Ti[OCH(CH_3)_2]_4$, according to Scheme 1.

The overall properties of these nanocomposites are strongly dependant not only on the individual properties

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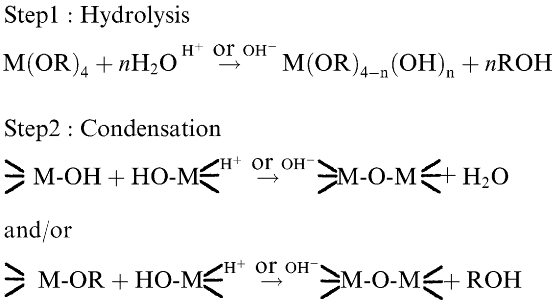

Step1 : Hydrolysis

$$M(OR)_4 + nH_2O \xrightarrow{H^+ \text{ or } OH^-} M(OR)_{4-n}(OH)_n + nROH$$

Step2 : Condensation

$$\geqslant M\text{-}OH + HO\text{-}M\leqslant \xrightarrow{H^+ \text{ or } OH^-} \geqslant M\text{-}O\text{-}M\leqslant + H_2O$$

and/or

$$\geqslant M\text{-}OR + HO\text{-}M\leqslant \xrightarrow{H^+ \text{ or } OH^-} \geqslant M\text{-}O\text{-}M\leqslant + ROH$$

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

of each component but also on their morphological structure.

The commercial availability of telechelic perfluoropolyethers (PFPEs) containing terminal hydroxyl groups [9,10], has made it possible to produce triblock copolymers, such as poly(ε-caprolactone-b-perfluoropolyether-b-ε-caprolactone) (PCL–PFPE–PCL) by the ring opening polymerisation of the monomeric ε-caprolactone (CL), initiated by the hydroxyl end groups of PFPE oligomer [11].

These α,ω-hydroxy terminated triblock copolymers are materials that combine the unusual properties of PFPEs (low glass transition temperatures, in the range −100 to −120 °C, solvent and high temperature resistance, barrier properties, low coefficient of friction, hydrophobicity and in particular very low surface energy) with those of PCL, such as miscibility with a wide variety of organic polymers [12], biocompatibility and biodegradability [13]. The fluorinated phase of PCL–PFPE–PCL triblock copolymers tends to be segregated towards the outer surface due to the strong thermodynamic drive to minimise the surface energy. Furthermore, thermal characterisation of PCL–PFPE–PCL copolymers evidenced the presence also in the bulk of two different phases: one phase located at low temperature was attributed to the fluorinated moiety, while the melting temperature values, related to the PCL blocks, were found to increase by increasing the PCL block length reaching the typical values of homopolymer PCL [14].

PCL–silica hybrids have been extensively studied by Jerome and co-workers [15–18] who have prepared transparent hybrid materials by reacting tetraethoxysilane (TEOS) with hydroxy and triethoxysilane terminated PCL by the sol–gel process. The morphology of these materials was found to be co-continuous, particularly at silica contents greater than 50 wt.%, with surface to surface distance between PCL and silica domains in the region of 5 nm.

In a recent work by Mascia and Tang [19], α,ω-hydroxy terminated PFPE was pre-reacted with chlorendic anhydride in order to convert hydroxy groups into carboxylic groups. Further telechelic chain extension reaction were carried out with unitary CL segments, followed by an end-capping reaction with γ-glycydiloxypropyltrimethoxysilane. This structure modification of pure PFPE was found to be essential to control the morphology of hybrids to dimensions in the nanometer scale length.

The present study is concerned with the preparation and the characterisation of hybrid materials based on PCL–PFPE–PCL, where the CL to PFPE molar ratio is 20:1 and the average molecular weight of each PCL block is 1140. The longer chain lengths of PCL segments makes such systems more miscible in solvents which are more commonly used in sol–gel processing of organic–inorganic hybrid materials. It is primarily in this respect that the present study differs from the previous work cited earlier.

