

Short communication

New nanocomposites constituted of polyethylene and organically modified ZnAl-hydrotalcites

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Abstract

The thermal properties and combustion behaviour of new PE–hydrotalcites nanocomposites are described. Hydrotalcites were synthesized and then intercalated with stearate anion, because of the compatibility of long alkyl chain with polyethylene chains. The presence of inorganic filler shields PE from thermal oxidation, shifting the temperature range of volatilisation towards that of thermal degradation in nitrogen, and brings to a reduction of 55% in heat release rate during combustion.

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1. Introduction

The dispersion of a low loading (ca. 5%) of inorganic particles of nanometre dimensions into organic polymers is a recent challenge for the preparation of new composite materials with enhanced mechanical, gas barrier and flame retardant properties when compared with those of composites prepared with micron size particles [1]. Furthermore, the addition of inorganic components to the polymer may induce optical, electrical or magnetic properties of interest for high-tech applications. The challenge to succeed regards both the nanoparticles preparation, their homogeneous dispersion into the polymeric matrix and the compatibility

of polymer/inorganic blends to obtain thermodynamically stable systems.

Layered inorganic compounds possess unique properties to be active as fillers in polymeric nanocomposites. They can be, in fact, exfoliated into single layers each of them having thickness of the order of 1 nm and the surface of the layers may be functionalised, by ion exchange or grafting reactions, with organic groups that increase the compatibility with the polymers. In addition, layered solids may intercalate polymeric chains into their interlayer regions. In this context, much work has been reported on the use of organically modified smectite clays, in particular montmorillonites, as fillers of polymeric composites [2], while scarce attention has been paid to anionic layered inorganics of hydrotalcite type, even if these latter materials compare favourably with natural clays in terms of purities, control of crystallinity and particle size, wider possibility of functionalisation.

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Hydrotalcite-like compounds, also known as “anionic clays” or “layered double hydroxides” constitute a large family of materials with general formula $[M(II)_{1-x}M(III)_x(OH)_2](A_x^{n-}) \cdot mH_2O$ where M(II) is a divalent cation such as Mg, Ni, Zn, Cu or Co and M(III) is a trivalent cation such as Al, Cr, Fe or Ga with A^{n-} an anion of charge n such as CO_3^{2-} , Cl^- , NO_3^- or organic anion. The x value generally ranges between 0.2 and 0.4 and determines the layer charge density and the anion exchange capacity. The structure of the hydrotalcite-like compounds (hereafter indicated as HTlc) is similar to that of the mineral brucite ($Mg(OH)_2$) which crystallises in a layer-type lattice, each layer being obtained by the edge concatenation of $Mg(OH)_6$ octahedra, the layers being stacked one on the top of the other and held together by weak interactions. HTlc structure may be described by considering that of brucite, in which isomorphous replacement of a part of the divalent cations by trivalent cation occurs. The excess of positive charge, generated by the presence of trivalent cations into the brucite-like sheet, is balanced by anions located in the interlayer region where hydration water molecules are also accommodated. The interlayer anions can be exchanged by other inorganic, organic or metallo-organic anions and even by biomolecules containing ionisable acidic groups [3,4]. This offers the possibility to modify the chemical environment of the inorganic lamella and render it compatible with the polymeric chain.

In the present paper the stearate anion was selected to organically modify the HTlc, because of the expected compatibility of this long alkyl chain carboxylate with the polyethylene (PE) chains. Furthermore, previous studies have shown that stearate anions, intercalated into the MgAl hydrotalcite give rise to organic–inorganic hybrids with a large interlayer distance [5].

2. Experimental

2.1. Materials

A large batch of HTlc of composition $[Zn_{0.69}Al_{0.31}(OH)_2](CO_3)_{0.155} \cdot 0.48H_2O$ (interlayer distance: 7.58 Å; BET-surface area: 24.1 m²/g) has been obtained by the method of homogeneous precipitation accomplished by urea hydrolysis [6]. To an aqueous solution, obtained by mixing 0.5 M $ZnCl_2$ and 0.5 M $AlCl_3$ solutions in the volume ratio 2:1 solid urea was added until the molar ratio of urea/Al(III) was 10. The solution was refluxed for 36 h. The precipitate obtained was separated from the mother solution and suspended in a 0.05-M Na_2CO_3 solution (about 20 mL/g of precipitate) for 1 day. After equilibration the solid was recovered, washed with de-ionised water and finally dried at room temperature over P_4O_{10} . The carbonate form was converted into the

