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Titanosilsesquioxanes Embedded in Synthetic Clay as a Hybrid Material for Polymer Science**

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Polyhedral oligomeric silsesquioxanes (POSSs) are attracting growing interest in catalysis and materials science.[1–3] Metal centers in their silica framework show catalytic properties,[4–6] and POSS cages have been used as building blocks for multifunctional composite solids[7,8] and for hierarchical inorganic/organic hybrid architectures.[9–11] This success is due to the versatility of these compounds, which may include almost inert hydrocarbon moieties (R), reactive groups, and metal centers, which can be exploited to catalyze different organic reactions, in the same skeleton (Figure 1).

The combination of these three components provides a very large number of units suitable for “Lego” chemistry, which may lead to functional hybrid materials with ordered arrays of pores if functional groups capable of polymeric reactions are present in the cage.[10] Moreover, POSS-based compounds can be embedded into porous[11] or layered[12,13] inorganic matrices to give a large number of inorganic/organic hybrids or composite materials. For example, the intercalation of NH_2POSS on montmorillonite provided hybrid additives used for polystyrene nanocomposites.[14,15]

Herein, we describe the intercalation of a bifunctional protonated titanium-containing aminopropyl isobutyl POSS, Ti-NH_3POSS, within the interlayer space of a synthetic sodium saponite,[16] Na-SAP. The application of the resulting material as a filler for the preparation of a polystyrene-based nanocomposite with enhanced thermooxidative properties was tested successfully. The catalytic properties of the Ti centers were exploited for the production of charring products, a strategy which has proved to be effective in increasing the thermal stability and enhancing the fire-retardancy properties of polymer nanocomposite materials.[17]

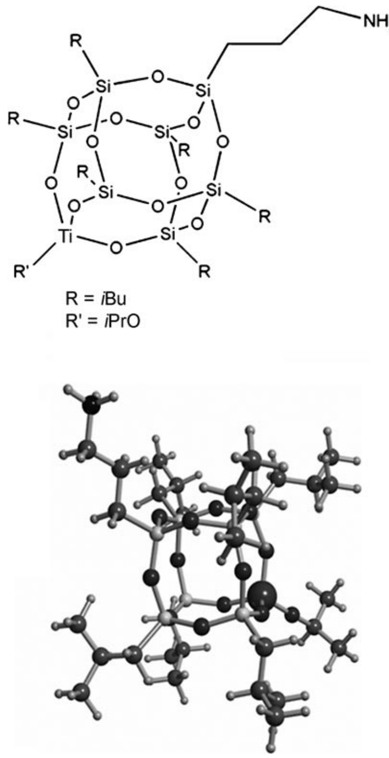

Figure 1. Structure of the protonated aminopropyl isobutyl titanosilsesquioxane, Ti-NH_3POSS, used for the preparation of the Ti-NHM-1 hybrid material.

Ti-NH_2POSS[18] displays two functionalities directly bonded to the silica cage: a catalytic titanium metal center[19,20] and a functional amino group suitable for intercalation in layered solids.[21] Ti-NH_2POSS was inserted under acidic conditions (i.e. NH_3^+ groups were present in the POSS compound) into Na-SAP through an ion-exchange procedure, which led to a hybrid material named Ti-NHM-1 (NHM is an acronym derived from Nano-SISTEMI Hybrid Materials). A virtually complete exchange of the saponite sodium ions with Ti-NH_3POSS was found (see Table 1 in the Supporting Information).

High-resolution transmission electron microscopy (HRTEM) of Ti-NHM-1 (Figure 2 A) indicated that the ion-

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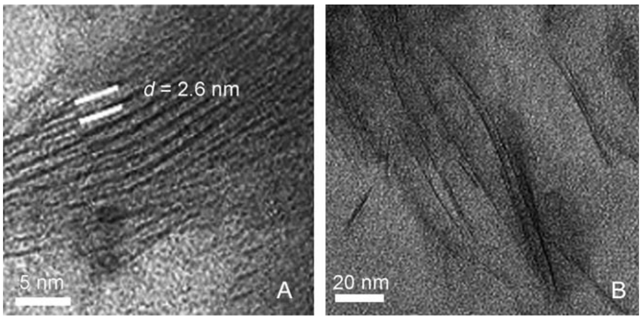

Figure 2. HRTEM micrographs of samples of A) Ti-NHM-1 and B) PS/Ti-NHM-1.

