Structural characterization and thermal properties of polyamide 6.6/Mg, Al/adipate-LDH nanocomposites obtained by solid state polymerization

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ABSTRACT

A new nanocomposite was obtained by dispersing an adipate-modified layered double hydroxide (Ad-LDH) with adipic acid and hexamethylene diamine. These samples were polymerized in the solid phase under a nitrogen flow for 200 min at 190 °C. The structural and compositional details of the nanocomposite were determined by powder X-ray diffraction (PXRD), fourier transform infrared (FTIR) spectroscopy, focused ion beam (FIB), thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The PXRD patterns and FIB images show a partially intercalated and partially exfoliated dispersion of layered crystalline materials in the polyamide 6.6 matrix. The best dispersion level is achieved in polyamide 6.6/LDH nanocomposites with low LDH loading. Some residual tactoids and particle agglomerates are also evident at high concentration. The best thermal stability of the nanocomposites is shown by the sample with 0.1% LDH content, for which it is higher than that of pure polyamide.

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1. Introduction

In recent years, the dispersion of low loadings (ca. 5%) of inorganic particles in the nanosize scale in organic polymers is a challenge for the preparation of new composite materials with enhanced mechanical, gas barrier and flame retardant properties, when compared to those of composites prepared with micron size particles [1,2]. A homogeneous dispersion of nanoparticles is believed to contribute better to the property improvement.

Although fillers like alumina, silica, etc., can be added, 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 a thickness of the order of nanometers (from ca. 0.7 to 2.5 nm) and by ion exchange or grafting reactions the surface of the layers may be functionalized with organic groups that increase the compatibility with the polymers [3]. In addition, layered solids may intercalate polymeric chains in their interlayer regions. Until now, however, the clay materials involved in this field have been mostly focused on montmorillonite-type layered silicates whose layers have a relatively low charge density and from which exfoliated montmorillonite-type layered silicate/polymer nanocomposites can be easily obtained [4–6]. However, scarce attention has been paid to anionic layered inorganic materials of the hydrotalcite type, even if these latter materials compare favourably with natural clays in terms of purity, control of crystallinity and particle size, and wider possibility of functionalization [7–10].

Hydrotalcite-like compounds, also known as layered double hydroxides (LDHs), are brucite-like layered materials, with hydrated anionic counterions in the gallery space [11–13]. The positive layer charge is originated by the partial isomorphic substitution of divalent cations by trivalent ones. In order to attain electroneutrality, an appropriate number of anions must be incorporated into the interlamellar domain. Their general chemical formula is $[M^{2+}_{1-x}M^{3+}_x (OH)_2]^{x+} A^{m-}_{x/m} \cdot nH_2O$, where M^{2+} is a divalent cation, M^{3+} is a trivalent cation and A is an interlamellar anion with formal charge m^-. The identities of M^{2+}, M^{3+} and of the interlayer anion, together with the value of the stoichiometric coefficient (x), may be varied over a wide range, giving rise to a large class of isostructural materials. This flexibility in composition allows preparing LDHs with a wide variety of properties [14], finding a wide range of applications; they can be used as catalysts or catalyst supports, anion exchangers, polymer stabilizers, etc. [2,15,16]. When these materials are to be used as hydrophobic polymer filler, pristine LDHs is not suitable and the insertion of anionic organic species with a long hydrophobic tail is necessary, which on one hand causes the expansion of the interlayer distance and on the other makes the LDH materials more compatible with organic polymers [2,17].

Several methods have been developed to produce clay/polymer nanocomposites [1,18,19]. Three methods were developed in the early stages of this field and have been applied widely. These are: in situ polymerization [20,21,22], solution induced

intercalation [23,24], and melt processing [25]. The most appropriate method, in order to produce well-exfoliated nano-composites, is the *in situ* polymerization. This method consists in swelling the inorganic material by the monomer, followed by polymerization initiated well thermally or by addition of a suitable catalyst [3]. The chain growth in the interlayer space accelerates particle exfoliation and composite formation. This technique is also particularity attractive due to its versatility and compatibility with reactive monomers and is beginning to be used for commercial applications [26]. *In situ* intercalation polymerization enables significant control over both the polymer architecture and the final structure of the composite [27].

In a previous paper, we reported the synthesis of the intercalated nanocomposite based on Mg, Al-adipate LDH and polyamide 6.6 [28] through the solid state polymerization (SSP) method [29]. Previously to the SSP, polyamide 6.6 salt (PA6.6sal), a low molecular weight condensate, was obtained by a stoichiometric stepwise reaction between adipic acid (AA) and hexametilenediamine (HMDA). In such condensation process, there is an equilibrium such as: $AA + HMDA \leftrightarrow PA6.6$ salt $+ H_2O$ [29]. Polyamide 6.6 is an important semi-crystalline engineering polymer widely used due to its combination of properties such as high stiffness and strength at elevated temperatures, toughness, good abrasion and wear resistance, coupled with an excellent short term heat resistance due to its high melting point of $\sim 260\,°C$ [30]. The morphology and dispersion of LDH particles in LDH/PA6.6 sal nanocomposites were investigated using focused ion beam (FIB) techniques, transmission electron microscopy (TEM) and X-ray diffraction (XRD). In this paper, the samples characterization has been completed, the interactions between LDH and PA6.6 were discussed by FTIR spectroscopy and the thermal stability was determined by TG and DTA analyses.