chloride form by titrating the HTlc dispersed in a 1-M NaCl solution (1 g/25 mL) with a 0.1-M HCl solution by means of an automatic titrator operating at pH-stat method and pH equal to 5. The chloride form was finally equilibrated with a 0.5-M $NaNO_3$ solution (1 g/40 mL) at 80 °C for 1 day to obtain the nitrate form. This latter material was washed with de-ionised, CO_2 -free water and dried in a desiccator containing phosphorus pentoxide and soda lime.

A standard sodium stearate solution (8×10^{-3} mol/dm³) was prepared by dissolving stearic acid in a water/methanol solution (volume ratio 1:1) containing NaOH in stoichiometric amount to neutralize the stearic acid, at 60 °C. The solution remains clear after cooling at room temperature.

2.2. Stearate ion intercalation

Five grams of the nitrate form of composition $[Zn_{0.69}Al_{0.31}(OH)_2](NO_3)_{0.31} \cdot 0.4H_2O$ (interlayer distance: 8.9 Å), was dispersed in 110 mL of the sodium stearate solution. After 2 days of equilibration, under stirring at room temperature, the solid was separated from the solution, washed with de-ionised, CO_2 -free, water and stored over phosphorus pentoxide. The supernatant solution was analysed for the nitrate and sodium ion content.

2.3. Analyses

The Zn and Al content of the HTlc was obtained using standard EDTA titrations after having dissolved a weighed amount of the samples (≈ 100 mg) in few drops of concentrated HCl solution and diluting to 50 mL with water. The nitrate content was obtained by Ion Chromatography using a Dionex DX500 Ion Chromatographer. Water and stearate content of the solid was obtained by thermogravimetry carried out with a Stanton Redcroft 781 thermoanalyzer, under air flow and at 5 °C/min heating rate. The amount of inorganic content in the composite has been deduced from the residue of the thermogravimetric analysis at 800 °C.

Sodium ions were determined with a Perkin–Elmer A. A. Spectrophotometer. X-ray powder diffraction patterns (XRPD) were obtained with a computer-controlled Philips 1710 diffractometer (40 kV, 20 mA, step scanning 1°/min) provided with a graphite monochromator. The BET-surface area was calculated from an N_2 -adsorption isotherm obtained with C. Erba Sorptomatic 1800.

2.4. Composites preparation

PE nanocomposites were prepared using an internal mixer, Brabender W50E. Medium density PE (Aldrich no. 332119) and the stearate HTlc were melt blended at

120 °C, rotor speed 60 rpm, residence time 3 min. The amount of stearate HTlc was calculated in order to prepare composites containing 5% (w/w) of inorganic fraction (ZnO and Al₂O₃).

Test specimen 30 mm², 3 mm thick for the oxygen consumption calorimeter have been obtained through compression moulding with a Specac 15011 Film Maker.

Thermal and thermo-oxidative behaviour of PE nanocomposites was studied through thermogravimetric analysis, using a TA instrument Q500 thermobalance with a heating ramp of 10 °C/min from 50 °C to 800 °C both in nitrogen and air (60 cm³/min).

Combustion studies were performed using an oxygen consumption calorimeter (Fire Testing Technology Limited FFT Cone Calorimeter model). Heat flux: 50 kW/m². Heat Release Rate (HRR, kW/m²), Total Heat Released (THR, MJ/m²), Mass Loss (ML, g), Mass Loss Rate (MLR, g/s) and Time To Ignition (TTI, s) measurements are average values of duplicate or triplicate experiments. Experimental error was evaluated to be ±10%.

