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Recent findings in (Ti)POSS-based polymer systems

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Abstract Novel polymer hybrids based on a Ti-containing polyhedral oligomeric silsesquioxane—(Ti)POSS—and two polymer matrices—polyamide 6 (PA6) and a styrene-maleic anhydride copolymer (PSMA)—have been prepared by different approaches (namely, in situ polymerization, melt blending, grafting) in order to investigate the dispersion level of (Ti)POSS within the organic polymer matrices in view of potential in situ catalytic activity of the metal. The chemical characterization of the prepared hybrid systems, performed by infrared spectroscopy and nuclear magnetic resonance, and their morphological analysis, evaluated by electron microscopy and X-ray diffraction, have shown that it is possible to homogeneously distribute and finely disperse (Ti)POSS at nanometric level within PA6 and PSMA. In this manner, an easy incorporation of metal functionalities into the above polymer matrices has been achieved and extension to other polymer systems can be foreseen.

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Introduction

Polyhedral oligomeric silsesquioxanes, known with the acronym of POSS and often referred to as molecular silica, are emerging as a new class of very interesting chemical compounds, easily functionalized and inserted in a variety of organic/inorganic hybrids. The family of POSS molecules consists of a thermally and chemically robust cage made of Si and O atoms, with suitable R substituents able to improve solubilization of the cage in various media and its compatibilization, on one hand, and X groups, when present, capable to promote coupling or polymerization or grafting, on the other. Owing to POSS size (1–3 nm) comparable to that of polymer segments and coils, under the most favorable circumstances the above hybrids exhibit a nanoscale distribution of POSS, particularly interesting in that POSS is close to be molecularly dispersed in the polymer matrix. As a consequence, high performance nanostructured systems can be obtained with enhanced properties such as, for example, better thermal resistance.

In general, in the wide field of materials science the applications of POSS in hybrid/nanocomposite areas have grown almost exponentially in recent years for their very ample range of applications, including a relevant catalytic behavior. In this respect, POSS molecules containing transition metals in their cage—(M)POSS—have been prepared and characterized by several research groups with the aim of incorporating metal functionalities into the polymer matrices. Indeed, (M)POSS molecules, advantageously applied to the field of homogeneous and heterogeneous catalysis by Abbenhuis et al. among others, [1–4] have been found to greatly enhance thermo-oxidative stability of polymer matrices, such as polystyrene, either alone [5] or in combination with a synthetic clay [6]. Furthermore, the dispersion of (M)POSS molecules containing Al or Zn as metal centers has been found to improve the thermal stability and flame retardancy of PP [7, 8].

Our studies, dealing with hybrid systems based on two polymers (PA6 and PSMA) and (Ti)POSS, have adopted different methods of preparation (in situ polymerization, melt blending, grafting) and are described in detail in the present study. Characterization and properties of the prepared hybrids, evaluated by a number of experimental techniques (FT-IR, ^{1}H-NMR, solution viscosity, DSC, SEM, and WAXD), have been compared with those of the neat polymer matrix in order to define the role of (Ti)POSS in the material end properties.

It is well known that hybrid polymer-POSS systems can be obtained by either a physical or a chemical approach, and both of them, when optimized, will lead to a nanometric distribution of POSS molecules in the matrix polymer and to an improvement of properties and performances of the resultant material. Our attempts to obtain a homogeneous, possibly nanometric distribution of (M)POSS molecules in the above polymer matrices will be herein described, with only a brief mention of some of their envisaged property improvements.

Experimental

Materials

Ti-containing aminopropylisobutylPOSS, (Ti)POSS-NH_2, was synthesized according to the procedure described in the literature [9]. The chemical structure of (Ti)POSS-NH_2 with an isopropoxide group linked to Ti is given in Fig. 1.

ε-Caprolactam (CL), kindly supplied by DSM Research, Geleen, The Netherlands, and ε-aminocaproic acid (ACA, from Fluka) were used as received. Polyamide 6 (PA6) chips were supplied by Rhodia Engineering Plastics Co., Ltd., France, and used as received.

Poly(styrene-*co*-maleic anhydride) (PSMA, Dylark 332), kindly supplied by Nova Chemicals, was characterized by a nominal concentration of maleic anhydride of 14 mol%, checked by ^{1}H-NMR.

Preparation of PA6/(Ti)POSS and PA6/(Ti)POSS: PA6 systems

Hydrolytic PA6 samples were synthesized at high temperature using an aluminum block heated by electric resistors connected to a rheostat. Mixtures of CL, ACA (initiator) and (Ti)POSS were introduced at room temperature into a glass polymerization vessel connected to a vacuum pump and then heated to the polymerization temperature (250 °C) by placing it in the aluminium block under argon flow. Polymerization time was usually set at 4 h. At the end of the reaction, the vessel was rapidly cooled to room temperature under a continuous stream of argon.

In order to prepare the blend with additional PA6, a typical recipe was as follows.

An inorganic/organic hybrid, e.g., that based on 20 wt% of POSS, was finely ground and then diluted with commercial PA6 down to 5 wt% of POSS, using a laboratory internal mixer provided with a mechanical stirrer (Heidolth, type RZR!)

