Polymer Degradation and Stability 96 (2011) 1793–1798

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Novel hybrid systems based on poly(propylene-g-maleic anhydride) and Ti-POSS by direct reactive blending

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ARTICLE INFO

Article history:
Received 28 February 2011
Received in revised form
15 July 2011
Accepted 24 July 2011
Available online 28 July 2011

Keywords:
Ti-POSS
Reactive blending
PPgMA
Thermal degradation
XPS

ABSTRACT

Novel hybrid systems based on maleic anhydride-grafted polypropylene (PPgMA) and home-made Ti-containing amino polyhedral oligomeric silsesquioxanes (Ti-POSS-NH_2) have been prepared by one-step reactive blending, and their properties have been compared with those of systems based on a non-reactive POSS (POSS). The occurrence of a reaction between PPgMA and the reactive POSS molecules has been assessed by Fourier Transform Infrared Resonance (FTIR) measurements, whereas dispersion of POSS into the polymer was evaluated by Scanning Electron Microscopy (SEM), showing a nanometric dispersion only for the reactive POSS. Thermo-oxidative behaviour was studied by Thermogravimetric Analysis (TGA), showing a delayed volatilization of the PPgMA/Ti-POSS-NH_2 with respect to both PPgMA/POSS and pristine PPgMA, which is attributed to the chemical activity of Ti in Ti-POSS-NH_2. To highlight the mechanism of the hybrid system decomposition, samples which underwent a thermal treatment at 250 °C, *i.e.* the onset temperature for polymer matrix decomposition in thermo-oxidative conditions, have been studied by FTIR and X-Ray Photoelectron Spectroscopy (XPS) measurements.

1. Introduction

Nanostructured polymers based on polyhedral oligomeric silsesquioxanes (POSS) and their metal-containing derivates (M-POSS), represent a research topic of large and growing interest [1–3]. The main reason for such interest is the high versatility of POSS materials that show a well defined siliceous structure which can be easily tuned for a large variety of applications. The incorporation of POSS molecules is responsible for modifications of the thermal and mechanical properties as well as reduction of both flammability and heat evolution in combustion [4–9].

POSS are organic/inorganic molecules, sizing approximately 1–3 nm, with general formula $(RSiO_{1.5})_n$ where R is hydrogen or an organic group, such as alkyl, aryl or any of their derivatives [10–12]. As far as M-POSS are concerned, they can be prepared from incompletely condensed structures, *i.e.* open-corner POSS molecules. These latter compounds, obtained by either direct synthesis using chlorosilanes [12,13] or by cleavage of completely condensed POSS [14,15], can react with transition metal compounds to form M-POSS. The use of metal-containing silsesquioxanes represents a novel method to incorporate metal functionalities into polymer matrices. M-POSS have been exploited in the field of both homogeneous and heterogeneous catalysis (such as alkene polymerization, metathesis and epoxidation) [16–20] and more recently have turned out to strongly affect thermo-oxidative stability of polymers. M-POSS containing Fe and bringing alkene groups as the organic substituents on Si–O core were used to prepare, via bulk free radical polymerization, hybrids based on polystyrene (PS) which showed an improved thermal stability with respect to that of the neat polymer matrix [21]. In a recent work, we reported on the preparation of polymer nanocomposites based on PS and home-made heptaisobutyl-Ti-POSS (HEI-Ti-POSS) [22]. The presence of HEI-Ti-POSS turned out to enhance the thermo-oxidative stability of PS-based nanocomposites and did not significantly affect the polymer molecular mass.

Incorporation of POSS into thermoplastic polymers by melt blending was also explored, especially with polyolefins [23–27]. In polypropylene (PP), the dispersion of different M-POSS containing Al, Zn, Ti or V metal centres was found to strongly improve the thermo-oxidative stability of PP [28–30].

Recently, together with the widely applied melt blending also the reactive blending procedure, *i.e.* the occurrence of chemical

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doi:10.1016/j.polymdegradstab.2011.07.018

reactions during melt blending, has been exploited [3]. In general, the possibility to perform a chemical reaction between POSS and a polymer to prepare POSS hybrids through a one-step melt blending process represents a very appealing, economic and environmentally friendly approach to modify polymer properties and/or to obtain new functionalities [31].

Recently, Fina et al. [32] reported successful grafting of monofunctional amino POSS onto maleic anhydride-grafted PP (PPgMA), in a one-step reactive blending process, showing improved degree of POSS dispersion thanks to the occurrence of grafting reactions. The presence of POSS moieties grafted on PPgMA was found to improve the thermo-oxidative stability, in terms of delayed mass loss during thermal degradation under air, as compared to both neat PPgMA and PPgMA containing the correspondent non-reactive POSS. The higher stability towards thermo-oxidative degradation was explained by the accumulation of POSS on the sample surface during the early stage of PPgMA/amino POSS degradation, thus reducing the radical initiation action of oxygen in the thermal degradation of the polymer.