3. Results and discussion

The ZnAl HTlc in carbonate form does not exfoliate nor it is able to intercalate the PE chains when dispersed into the melted PE. In order to decrease the layer–layer interaction and thus render layered material exfoliable and, at the same time, to make the inorganic lamellae compatible with the hydrophobic PE chains, it was decided to convert the HTlc into stearate form with a sequence of anion exchange processes. The HTlc was first converted into the chloride and then into the nitrate form (interlayer distance: 8.9 Å) which was then used to perform the nitrate/stearate anion exchange to prepare a pure phase of composition [Zn_{0.69}Al_{0.31}(OH)₂](CH₃(CH₂)₁₆CO₂)_{0.24}(NO₃)_{0.07}·0.4H₂O. From Fig. 1

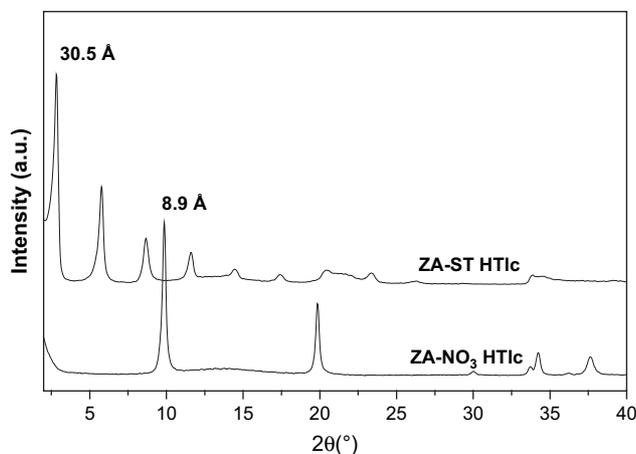


Fig. 1. XRPD patterns of the nitrate (ZA–NO₃) and of the stearate (ZA–ST) forms of the ZnAl hydroxycarbonate.

showing the XRPD patterns in comparison with that of the nitrate form it may be seen that the first diffraction maximum, associable to the interlayer distance, moves to lower angles as a consequence of the replacement of the nitrate ions with stearate ions with increase in interlayer distance of HTlc from 8.9 Å to 30.4 Å. Since the thickness of the hydroxycarbonate layer is evaluated to be 4.8 Å, the gallery height of the stearate form is 25.6 Å. If the composition, the charge density and the gallery height are considered, a structural model that foresees the stearate anions present into the interlayer region of HTlc as a monofilm of interdigitated alkyl chains can be drawn. The large interlayer distance and the presence of stearate alkyl chains favour the dispersion of the HTlc into melted PE of medium density. Composites, containing increased amounts of inorganic filler (5, 10, 15% w/w) have been obtained by melt mixing. The XRD patterns of all the composites are identical to that reported in Fig. 2 showing the absence of the typical X-ray reflection peaks of the HTlc, which is a strong indication of exfoliation, as is reported in literature [7,8], of the HTlc-stearate into the PE, with formation of nanocomposites. Additional and definitive proof of the presence of exfoliated lamellae into the composites will be obtained by transmission electron microscopy (TEM) analyses in due course.

In Fig. 3 the thermo-oxidative behaviour of pure PE and of its nanocomposite with 5% of HTlc are compared with the pure polyethylene thermal degradation in inert atmosphere. The destabilization effect of oxygen is evident comparing TGA curves of PE in nitrogen and in air. Indeed, the thermal degradation of PE in inert atmosphere takes place in a single step between 370 °C and 510 °C, whereas the oxidative degradation begins at a lower temperature (250 °C) and takes place in a more complex process due to reaction of degrading polymer radicals with oxygen in air.

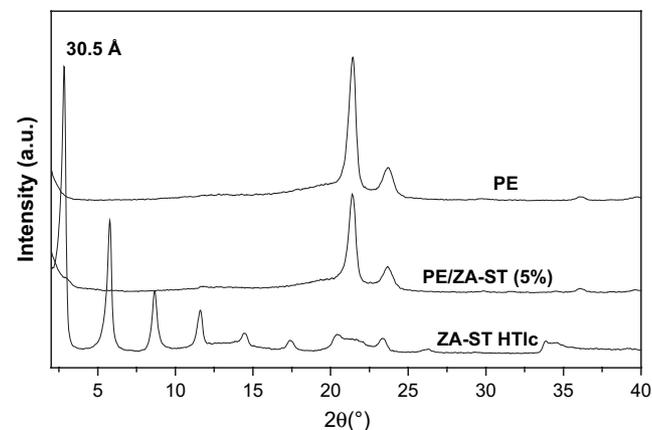


Fig. 2. Comparison between the XRPD patterns of the polymer (PE), of the filler (ZA–ST) and of the composite at 5% of inorganic loading.