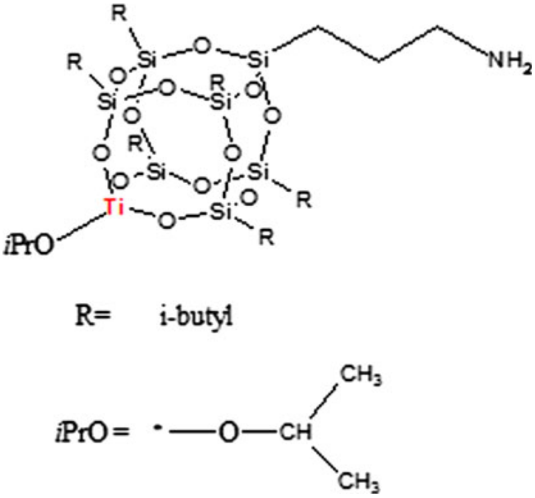

Fig. 1 Structures of (Ti)POSS-NH_2

at a mixing speed of 60 rpm, melt blending the components at 250 °C under nitrogen for 10 min.

Preparation of PSMA/(Ti)POSS hybrid systems

PSMA and (Ti)POSS were mixed under nitrogen in a glass mixer equipped with a mechanical stirrer (Heidolth, type RZR1), applying different mixing times, typically 10 min, at 240 °C. Neat PSMA was processed and characterized under the same conditions as the reference material. In order to evaluate the grafting yield, after melt blending all solid samples were broken in small pieces and unreacted POSS was removed by soxhlet extraction with petroleum ether for 48 h. On the basis of preliminary tests, petroleum ether was found to be an excellent solvent for both POSS-NH_2 and (Ti)POSS-NH_2, while PA6 and PSMA were completely insoluble in it.

The grafting yield was calculated by weighting hybrid samples before and after the washing treatment.

Characterization

The different hybrid materials prepared as described above were characterized in terms of reaction parameters, material appearance, physical properties, etc., by using different characterization techniques as detailed below.

The chemical characterization was carried out using Fourier transform infrared spectroscopy (FT-IR), nuclear magnetic resonance spectroscopy (NMR) and solution viscosity. FT-IR spectra were recorded by a Bruker IFS 66 spectrometer. The KBr pellets were prepared by mixing the sample with KBr powder (ca. 1:100) and hydraulically pressing the mixture at the pressure of 10 tons. All samples were dried at 120 °C for 4 h under inert atmosphere and scanned in the 400–4,000 cm^{-1} range with nitrogen purge. ^1H-NMR spectra were obtained by a Varian 300 MHz NMR, preparing $CDCl_3$ solutions of the samples for PSMA-based hybrids, while PA 6—(Ti)POSS systems were characterized by using a $CDCl_3$/2,2,2-trifluoroethanol (TFE) (50/50 v/v) mixture as the solvent. A Ubbelohde viscometer was used to determine solution viscosities and evaluate molar masses. For the PSMA samples the measurements were performed on polymer solutions in toluene ($c = 0.5$–1 g/dl) at 20 °C while, for PA6 solution viscosities, the measurements were carried out on polymer solutions in H_2SO_4 ($c = 0.5$–1 g/dl) at 20 °C.

The morphological analysis was performed by X-ray diffraction (WAXD) and Scanning Electron Microscopy (SEM). WAXD diffraction patterns were obtained by a Philips powder diffractometer Mod. PW1050 (Ni-filtered Cu $K_{\alpha 1}$ radiation, $k = 1.540562$ Å). WAXD spectra were used to evaluate the crystalline/amorphous content of the polymer material after dispersion with (Ti)POSS. A Leica Stereoscan 440 scanning electron microscope equipped with a backscattered electron detector was used to examine morphologies and Si distribution of the composite sample. The specimens were submerged in liquid nitrogen for 30 min and fractured cryogenically. All samples were thinly sputter-coated with carbon, using a Polaron E5100 sputter coater.

The thermal properties were studied by differential scanning calorimetry (DSC) performed under a continuous nitrogen purge in a Mettler calorimetric apparatus, model TC10A. Data were gathered using a scan rate of 10 °C/min.

Results and discussion

PA6/(Ti)POSS-NH_2

Hybrid systems based on PA6 and (Ti)POSS-NH_2 have been prepared by the in situ hydrolytic polymerization of CL. The above POSS molecule, which show a good solubility in molten CL even at high loadings, has been added to the reaction medium in various concentrations (from 2.5 to 20 wt%). The properties of the prepared hybrids have been compared with those of neat PA6. Table 1 shows bound (Ti)POSS yield and the apparent molar masses of the PA6/(Ti)POSS-NH_2 systems, as well as that of neat PA6. Molar masses have been calculated assuming that the Mark–Houwink–Sakurada relationship adopted for PA6 can be considered roughly valid also for our PA6/(Ti)POSS-NH_2 system. In order to define the amount of (Ti)POSS chemically bound to the polymer matrix, the reaction yield has been evaluated by weighting the sample before and after soxhlet extraction by petroleum ether on ground samples for 24 h. Clearly, this procedure can provide useful information on the kind of interactions occurring between the system components and on the overall amount of bonded (Ti)POSS, as referred to its nominal content in the feed and in the hybrid.