2. Experimental

2.1. Materials

(a) The perfluoroether oligomer used in this study was Fomblin Z-DOL TX (supplied by Ausimont), which can be represented by the following formula:

$$H\text{–}(OC_2H_4)_{1.5}\text{–}OCH_2CF_2O\text{–}(C_2F_4O)_p(CF_2O)_q\text{–}CF_2CH_2O\text{–}(C_2H_4O)_{1.5}\text{–}H$$

where the constituent units $-C_2F_4O-$ and $-CF_2O-$ are randomly distributed along the macromolecular chains with p/q ratio of 0.9. The molar mass of this fluorinated macromer is 2200 $g\,mol^{-1}$. For the purpose of identification this will be referred to as TX2.

(b) High purity tetraethoxysilane (TEOS, Aldrich), 3-isocyanatopropyltriethoxysilane (ICTES, Fluka), 1,4-diazobicyclo(2,2,2) octane (DABCO, Aldrich), hydrochloric acid at 37% concentration (Carlo Erba), ethanol (Carlo Erba), tetrahydrofuran (Carlo Erba) and tin(II) octoate (Aldrich) were used without further purification.

(c) CL and toluene (both from Aldrich) were both dried over calcium hydride and distilled before use.

2.2. Preparation of α,ω-hydroxy terminated PCL–PFPE–PCL block copolymers

α,ω-hydroxy terminated PCL–PFPE–PCL block copolymers were prepared in bulk by ring opening polymerisation of CL at 120 °C, using TX2 as transfer agent (TX2/CL = 1/20 mol/mol) in the presence of tin(II) octoate as initiator. The procedure is very versatile and makes it possible to prepare copolymers containing precise lengths of PCL block, thereby permitting to alter considerably the solubility characteristics [11].

For the purpose of this paper the structure of the block copolymer:

$$H[O–(CH_2)_5–CO]_{10}–(OC_2H_4)_{1.5}–OCH_2CF_2O–(C_2F_4O)_p(CF_2O)_q–CF_2CH_2O–(C_2H_4O)_{1.5}–[CO–(CH_2)_5–O]_{10}H$$

will be abbreviated to HO–PCL–PFPE–PCL–OH and coded as TXCL. The product was dried overnight at room temperature under reduced pressure before use.

2.3. Preparation of α,ω-triethoxysilane terminated PCL–PFPE–PCL block copolymers

α,ω-hydroxy terminated PCL–PFPE–PCL oligomer was dissolved in toluene and dried by repeated azeotropic distillation of the solvent just before use. It was then redissolved in dry toluene (5 wt.%/vol) and ICTES was added to a TXCL/ICTES molar ratio of 1:2.2 followed by the addition of DABCO at a molar ratio of 1:1 with respect to hydroxyl groups. The reaction was carried out under refluxing conditions for about 7 h and the product was recovered by precipitation in cold methanol, thereby removing DABCO and the excess ICTES which remained in solution. The product was dried overnight at room temperature under reduced pressure before use.

2.4. Preparation of PCL–PFPE–PCL/silica hybrids

PCL–PFPE–PCL/TEOS mixtures at three weight ratios, respectively 2:1, 1:1 and 1:2, were dissolved in tetrahydrofuran (about 20 wt.%/vol) and a stoichiometric amount of water with respect to ethoxide groups was added, for the hydrolysis reaction, together with appropriate amounts of ethanol to miscibilise the water and hydrochloric acid (5 mol%/mol with respect to ethoxide groups) as catalyst. These are expected to give a theoretical concentration of organic component in the final hybrid equal to 63.4%, 77.5% and 87.3% by weight, respectively.

A typical preparation was as follow: 1.0 g of TEOS and 1.0 g of PCL–PFPE–PCL (either hydroxyl or triethoxysilane terminated) were added to 10 ml of tetrahydrofuran and mixed until a homogeneous solution was obtained. Then ethanol (1.15 ml), water (0.29 ml) and hydrochloric acid (12 N solution, 0.10 ml) were added under vigorous stirring at room temperature for about 10 min. The clear solution was subsequently cast into a closed Petri dish and the solvent was slowly evaporated at room temperature for one week. These systems were also subjected to a "post-cure" treatment at 100 °C overnight.