2. Experimental

2.1. Materials and preparation of the organomodified-LDH

The reagents, $Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, NaOH, adipic acid (AA) and hexamethylene diamine (HMDA), were from Panreac (Spain). All of them were used without further purification.

A Mg–Al LDH with Mg:Al molar ratio 2 (Mg,Al/Ad) with adipate (Ad) in the interlayer was prepared by the co-precipitation method at a constant pH [31]. A solution (solution A) was prepared by dissolving $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ in 250 mL of water with a total Mg/Al concentration of 0.6 mol/L. A second solution (solution B) was prepared by dissolving NaOH in 800 mL of water (NaOH concentration 1 mol/L). A third solution (solution C) was prepared by dissolving AA in 100 mL water; the quantity of AA used was twice the anionic exchange capacity of the LDH (i.e. AA/Al molar ratio=2). Solution C was neutralized directly in the 3-neck vessel used for the synthesis by adding solution B until a pH=10 was reached. Solutions A and B were added drop-wise to solution C with intense stirring, the pH being maintained at a value of 10.0. Addition was completed in 4 h. The slurry was aged, in order to obtain well crystallized and uniform particle size distribution, for 3 h at 125 °C in a microwave oven. The microwave–hydrothermal experiments were carried out in a Milestone Ethos Plus microwave oven where reactants were treated in teflon liners. The microwave oven used a 2.45 GHz frequency radiation and the power supplied was that necessary to attain the temperature previously programmed. In order to minimize contamination with atmospheric CO_2, the preparation of this compound (Ad-LDH) was carried out under a nitrogen purge.

2.2. Preparation of LDH/PA6.6 nanocomposites

The nanocomposites were prepared by *in situ* intercalative polymerization, following a method similar to those used on a laboratory scale to prepare polyamide 6.6 [32,33]. A given amount of HMDA and AA with a molar ratio 1 was added to 50 mL of Ad-LDH slurry. The mixture was refluxed under nitrogen for 3 h at 100 °C. Several mixtures with different LDH/polymer ratios (0%, 0.1%, 0.5%, 1%, 2% and 5%, mass fraction of LDH content) were prepared. Then, the polyamide 6.6 salts were obtained by recrystallization upon vaporization of water.

In order to polymerize the monomer, the samples were heated under an inert atmosphere for 200 min at 190 °C. The temperature was chosen because it is in the vicinity of the melting point of the polyamide salt, to avoid thermal decomposition [34].

The formulations (0.1%, 0.5%, 1%, 2% and 5%) were chosen because no improvements were obtained on using higher LDH loading by *in situ* polymerization. The samples are named as XPA6.6, where *X* is the weight concentration of LDH.

2.3. Characterization and measurements

Powder X-ray diffraction (PXRD) patterns were recorded in a Siemens D-500 instrument using Cu-$K\alpha$ radiation ($\lambda = 1.54050$ Å) and equipped with Diffract AT software. Identification of the crystalline phases was made by comparison with the JCPDS files [35].

The FTIR spectra were recorded in a Perkin-Elmer FT1730 instrument, using KBr pellets; 100 spectra (recorded with a nominal resolution of 4 cm^{-1}) were averaged to improve the signal-to-noise ratio.

Thermogravimetric (TG) and differential thermal analyzes (DTA) were carried out in TG-7 and DTA-7 instruments from Perkin-Elmer, in flowing oxygen or nitrogen (from L'Air Liquide, Spain), respectively, at a heating rate of 10 °C min^{-1}.

An FEI FIB201 gallium focused ion beam (FIB) instrument was used for sectioning and high-resolution imaging.
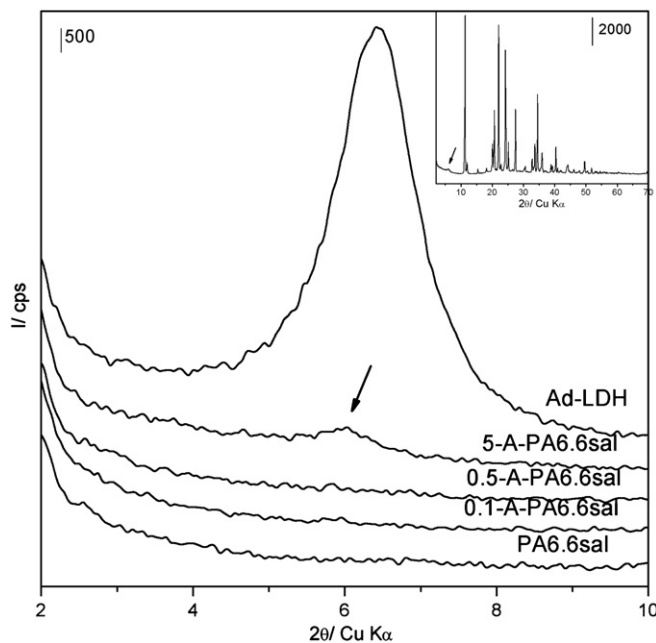

Fig. 1. Powder X-ray diffraction patterns of Mg, Al/Ad-LDH, 5PA6.6 sal, 0.5PA6.6 sal, 0.1PA6.6 sal and PA6.6 sal. Inset: full range diagram for sample 5PA6.6 sal. The arrows indicate the expected position for diffraction by (003) planes of hydrotalcite.