As can be clearly inferred from Table 1, the introduction of the metal silsesquioxane with primary amine functionality acts, as expected, as a PA6 chain terminator and causes a sharp reduction of polyamide molar mass, somehow lowering also the amount of linked (Ti)POSS, although to a very limited extent.

In order to better evaluate the kind of interactions and/or reactions occurring between (Ti)POSS-NH_2 and the polyamide, the prepared hybrids, as well as neat PA6 and (Ti)POSS-NH_2 have been analyzed by FT-IR. IR spectra of (Ti)POSS-NH_2 (a), neat PA6 (b), and AMN-47 sample (based on 20 wt% of (Ti)POSS-NH_2), before (c), and after washing (d) with petroleum ether, a solvent capable to remove unreacted silsesquioxane, are reported in Fig. 2.

Table 1 Characteristics of the samples prepared using different (Ti)POSS concentrations

Sample code	(Ti)POSS-NH_2 concentration in the feed		$M_w \times 10^{-3}$ [a]	Linked (Ti)POSS-NH_2 (%)
	(wt%)	Mole (%)		
PA6	–		30.2	–
AMN-6	2.5	0.2	20.0	100
AMN-10	5	0.5	13.5	100
AMN-47	20	2.2	9.0	97

[a] $[\eta] = 0.51 \times 10^{-3} M_w^{0.74}$ [10]

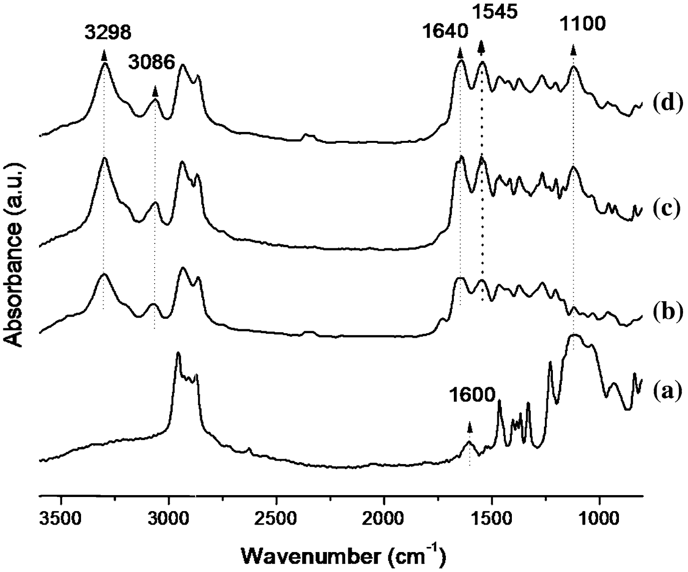

Fig. 2 FT-IR spectra of (Ti)POSS-NH_2 (*a*), neat PA6 (*b*), AMN-47 (before purification) (*c*), AMN-47W (washed to remove unreacted POSS) (*d*). The curves are vertically shifted for clarity

(Ti)POSS-NH_2 shows a strong Si–O–Si stretching absorption band at ca. 1,100 cm^{-1}, which is the typical absorption peak of the silsesquioxane inorganic framework, a band at 920 cm^{-1}, due to Ti–O–Si band, and a peak at 1,600 cm^{-1}, assigned to NH_2 bending of the aminopropyl group, as discussed in detail in Ref. [9]. Neat PA6 shows a characteristic absorption band at 1,640 cm^{-1}, attributed to the amide I band as a result from the C=O stretching vibration of the amide group coupled to the bending of the N–H bond, and a band at 1,545 cm^{-1} due to N–H bending and C–N stretching vibrations [11–13], together with bands at 3,086 and 3,298 cm^{-1}.

The FT-IR spectra of the AMN-47 hybrid, before and after the washing treatment, come out to be very similar between them, being characterized by the absorption bands belonging to both PA6 (1545, 1640, 3086, and 3298 cm^{-1}) and the silsesquioxane (1,100 cm^{-1}). Indeed, it is relevant to underline that the latter band, which is due, as reported above, to Si–O–Si stretching vibration, and the Ti–O-Si band at 920 cm^{-1}, give evidence of the presence of POSS linked to the polymer matrix, as the intensity of these peaks does not disappear in the sample after the attempt of extraction of the unbound POSS.

In addition to the FT-IR investigation on the possible reactions between (Ti)POSS-NH_2 and PA6, the above results have been further confirmed by NMR. Figure 3 shows the ^{1}H-NMR spectrum of the sample AMN-47W, obtained with 20 wt% of (Ti)POSS-NH_2 in the feed and washed in order to remove unreacted POSS, if any. The methylene and isobutyl moieties of the POSS units are evidenced by the peaks at $\delta = 3.2$ [–CH_2CH_2–NH], 1.46 [–CH_2CH_2–CH_2], $\delta = 0.60$ [–Si–CH_2], $\delta = 0.96$ [–CH–$(CH_3)_2$], and $\delta = 1.85$ ppm [–Si–CH_2–CH] [14].