Reactive blending may also be exploited to obtain a finer dispersion of M-POSS molecules within the polymer, thus possibly enhancing the efficiency of POSS in the thermal stabilisation of polymers. Taking into account the above considerations, in this work novel systems based on a home-made Ti-containing amino POSS (Ti-POSS-NH_2) and PPgMA have been developed and fully characterized.

2. Experimental

2.1. Materials

Octaisobutyl POSS (referred as POSS in the following) was purchased from Hybrid Plastics (USA) as crystalline powders and used as received. Chemical structures for POSS ($M = 873.6$ g/mol) and amino heptaisobutyl Ti-POSS (refereed as Ti-POSS-NH_2 from now on) are reported in Fig. 1. Ti-POSS-NH_2 was synthesized according to the procedure given in [33].

Unstabilised PPgMA was obtained from Crompton Corp. (USA) (Polybond 3200 containing 1 wt.-% of maleic anhydride function) and was used as received. Neat PPgMA was processed and characterized under the same conditions as the reference material.

2.2. Hybrid system preparation

Hybrid systems were prepared by mixing the neat polymer and 5 wt.-% of POSS molecules in a laboratory internal mixer (180 °C) provided with a mechanical stirrer (Heidolth, type RZR1), applying a mixing time of 10 min.

Neat PPgMA was processed and characterized under the same conditions, as reference material.

Composites obtained by melt blending were purified from unreacted POSS by solubilisation of PPgMA/POSS in 15 ml of boiling xylene, followed by precipitation in 150 ml cold chloroform. The collected precipitate was then washed with chloroform and finally dried under vacuum to remove all solvents.

2.3. Characterization

A Leica Stereoscan 440 scanning electron microscope equipped with a back scattered electron detector was used to examine the composite sample morphologies and Si distribution. 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.

Fourier transform infrared spectroscopy (FTIR) spectra were recorded by a Bruker IFS66 spectrometer. The KBr pellet were prepared by mixing the sample with KBr powder (around 1:100) and using a hydraulic press at the pressure of 10 tons. All the samples were dried at 120 °C for 4 h under inert atmosphere and were scanned in the range 400–4000 cm^{-1} with nitrogen purge. FTIR on thermally treated PPgMA/POSS and PPgMA were obtained after a treating a polymer film (≈ 50 μm) for 4 h at 250 °C supported on a silicon wafer, in transmission mode through the silicon wafer and the supported residue.

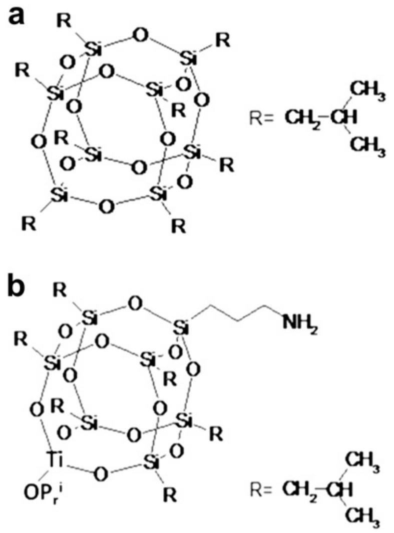

Fig. 1. (a) Octaisobutyl POSS (POSS); (b) amino heptaisobutyl Ti-POSS (Ti-POSS-NH_2).

X-Ray Photoelectron Spectroscopy (XPS) analyses were performed using a PHI 5602 Multi-technique instrument, featuring a charge neutralizer and a monochromated Al X-ray source (1486.6 eV) set at 350 W anode power. The data were acquired in multi-region mode, with 5.85 eV pass energy, take-off angle of 68°. and 0.025 eV energy resolution. Samples were prepared by pressing powders onto a thick indium film; then, they were set into a prepumping chamber ($\cong 10^{-7}$ torr) for 10 min and transferred in the main chamber ($\cong 10^{-9}$ torr) for analysis. PHI MultiPak software was used for data treatment and analysis. Due to the intrinsic insulating nature of the samples and the need of a charge neutralization device, all XPS spectra were software shifted to set the main carbon peak binding energy to 285 eV. Curve fits were performed without smoothing, using Gaussian templates and Shirley background subtraction.

Thermogravimetry Analysis (TGA) was performed on a TA Q 500 instrument, on *ca.* 6 mg samples, in Platinum pans, in isothermal conditions. Specimens were first heated in nitrogen to 250 °C to avoid significant weight loss during heating. When temperature was reached, atmosphere was switched to air (60 ml/min) and temperature kept constant for 4 h.

3. Results and discussion

In order to compare the effects of graftable M-POSS with an unreactive POSS containing no metal centre, both kinds of POSS have been blended with PPgMA.

The interactions and/or reactions occurring between the components of the system PPgMA/POSS, neat PPgMA, the two kinds of POSS and the prepared composites have been assessed by FTIR measurements. In Fig. 2, IR spectra of PPgMA and of Ti-POSS-NH_2 are shown.

In the of spectrum of PPgMA together with the characteristics absorption bands of PP, the signals centred at *ca.* 1780 and