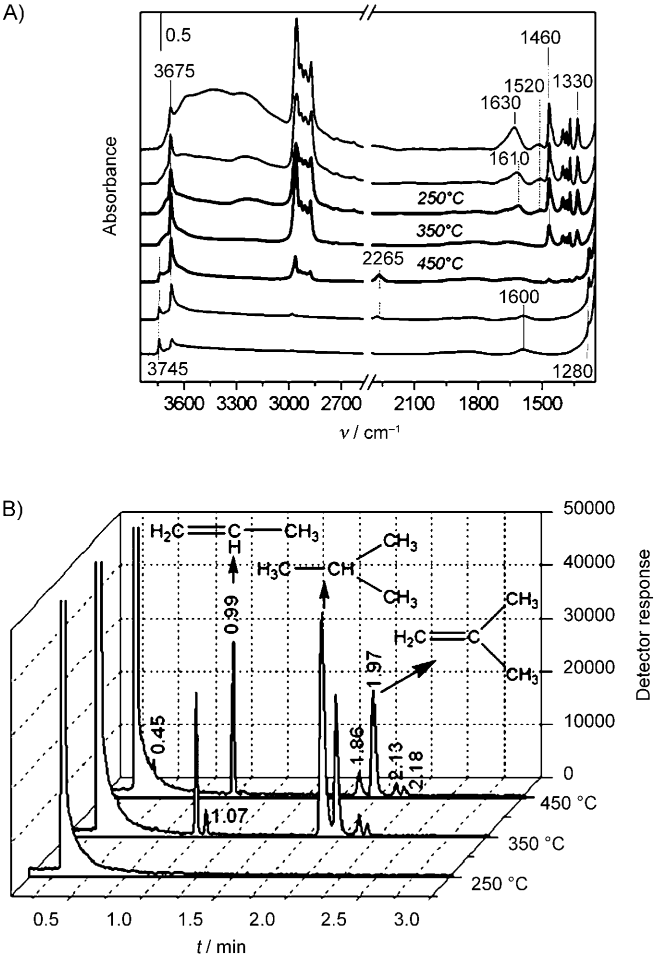

Figure 3. A) IR spectra of Ti-NHM-1 heated under nitrogen flow at various temperatures and B) related chromatograms (GC) recorded after heating the same sample at 250, 350, and 450 °C. The 0.5 value in the upper left-hand corner of (A) represents absorbance units.

exchange process does not alter the saponite lamellar morphology but does lead to a significant modification of the interlayer distance. These conclusions are in agreement with XRD data (see Figure 1 in the Supporting Information). Ti-NHM-1 showed regions with a larger interlayer distance (2.6 nm, Figure 2 A) than that observed for the pristine saponite (with a *d* spacing of ca. 1.2 nm). The Ti-NH_3POSS monomer has an ellipsoidal shape (with axes of 0.8 and 1.6 nm in length) and is arranged in different spatial configurations within the saponite layers (see Figures 2 and 3 in the Supporting Information).

The Ti-NH_3POSS intercalation was also monitored by infrared spectroscopy (see Figure 4 in the Supporting Information). The presence of two peaks at approximately 1610 and 1520 cm^{-1}, assigned to the out-of-phase and in-phase deformation vibrations of the NH_3^+ group, respectively, was clear-cut evidence that Ti-NH_3POSS units act as countercations of the saponite anionic layers.

Precious hints at the thermal stability and chemical reactivity of the hybrid materials were derived by infrared spectroscopy in conjunction with gas chromatography/mass spectrometry (Figure 3). When embedded in Na-SAP, Ti-NH_3POSS starts to decompose at $T > 250\,°C$ by Hoffmann degradation of the NH_3^+ group (Figure 3 A, IR bands at 3300–3000, 1520, and 1460 cm^{-1}). Differential thermal gravimetry (DTG) analysis (see Figure 5 in the Supporting Information) showed that the maximum rate of decomposition occurred at 405 °C; thus, decomposition was delayed significantly with respect to that of pure Ti-NH_2OSS (maximum rate at 325 °C). It is evident that the clay structure plays a key role in the thermal stabilization of Ti-NH_3POSS.

The hydrocarbon chains of the POSS cages decomposed at $T > 350\,°C$ to give propene, isobutane, and isobutene (Figure 3 B), in agreement with the IR spectra. Furthermore, amorphous silica and silicon carbide species (IR band at ca. 2265 cm^{-1})[22] were formed upon heating the Ti-NHM-1 sample at 450 °C (Figure 3 A). These products are derived either from the collapse of the siliceous POSS cage or from the decomposition of its organic moieties. At 450 °C, the major products were propene and isobutene (Figure 3 B), which evolved to charring products (IR band at 1600 cm^{-1}, Figure 3 A). Thus, it appears that dehydrogenation processes may be promoted by the Ti centers. The formation of carbonaceous species in Ti-NHM-1 material was also observed by thermal analysis (see Figures 5 and 6 in the Supporting Information).