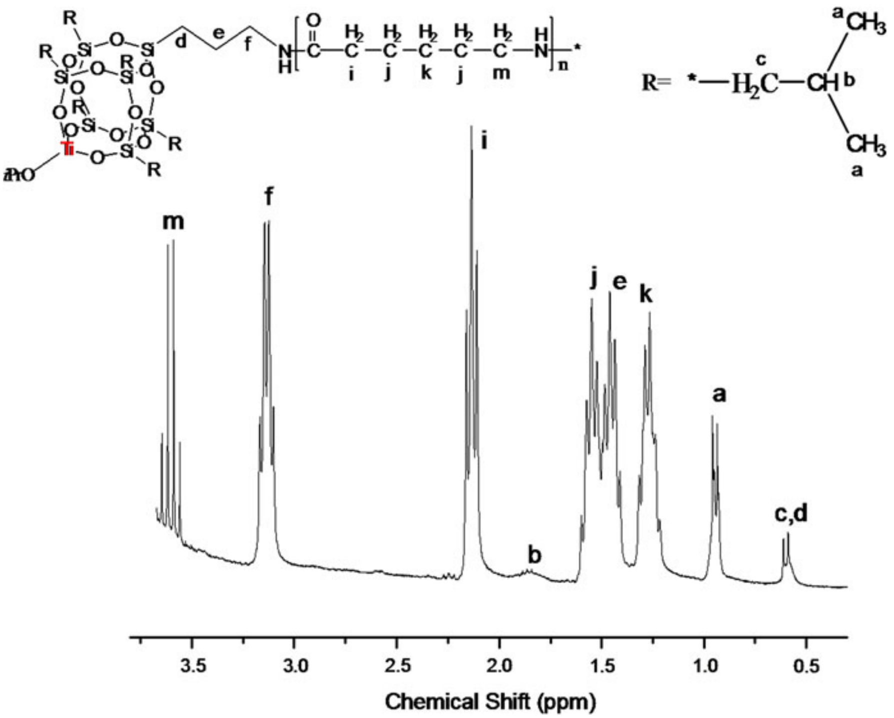

Fig. 3 ^{1}H-NMR spectrum of AMN-47W hybrid

The disappearance of the absorption peak pertaining to the amino group at $\delta = 2.73$ ppm which, on the contrary, is clearly present in neat (Ti)POSS-NH$_2$, also supports its incorporation into PA6. The peaks corresponding to the methylene portion of the PA6 chain have been observed at the δ values of 1.32, 1.43, 1.57, 2.16, and 3.61 ppm [15, 16]. Furthermore, the typical signal of an amide proton around 6.47 ppm has been also detected.

The above results definitively support the insertion of the (Ti)POSS molecules at the end of the polyamide chain (Fig. 4).

SEM investigation, coupled with elemental analysis, has been performed to study the morphology of the various hybrid systems. The prepared samples have been characterized in detail in order to investigate the Si dispersion, the domain size and the adhesion of (Ti)POSS-NH$_2$ particles to the polymer matrix. Figure 5 shows the SEM micrograph of the AMN-10 sample based on PA6 and 5 wt% of (Ti)POSS-NH$_2$. BS emission allowed us to identify the presence and distribution of Si in the polymer matrix and hence to study POSS dispersion.

Examination of the above micrograph does not reveal any POSS aggregates on the sample surface (a), while elemental analysis (b) shows a uniform Si distribution, thus evidencing submicrometer POSS dispersion. Figure 6 shows the micrograph obtained by back scattering emission (BS) of the AMN-47 sample, based on 20 wt% of (Ti)POSS-NH$_2$.

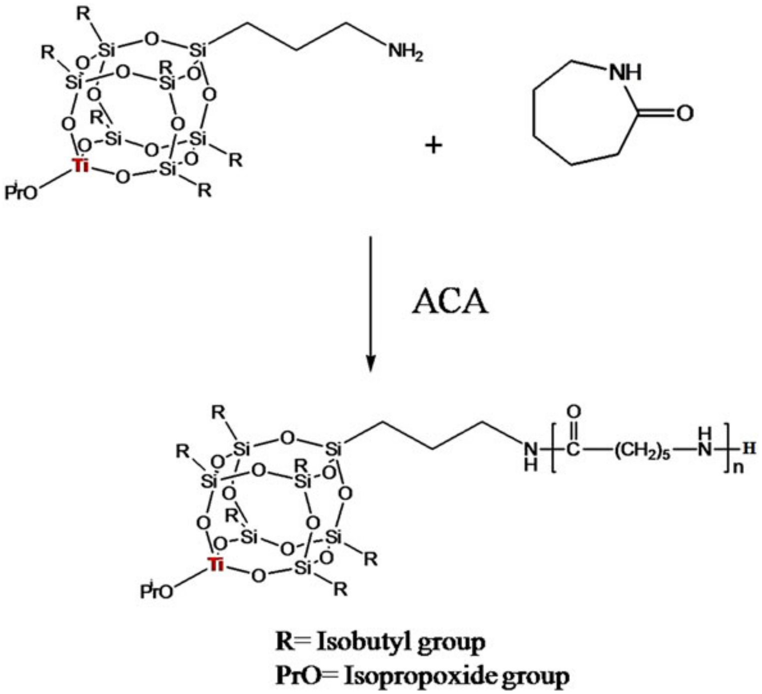

Fig. 4 Reaction scheme for the synthesis of PA6/(Ti)POSS-NH_2 hybrids

No POSS aggregates have been observed on the sample surface, while the elemental analysis has shown a uniform Si distribution, thus evidencing again submicron POSS dispersion.