2.5. Characterisation

FT-IR analysis was performed with a Brucker IFS48 spectrometer. A minimum of 64 scans of a resolution of 2 cm^{-1} was used. Samples were analysed as thin films cast on sodium chloride window. ^1H-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 Perkin Elmer DSC 7 instrument in the range −20 to 100 °C with a heating rate of 20 °C/min and using two heating cycles in order to estimate the extent of residual reactions and/or physical transitions.

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

3. Results and discussion

The progress of the reaction between α,ω-hydroxy terminated PCL–PFPE–PCL and ICTES was monitored using FT-IR spectroscopy analysis by comparing the broad absorption band of the hydroxyl groups of HO–PCL–PFPE–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.

It was found that, under the experimental conditions used in this study, the reaction goes to completion within 7 h.

The expected structure was also confirmed by the ^1H-NMR spectra of the reactants α,ω-hydroxy terminated PCL–PFPE–PCL and ICTES. Typical spectra for the reaction product and the corresponding signal assignment are reported in Fig. 2 and in Table 1, respectively.

The spectrum of the final product reported in Fig. 2(c) shows the presence of signals attributable to both reactants, which is a clear indication that they were linked together, bearing in mind that the purification procedure used ensures that no residual reactants would be present. Furthermore, the signal at 3.65 ppm, related to the methylene groups adjacent to hydroxyl end groups of HO–PCL–PFPE–PCL–OH (1-f in Table 1), was not present in the spectra, indicating that the reaction between terminal groups of TXCL and isocyanato groups has gone to completion. (Note that the signal of the above mentioned methylene groups after reaction is probably covered by other signal.)

Finally, the ratio between signals related to internal PFPE segment (4.25 ppm, 1-b in Table 1) and to propylsilane groups (0.70 or 3.30 ppm, 2-c and 2-e in Table 1,

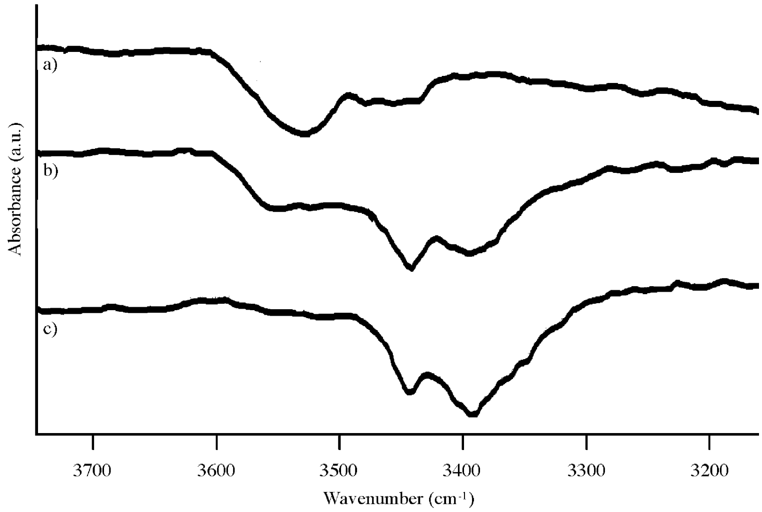

Fig. 1. FT-IR spectra of the reaction product with α,ω-hydroxy terminated PCL–PFPE–PCL and ICTES at different reaction times: (a) 0 h; (b) 2 h and (c) 7 h.

respectively) within the experimental error, is approximately 1:1. This points to the presence of two triethoxysilane terminal groups for each PCL–PFPE–PCL chain, according to reaction shown in Scheme 2.

The final product is coded TXCLSi and its structure can be abbreviated to $(EtO)_3Si$–PCL–PFPE–PCL–$Si(OEt)_3$, neglecting the urethane groups between Si atoms and PCL segments.

The thermal properties of TXCL and TXCLSi oligomers are reported in Table 2. These show that both samples exhibit a melting transition, attributable to PCL segments, at the temperatures of 58.1 and 61.4 °C, respectively. The micrographs in Fig. 3 showed the α,ω-triethoxysilane terminated PCL–PFPE–PCL block copolymers displays a finer spherulitic structure, probably due to the presence of end groups which may hinder the growth of spherulites by steric effects.