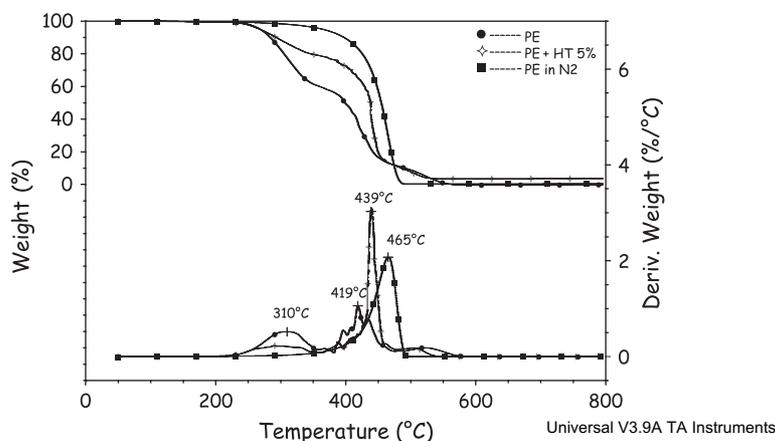


Fig. 3. TGA in air of PE and its nanocomposite; comparison with thermal degradation of pure PE in inert atmosphere.

The presence of inorganic filler strongly modifies the PE thermo-oxidation behaviour shifting the temperature range of volatilisation towards that of thermal degradation in nitrogen.

These behaviours point out that the presence of the HTlc lamellae produces a barrier effect to oxygen diffusion into the heated polymer due to the accumulation of the oxides produced by thermal degradation of the HTlc on the surface of the volatilising polymer [9].

The formation of this protective layer on the specimen surface is well evident during the combustion in the cone calorimeter test. In Fig. 4A, the heat release rate and total heat release curves for the pure polymer

and its nanocomposite with 5% of HTlc are displayed. The presence of 5% of HTlc brings a reduction of 55% in the maximum of heat release rate (Peak HRR) and a delay of about 50 s. Fig. 4B presents the mass loss and the mass loss rate (MLR) curves for PE and PE/HTlc nanocomposites during combustion in the cone calorimeter at 50 kW/m².

The shape of the mass and mass loss rate and of heat release and rate of heat release curves is correspondingly similar, suggesting that the lower HRR of nanocomposites is caused by the reduction of MLR and that the enhanced flame retardancy of PE/HTlc nanocomposites is due to modifications taking place in the condensed phase during polymer combustion. Finally, the Fire Performance Index (FPI = Peak HRR/TTI) from 70.5 kW/m²s for the pure polymeric matrix is decreased to 37.6 kW/m²s in the case of the nanocomposite showing a consistent reduction of fire risk. The results of thermal and combustion properties obtained by the use of hydrotalcites dispersed in the PE matrix are similar to analogous organoclay system [10].

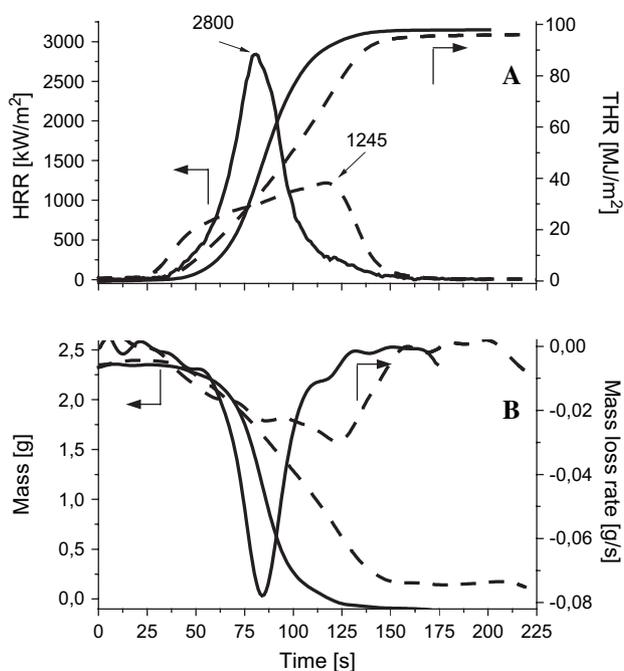


Fig. 4. Cone Calorimeter test: HRR and THR (A), mass loss and mass loss rate (B) of PE (solid curves) and PE + 5%HTlc (dash curves).

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