Besides SEM analysis, X-ray diffraction patterns of neat PA6 and the three PA6/(Ti)POSS-NH_2 systems have been performed in order to confirm the level of POSS dispersion in the polymer matrix and give insights into the system microstructure.

Figure 7 shows the WAXD patterns of (Ti)POSS-NH_2(a), neat PA6(b), AMN-6 (PA6/(Ti)POSS-NH_2 (2.5 wt%)) (c), AMN-10 (PA6/(Ti)POSS-NH_2 (5 wt%)) (d), and AMN-47 (PA6/(Ti)POSS-NH_2 (20 wt%)) (e).

(Ti)POSS-NH_2 is crystalline and shows strong reflections at 2θ of 7.9° (11.2 Å), and 19.9° (4.44 Å). X-ray diffraction patterns of neat PA6 and PA6/(Ti)POSS hybrids are similar, showing the characteristic polyamide crystalline peaks at 2θ of 20.03° and 23.98° which are attributed to the (200) and (002)/(202) plane reflections of α-form, respectively.

It is evident that the silsesquioxane reflections are absent in the WAXD patterns of the hybrid systems, even in the case of AMN-47, which contains 20 wt% of (Ti)POSS. It is worth underling that, in general, the disappearance of (Ti)POSS X-ray peaks in the hybrid systems has always been considered as the proof of full silsesquioxane dispersion in the polymer matrix by grafting and/or reaction.

The above results confirm the obtainment of hybrid systems formed by the reaction of the amino group of (Ti)POSS-NH_2 with the COOH groups of the

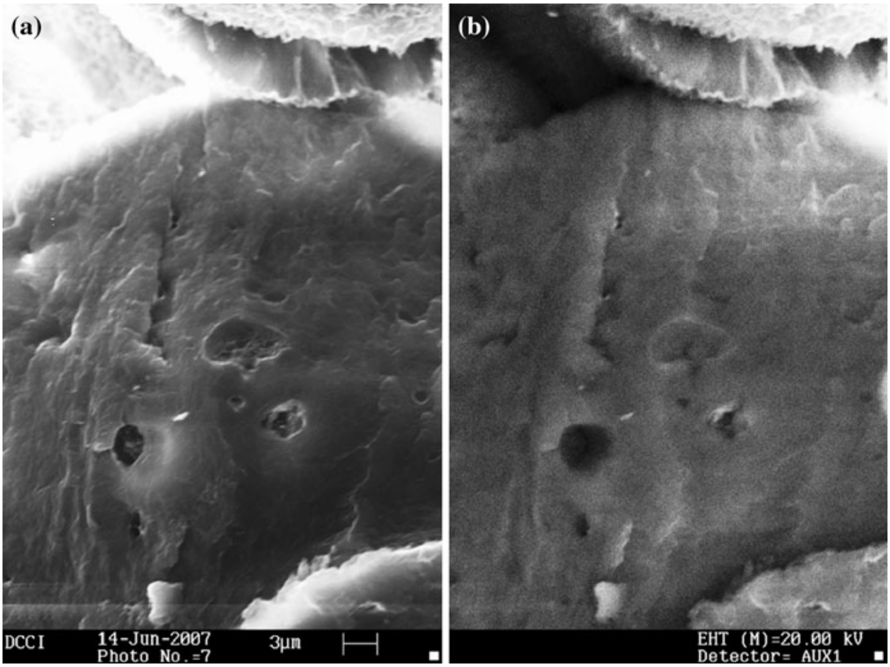

Fig. 5 SEM micrographs of AMN-10: secondary electron (**a**) and back scattering emission (**b**)

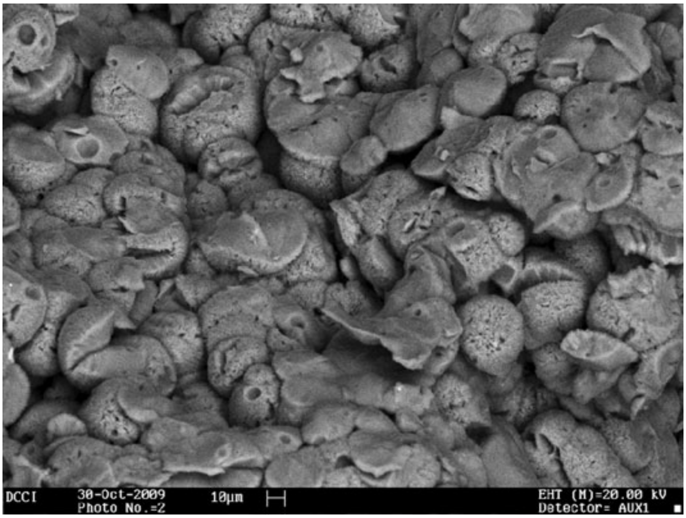

Fig. 6 SEM micrograph of AMN-47

polymer chain, which stops the macromolecular chain growth. Moreover, as the fixation of POSS by PA6 is almost complete even when present at high concentrations (i.e., 20 wt%) in the reaction medium, it is thus possible by this