Scheme 3 shows a simplified reaction scheme for the preparation of PCL–PFPE–PCL/silica hybrids from α,ω-triethoxysilane and α,ω-hydroxy terminated PCL–PFPE–PCL block copolymers. It is possible, however, that there will be also a direct reaction between the hydroxyl and ethoxy end groups.

The main characteristics of PCL–PFPE–PCL/silica hybrids are summarised in Table 3.

A large difference in structure is clearly evident between hybrids produced from α,ω-triethoxysilane terminated PCL–PFPE–PCL block copolymers and those obtained from α,ω-hydroxy terminated systems, even by simple visual inspection. TXCL based hybrids were opaque in appearance at high contents of organic component (i.e. TXCL-H and TXCL-M) and were only transparent for systems with a low organic phase content (TXCL-L), indicating the occurrence of a considerable phase segregation which allows the PCL segments to crystallise (see optical micrographs in Fig. 3).

On the contrary, TXCLSi based hybrids gave only slightly translucent products at the highest content of organic matter (TXCLSi-H) and fully transparent for low contents of the organic component (TXCLSi-M and TXCLSi-L). This is a clear indication of the better degree of interpenetration between inorganic and organic phases obtained with α,ω-triethoxysilane terminated PCL–PFPE–PCL block copolymers. The transparency of the systems confirms that the domains are very small; further investigation on the phase morphology of the hybrids with SEM and/or TEM will be carried out in a future work.

On the basis of these data it is clear that the functionalisation of the triblock copolymers through the introduction of triethoxysilane end groups enhances considerably the compatibility of the organic and inorganic components of the hybrid system. At the same time it is remarkable to note that a quite high level of compatibility can be achieved even when hydroxyl functional end groups are present in the triblock copolymers. This is to be attributed to the high affinity of the ester groups in the PCL segments with the hydroxyl groups in the silica phase, as pointed out by Jerome et al. [15–18].

From the results obtained, it is clear that functionalisation of PCL–PFPE–PCL block copolymers with triethoxysilane reactive end groups gives a much finer morphology, particularly at low silica concentration.

The thermal data show that the first heating scan trace for the hybrids only cured at room temperature