In the light of these results, Ti-NHM-1 was tested as an additive in polystyrene-based nanocomposite materials (PS/Ti-NHM-1). Na-SAP and Ti-POSS were also studied in comparison. XRD analysis (see Figure 7 in the Supporting Information) and HRTEM micrographs (Figure 2 B) provided evidence of a good dispersion of Ti-NHM-1 in the polystyrene matrix. When Na-SAP was used as an additive, it was not so well dispersed (see Figure 8 in the Supporting Information). Thus, the presence of intercalated Ti-NH_3POSS appears to facilitate the dispersion of the layered solid in the polystyrene matrix. This behavior is probably associated with both the significant increase in the saponite interlayer distance and the hydrophobic character of the Ti-NHM-1 hybrid (see Figures 5 and 6 in the Supporting Information). DTG data indicated that the thermal stability of polystyrene was improved slightly in the presence of Na-SAP because of the physical barrier of the lamellae to oxygen diffusion (compare curves a and b in Figure 4).

Interestingly, the addition of Ti-NHM-1 led to the formation of a polymer nanocomposite with enhanced thermooxidative stability: the decomposition of polystyrene

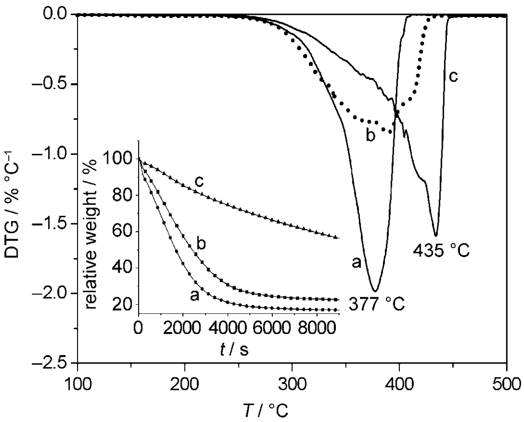

Figure 4. Thermogravimetric analysis under air flow (DTG curves) of the a) neat PS, b) PS/Na-SAP (dotted curve), and c) PS/Ti-NHM-1 materials. Inset: TG curves under isothermal conditions at 280 °C under oxygen flow for a) neat PS, b) PS/Na-SAP, and c) PS/Ti-NHM-1.

was delayed by approximately 60 °C with respect to the pure polymer matrix (Figure 4c). This behavior suggested that the catalytic activity of the Ti centers, which leads to the formation of stable charring products by secondary reactions (see above), enabled significant improvement of the thermal stability of the polymer nanocomposite material.[23] We recently described the catalytic role of bare Ti-POSS for the thermal stabilization of polystyrene.[24] Nevertheless, the thermooxidative stability of polystyrene was increased by about 30 °C in the presence of pure Ti-POSS, whereas for Ti-NMH-1, decomposition was delayed by about 60 °C with respect to neat polystyrene. Furthermore, when the temperature of the pure matrix was set at 280 °C prior to decomposition, the rate of weight loss was significantly decreased for PS/Ti-NHM-1 in comparison with that of PS and PS/Na-SAP (inset in Figure 4). The residue formed during the heating of PS/Ti-NHM-1 for these analytical studies was obtained in 55 % yield at the end of the analysis, whereas yields of 22 and 17 % were found for the residue formed from PS/Na-SAP and neat PS, respectively.

In summary, the embedding of Ti-NH_3POSS in a saponite clay leads to a remarkable thermal stabilization of the molecular compound. The resulting Ti-NHM-1 hybrid displays multifunctional properties, which act in a synergic fashion when it is used as an additive in a polystyrene matrix: the catalytic properties of titanium, which are relevant for the formation of charring products, in combination with the physical-barrier effects of the clay sheets play a fundamental role in improving the thermal stability of polystyrene, as indicated by the delayed thermal decomposition of the PS/Ti-NHM-1 composite material.

Experimental Section

Materials preparation: Ti-NH_2POSS was obtained by a previously described procedure.[18] Synthetic saponite clay (Na-SAP) was synthesized hydrothermally by mixing $Al(OCH(CH_3)_2)_3$, NaOH, $Mg(CH_3COO)_2$, SiO_2, and H_2O to form a gel (composition: $1\,SiO_2$, $0.834\,Mg(CH_3CO_2)_2$, $0.113\,Al(OCH(CH_3)_2)_3$, 0.113 NaOH, $18.6\,H_2O$), followed by ion exchange using a saturated solution of NaCl.

Intercalation of Ti-NH_3POSS in Na-SAP: Na-SAP was suspended in a solution of Ti-NH_2POSS in THF (Sigma Aldrich) and HCl (10 %) and stirred at 50 °C for 24 h. The product was filtered, washed several times with water, and dried in an oven at 80 °C.

Preparation of PS/Na-SAP and PS/Ti-NHM-1: A mixture of styrene and Ti-NHM-1 (5 wt %) was sonicated for about 1 h. Azobisisobutyronitrile (AIBN, 0.1 g) was then added, and the mixture was stirred at room temperature for 15 min. The resulting mixture was heated under nitrogen at 60 °C for 24 h (to effect polymerization), and then at 80 °C for 24 h.

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