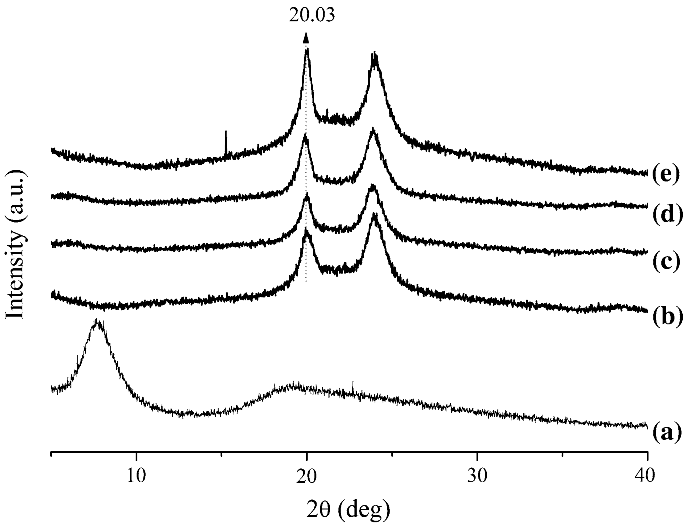

Fig. 7 X-ray diffraction patterns of (Ti)POSS-NH_2 (*a*), neat PA6 (*b*), AMN-6 (*c*), AMN-10 (*d*), and AMN-47 (*e*)

procedure to entirely avoid the formation of silsesquioxane aggregates and achieve their almost nanometric dispersion.

It is evident that, because of the obtainment of low molar mass polyamide even at low POSS concentrations, the above in situ polymerization is not a suitable method per se for the preparation of hybrid polymer materials based on amine-functionalized POSS molecules. However, it can be used as a Ti-conveying component of polymer blends. To verify the suitability of this approach, the synthesized low molar mass PA6/(Ti)POSS-NH_2 hybrid, based on the highest POSS concentration, has been melt mixed with neat PA6.

The SEM micrograph of the AMN-60 sample, prepared by melt mixing of PA6 and AMN-47, is shown in Fig. 8. The surface of this sample displays a uniform Si distribution without any visible aggregates, thus suggesting the formation of nanostructured materials, where the metal can be easily introduced and finely dispersed.

As widely reported, among the polymer features affected by POSS, either physically dispersed or chemically attached to polymer chains, it is relevant to consider the thermal behavior of the derived systems. On this basis, the PA6/(Ti)POSS-NH_2 systems prepared by our team have been investigated by DSC analysis. Table 2 shows the DSC results both of neat PA6 and the hybrids. It can be seen that the PA6/(Ti)POSS-NH_2 systems show a very little decrease, if any, of the melting temperature (T_m) compared to that of neat PA6, well inside the experimental errors, indicating that incorporation of (Ti)POSS-NH_2 does not appreciably affect the T_m of PA6. Conversely, the decrease of crystalline content from the first to the second heating is rather relevant and easily explained when the high cooling rate adopted for the thermal cycle is considered.

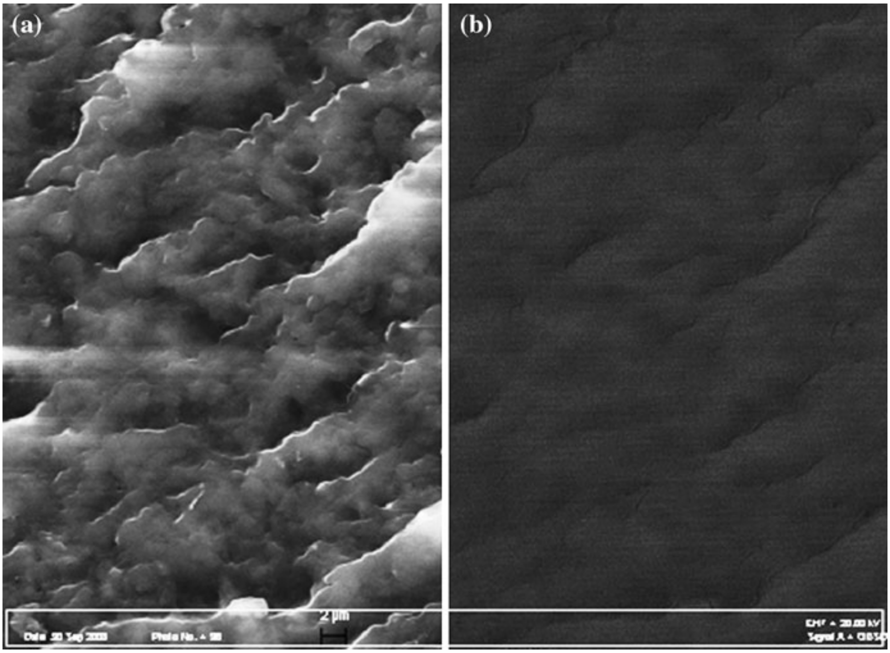

Fig. 8 SEM micrographs of AMN-60: secondary electron (**a**) and back scattering emission (**b**)