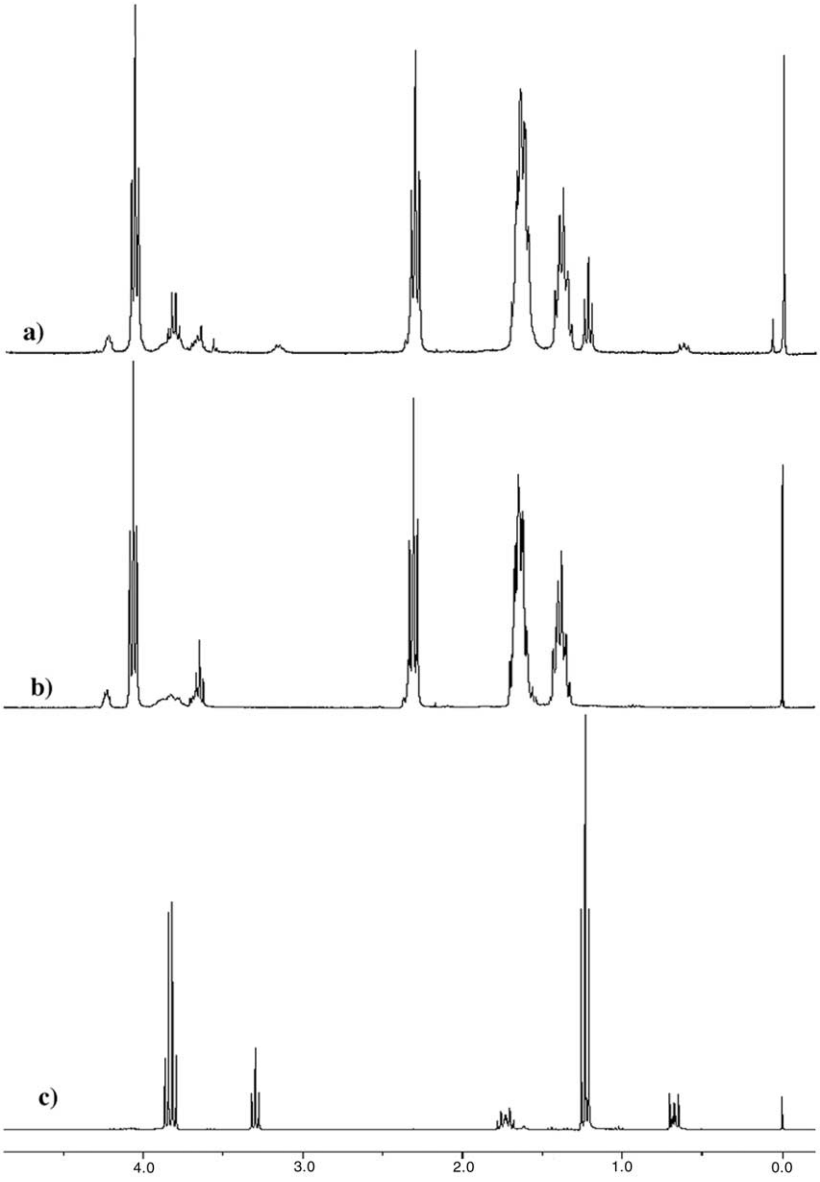

Fig. 2. ^{1}H-NMR spectra of (a) purified reaction product, (b) α,ω-hydroxy terminated PCL–PFPE–PCL and (c) ICTES.

Table 1
^{1}H-NMR assignments of the reactants TXCL and ICTES (m: multiplet; q: quadruplet; t: triplet; s: singlet)

1	$-PFPE-CF_2-\underset{a}{CH_2}-O(\underset{a}{CH_2}-\underset{a}{CH_2}-O)_{0.5}-\underset{a}{CH_2}-\underset{b}{CH_2}-O-(CO-\underset{c}{CH_2}-\underset{d}{(CH_2)_3}-\underset{e}{CH_2}-O)_n-CO-\underset{c}{CH_2}-\underset{d}{(CH_2)_3}-\underset{f}{CH_2}-OH$ a: 3.70–3.95 ppm, m, 6H; b: 4.25 ppm, m, 2H; c: 2.30 ppm, t, 2H; d: 1.40–1.65 ppm, m, 6H; e: 4.05 ppm, t, 2H; f: 3.65 ppm, t, 2H
2	$(\underset{a}{CH_3}-\underset{b}{CH_2}-O)_3-Si-\underset{c}{CH_2}-\underset{d}{CH_2}-\underset{e}{CH_2}-N{=}C{=}O$ a: 1.25 ppm, q, 9H; b: 3.85 ppm, t, 6H; c: 0.70 ppm, m, 2H; d: 1.75 ppm, t, 2H; e: 3.30 ppm, m, 2H

produces a very broad endothermic peak almost in all cases which is attributed to the combined effects of evaporation of residual volatiles (such as water, ethanol and solvent) and further loss of water from the sol–gel

$$\text{HO-PCL-PFPE-PCL-OH} + 2(\text{EtO})_3\text{Si}(\text{CH}_2)_3\text{NCO} \rightarrow$$
$$(\text{EtO})_3\text{Si}(\text{CH}_2)_3\text{-NH-CO-O-PCL-PFPE-PCL-O-CO-NH-}(\text{CH}_2)_3\text{-Si}(\text{OEt})_3$$

Scheme 2. Formation of α,ω-triethoxysilane terminated PCL–PFPE–PCL block copolymers.