Table 2 Glass transition, melting temperature and degree of crystallinity of PA6 and PA6 hybrids

Sample code	T_{mI} (°C)	x_{cI} (%)	T_g (°C)	T_{mII} (°C)	x_{cII} (%)
PA6	223	38	49	221	29
AMN-6	224	39	51	220	28
AMN-10	223	37	56	219	25
AMN-47	217	37	58	219	25

As compared to neat PA6, T_g increases in all samples, as POSS loading increases from 2.5 to 20 wt%. Indeed, the hindering effect of Si–O–Si cages on polymer chain motion may fully explain the enhancement of the glass transition temperature. From the above data, it is evident that the polyamide chain movements are reduced to a relevant extent by the bulky POSS moiety at the end of the chain.

PSMA/(Ti)POSS-NH_2

Systems based on PSMA and (Ti)POSS-NH_2 have been synthesized by chemical grafting. Neat Ti-based POSS seems to be poorly organized (Fig. 9), with a melting temperature of ca. 180 °C. For comparison, POSS-NH_2 without metal at a corner of the cage is highly crystalline and melts at ca. 260 °C.

On this basis, it is clearly evident that at the mixing temperature used (240 °C), (Ti)POSS-NH_2 is completely melted and the possible reactions and/or interactions

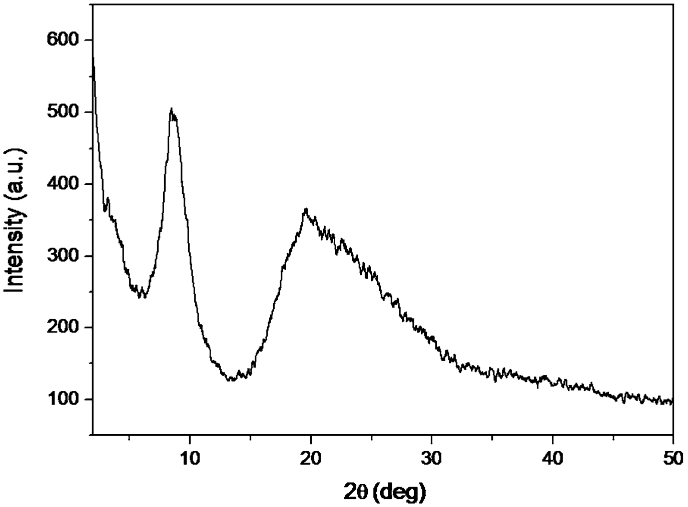

Fig. 9 WAXD spectrum of (Ti)POSS-NH_2

Table 3 Characterization of the hybrids based on POSS-NH_2 and (Ti)POSS-NH_2

Sample code	POSS type	POSS concentration (wt%)	Yield (%)	T_g (°C)
PSMA	–	–	–	134
AMN-27[a]	POSS-NH_2	20	50	121
AMN-46	(Ti)POSS-NH_2	20	100	137

[a] These data are taken from Ref. [17]

between the copolymer and silsesquioxane will take place in the liquid, possibly homogeneous phase. As previously described, the reaction yield has been evaluated by weighting the sample before and after the treatment with a solvent capable to solubilize unbound (Ti)POSS molecules. In Table 3 the yield, i.e., the relative amount of silsesquioxane retained by the polymer matrix, for a sample prepared by adding 20 wt% of (Ti)POSS-NH_2 to PSMA has been compared with that of a system based on neat POSS-NH_2 [17].

By analyzing the above table, it comes out that the grafting capability of the Ti-based POSS is much higher than that of POSS-NH_2, being the (Ti)POSS-NH_2 completely retained by PSMA. This result could be explained by taking in account, as previously underlined, that at the mixing temperature, the latter silsesquioxane is completely melted, allowing the reaction between the two system components to occur in the liquid, presumably homogeneous phase. Conversely, it is important to remind that in the case of PSMA/POSS-NH_2 system, the temperature applied during POSS-polymer mixing (240 °C) is lower than that of the silsesquioxane melting temperature and that reactions limited to those occurring at the POSS crystal/polymer boundary have similarly been proposed [17]. Clearly, this different behavior of the two silsesquioxanes might strongly influence the reaction kinetics.