Table 2
Melting temperature and enthalpy of TXCL and TXCLSi oligomers (from DSC data, second scan)

Code	T_m (°C)	ΔH (J/g)
TXCL	58.1	46.4
TXCLSi	61.4	42.0

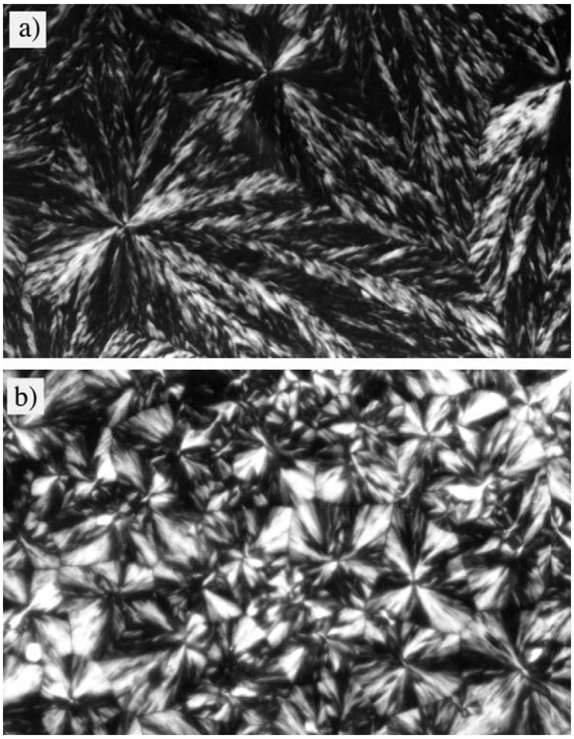

Fig. 3. Optical micrographs of (a) TXCL and (b) TXCLSi block copolymers (600×).

reaction. This is an indication that the condensation reactions at room temperature are not complete, due to vetrification of the gel which hinders the diffusion of reactants. Such a deduction is supported by the observation that the thermograms for the second heating scan were free from any broad endothermic peaks.

In the case of hybrids with high PCL–PFPE–PCL/silica ratio a melting peak attributed to PCL segments was observed in the range 45–46 °C suggesting a low level of interpenetration of the organic and inorganic phases.

For these systems the degree of crystallinity, α, was very high ($\alpha = 54.1\%$) and increased slightly after curing at 100 °C ($\alpha = 56.1\%$). For TXCL-M (medium content of organic component), on the other hand, crystallinity was hardly detectable. No melting transitions was recorded and only a small melting endotherm ($\alpha = 0.7\%$) was observed for systems cured at both room temperature and 100 °C. The system TXCL-L (low content of organic component) did not show any melting transition at all and the films were very transparent.

Conversely, the system TXCLSi-H (high content of organic matter) exhibited a degree of crystallinity much lower than the corresponding α,ω-hydroxy terminated oligomer based hybrid. Furthermore, curing at 100 °C had only a negligible effect on crystallinity. The α value decreased from 3.8% to 2.6%. Both TXCLSi-M and TXCLSi-L systems did not show a melting transition.

The above data for TXCL based hybrids can be explained by taking into account the fact that prolonged curing at high temperature (higher than T_m of the system) can increase the extent of segregation of the PCL containing phase, thereby allowing crystallisation to take place. In the case of hybrids prepared with α,ω-triethoxysilane terminated oligomers, on the other hand, the segregation is inhibited by the formation of covalent bonds between the organic and inorganic phases and the only effect observed after curing was to advance the sol–gel reaction.

A further support for the above explanations was obtained from the Soxhlet extraction data (reported in Table 4) which gave information related to the extent of the organic oligomers entering the silica network. In the case of hybrids cured at room temperature a large amount of the extracted fraction was noted, suggesting that there was only a low degree of interpenetration of the organic and inorganic phases.

The amount of extractable organic phase, on the other hand, decreased considerably for both TXCL and TXCLSi based hybrids after curing at 100 °C. Furthermore, the extracted matter for the samples having similar organic/inorganic content was found to be always higher in the case of α,ω-hydroxy terminated PCL–PFPE–PCL block copolymers (TXCL based hybrids) relative to α,ω-triethoxysilane terminated (TXCLSi based hybrids), due to the higher reactivity of the latter end groups.

The data on the extractable organic fraction from the hybrids are in agreement with those reported by Jerome et al. [15] for PCL/silica hybrids. It is to be noted that the ^{1}H-NMR analysis carried out on the extracted

1. $Si(OEt)_4 + 4H_2O \rightarrow Si(OH)_4 + 4EtOH$

2a. $(EtO)_3Si\text{-}PCL\text{-}PFPE\text{-}PCL\text{-}Si(OEt)_3 + 6H_2O \rightarrow (HO)_3Si\text{-}PCL\text{-}PFPE\text{-}PCL\text{-}Si(OH)_3 + 6EtOH$

2b. $(HO)_3Si\text{-}PCL\text{-}PFPE\text{-}PCL\text{-}Si(OH)_3 + Si(OH)_4 \rightarrow \text{-}O\text{-}Si\text{-}O\text{-}Si\text{-}PCL\text{-}PFPE\text{-}PCL\text{-}Si\text{-}O\text{-}Si\text{-}O\text{-} + H_2O$

3. $HO\text{-}PCL\text{-}PFPE\text{-}PCL\text{-}OH + Si(OH)_4 \rightarrow \text{-}O\text{-}Si\text{-}O\text{-}PCL\text{-}PFPE\text{-}PCL\text{-}O\text{-}Si\text{-}O\text{-} + H_2O$

Scheme 3. Preparation of PCL–PFPE–PCL/silica hybrids from, α,ω-triethoxysilane and α,ω-hydroxy terminated PCL–PFPE–PCL block copolymers (idealised reactions).

Table 3
DSC data of PCL–PFPE–PCL/silica hybrids

Code	Content of organic component (wt.%)[a]	Curing at 23 °C			Curing at 100 °C			
		T_m (°C)[b]	ΔH (J/g)	α[c]	Appearance[d]	T_m (°C)[b]	ΔH (J/g)	α[c]
TXCL-H	87.3	46.1	21.9	54.1	O	45.4	22.7	56.1
TXCL-M	77.5	n.d.	n.d.	0.0	O	56.4	0.2	0.7
TXCL-L	63.4	n.d.	n.d.	0.0	T	n.d.	n.d.	0.0
TXCLSi-H	86.9	44.7	1.4	3.8	TL	52.1	1.0	2.6
TXCLSi-M	76.8	n.d.	n.d.	0.0	T	n.d.	n.d.	0.0
TXCLSi-L	62.4	n.d.	n.d.	0.0	T	n.d.	n.d.	0.0

[a] Theoretical, according to the reaction scheme proposed.

[b] Melting temperature (second scan); n.d.: not detected.

[c] Percentage of crystallinity with respect to the theoretical (based on ΔH values of TXCL and TXCLSi pure macromers reported in Table 2.

[d] O: opaque; TL: translucent; T: transparent.

Table 4
Soxhlet extraction data

Code	PCL–PFPE–PCL content (wt.%)	Extracted fraction (wt.%)	
		Curing at 23 °C[a]	Curing at 100 °C[a]
TXCL-H	87.3	74.2 (85.0)	49.3 (56.5)
TXCL-M	77.5	63.2 (81.5)	37.5 (48.4)
TXCL-L	63.4	45.2 (71.3)	24.1 (38.0)
TXCLSi-H	86.9	57.4 (66.1)	37.4 (43.0)
TXCLSi-M	76.8	52.7 (68.6)	29.9 (38.9)
TXCLSi-L	62.4	38.8 (62.2)	23.2 (37.2)

[a] In bracket the percentage of extracted fraction with respect to the theoretical organic content is reported.

fraction has revealed the presence of PCL oligomers having both carboxylic and hydroxy end groups, thus the extracted organic fraction has to be attributed to simultaneous hydrolysis reactions within the PCL blocks during the production of the respective hybrids, particularly under acidic conditions.

4. Summary and conclusions

Hydroxy terminated PCL–PFPE–PCL triblock copolymers were readily functionalised with triethoxysilane end groups through reactions with ICTES, in the presence of DABCO, used as catalyst.

Transparent PCL–PFPE–PCL/silica hybrid materials with high organic content were obtained only in the case alkoxysilane functionalised oligomers. For such systems the PCL–PFPE–PCL copolymer was intimately interconnected with the inorganic network to prevent the crystallisation of the PCL segments.

The progress of the sol–gel reaction was curtailed by the early vetrification of the reactive system, while the interpenetration of the organic phase was enhanced by curing the samples at high temperature (100 °C).

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