Indeed, in the case of (Ti)POSS-NH_2, a hybrid with a homogeneous dispersion of POSS, namely a system characterized by a complete disappearance of maleic anhydride groups by the grafting reaction with silsesquioxane, should be attained much faster and more extensively than in the case of PSMA/POSS-NH_2 systems. This hypothesis is supported also by the thermal behavior of the prepared hybrid. Indeed, as shown in Table 3, while the sample AMN-27, prepared by mixing PSMA and 20 wt% of POSS-NH_2, has two T_gs, the single glass transition temperature of the AMN-46 sample, based on 20 wt% of (Ti)POSS-NH_2, underlines the achievement of a fully homogeneous system.

The reaction occurring between the polymer matrix and the Ti-containing silsesquioxane molecule has been studied by FT-IR (Fig. 10). The occurrence of the imidization reaction between the MA group of PSMA and the amino group of the POSS molecule, with the consequent formation of a cyclic imide linkage, has been confirmed by the appearance of the bands at ca. 1,100 and 1,700 cm^{-1} in the spectrum of the hybrid system. As already mentioned, the peaks at 1,100 and 920 cm^{-1} are due to Si–O–Si and Ti–O–Si, respectively, while that at higher wavenumbers can be attributed to imide groups (Fig. 10c). It is also pertinent to mention here that the disappearance of ring vibration at 910 cm^{-1} in the spectrum of PSMA-(Ti)POSS hybrid supports the successful occurring of the grafting reaction.

The dispersion of POSS in the polymer matrix has been studied by SEM coupled to elemental analysis. Figure 11 shows a SEM micrograph of the sample AMN-46, prepared by grafting 20 wt% of (Ti)POSS-NH_2 to PSMA.

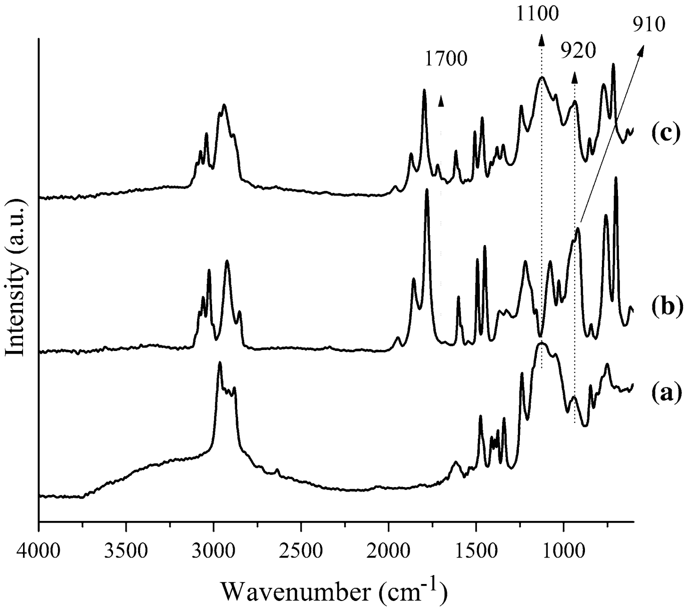

Fig. 10 FT-IR spectra of (Ti)POSS-NH_2 (*a*), PSMA (*b*), and AMN-46 (*c*). The curves are vertically shifted for clarity

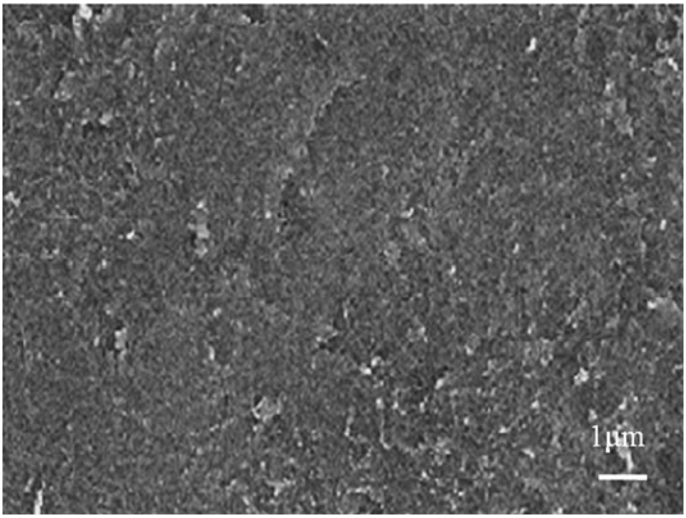

Fig. 11 SEM micrograph of AMN-46

By considering the above micrograph, it comes out that (Ti)POSS is uniformly dispersed in the polymer matrix without any visible aggregates, thus suggesting again the formation of nanostructured materials.

Conclusions

The possibility to introduce metals, homogeneously distributed and finely dispersed in organic polymer matrices, have been easily achieved for two polymers: polyamide 6 and poly(styrene-*co*-maleic anhydride). In both cases, Ti metal, inserted in a corner of a specific functionalised POSS cage, has been connected to the polymer chains by the formation of covalent links between the primary amine functionalities of POSS and reactive groups exiting in the PA6 (carboxy groups at a chain end) or PSMA (pendant maleic anhydride groups). As a carrier of metals into polymer matrices, amino-functionalised POSS has been found to be very suitable. Future developments and extensions to other hybrid systems can be foreseen.

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