

The role of the trivalent metal in an LDH: Synthesis, characterization and fire properties of thermally stable PMMA/LDH systems

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ABSTRACT

Two layered double hydroxides (LDHs), calcium aluminum undecenoate (Ca_3Al) and calcium iron undecenoate (Ca_3Fe), have been prepared by the co-precipitation method. XRD analysis of these LDHs reveals that they are layered materials and FT-IR and TGA confirmed the presence of the undecenoate anions in the material produced. The PMMA composites were prepared by bulk polymerization and the samples were characterized by XRD, TEM, TGA and cone calorimetry. Both additives greatly enhance the thermal stability of PMMA, while the calcium aluminum LDH gives better results when the fire properties were examined using the cone calorimeter.

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1. Introduction

Many investigations have shown that inorganic hydroxide fillers, especially magnesium hydroxide (MH) and aluminum tri-hydrate (ATH), are environmentally friendly additives [1,2]. However, they have disadvantages, such as the need for quite high loadings and poor compatibility with the polymeric matrix, which degrade the mechanical properties [3]. The search for other inorganic hydroxide to substitute for existing metal hydroxides (MH, ATH) has been of current interest [4].

In previous observations on polymer–clay nanocomposite flammability using montmorillonite (MMT) as the nano-dimensional material, it is observed that reduction in the peak heat release rate (PHRR) is dependent on the polymer matrix and the quality of the nano-dispersion. In the case of polystyrene (PS), polyamide-6 (PA-6) and ethylene vinyl acetate copolymer (EVA), the reduction in PHRR is quite significant, around 60% [5]. However, in the case of poly(methyl methacrylate) (PMMA), only a modest reduction in PHRR, 30%, can be achieved [6,7]. It was further observed that the typical small reduction in PHRR seems to be dependent on both the identity and amount of the surfactant [8,9].

The small reductions in PHRR observed for MMT/PMMA systems triggered a search for new additives for this polymer. Layered

double hydroxides (LDHs), also known as hydrotalcite-like materials, may be a good candidate for this, as the composition of the layers can be varied, which is not possible with an MMT-like material. This presents an advantage, since tuning the LDH may lead to enhancement in some properties, but a good understanding of the role of each component of the LDH is required for optimization of the properties.

The LDH structure is described with the ideal formula $[\text{M}_1^{II-x} \text{M}_x^{III}(\text{OH})_2]_{\text{intra}}[\text{A}_{x/m}^{m-} \cdot n\text{H}_2\text{O}]_{\text{inter}}$, where M^{II} is a divalent cation such as Mg, Co, Ni, Cu, or Zn and M^{III} is a trivalent cation such as Al, Cr, Fe, V, or Ga with $\text{A}_{x/m}^{m-}$ an anion of charge m such as NO_3^- , CO_3^{2-} , Cl^- , SO_4^{2-} , $\text{C}_{12}\text{H}_{25}\text{SO}_4^-$, various carboxylates, etc; intra and inter denote the intralayer domain and the interlayer space, respectively. The LDH structure consists of brucite-like layers constituted of edge-sharing $\text{M}(\text{OH})_6$ octahedra [10].

Anionic guest entities, like monomers and polymers [11,12], functional biomolecules [13,14], and complexes of reducible transition metals [15,16] have been intercalated within an LDH matrix. LDH nanocomposites have found applications in mechanical strengthening [11,12], as adsorbents [17], or magnetic nanostructures [15,16]. In contrast, their potential usage as fire retardants has not been widely explored.

In recent work on LDHs as fire retardants for polymers, it was observed that matching an LDH with a particular polymer is a key to use these nanomaterials effectively [18]. An Mg–Al LDH will disperse much better in a polar polymer, like PMMA, than in a non-polar polyethylene, polypropylene or polystyrene. This task is not simple, as there are many parameters to control: metals

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(divalent and trivalent), anion functional groups (carboxylate, sulfonate, sulfate, phosphate, etc), anion sizes, crystallite sizes, stoichiometry and the polymer. The variation of the divalent metal cation in an LDH has an influence dispersability and fire properties of the corresponding polymer (nano)composites [19]. Finally, the length of the carboxylate chain has been varied and the dispersability of the LDH and fire properties assessed with both PMMA and PS; the dispersion is much better with PMMA but there is still a substantial reduction in the peak heat release rate even with the LDH poorly dispersed in PS [20]. In this work, two trivalent metal ions, aluminum and iron, are used keeping the divalent metal and anion the same.

There are a few reports in the literature discussing the use of iron in the fire retardancy of polymers. Nangrani et al. [21] reported that ferric oxide actually increased the flammability of polycarbonate. Whelan [22] investigated iron oxide as an effective synergist with halogens in halogen-containing nitrile polymers. Recently, Jiao et al. [4] reported that EVA/(Mg/Al/Fe- CO_3) composites containing a variable amount of Fe^{3+} ion obtained a V-0 rating in the UL-94 protocol, while with EVA/MgAl- CO_3 (an iron-free hydrotalcite), dripping occurred. The presence of iron as a substitutional impurity in MMT has been shown to lead to radical trapping reactions and a reduction in the PHRR at low amounts of clay [23]. Kong et al. have recently reported on a synthetic iron-containing MMT analog and found that the iron has a significant effect on the degradation and fire properties [24].

2. Experimental

2.1. Materials

The materials used in the synthesis of the layered double hydroxides were analytical grade, obtained from the Aldrich Chemical Co. These include 10-undecenoic acid, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, sodium hydroxide. Methyl methacrylate (MMA) and benzoyl peroxide (BPO) were used to prepare the polymer composites. MMA monomer was passed through an inhibitor remover column before use.

2.2. Preparation of the LDHs

The Ca/Al and Ca/Fe LDHs undecenoate were synthesized using the co-precipitation method following the literature procedure [25]. The preparation was performed in a nitrogen atmosphere to exclude CO_2 from the LDHs: 2000 ml of deionized water was boiled for 30 min while purging with nitrogen, then cooled to room temperature. In a 3 L three-neck flask was placed 900 ml of the previously treated water, under a constant nitrogen flow. To this was added 50 g (0.27 mol) of undecenoic acid and 5 min later, 11 g (0.27 mol) of NaOH. After the solution became colorless, the nitrate solution was prepared in separate container by dissolving 64 g (0.27 mol) of calcium nitrate and 34 g (0.091 mol) of aluminum nitrate in 450 ml of previously boiled water. This solution was then added dropwise to the 10-undecenoate solution, maintaining the pH of the solution at 10.0 ± 0.1 . The slurry was aged at 60°C for 2 days, and washed several times with degassed deionized water and dried in a vacuum oven at 80°C for a day to yield the desired calcium aluminum undecenoate LDH (Ca_3Al). Ca_3Fe was obtained similarly, with iron nitrate replacing aluminum nitrate and this sample was aged at room temperature.

2.3. Preparation of LDHs/PMMA nanocomposites

The PMMA/LDHs nanocomposites were prepared by a two-stage process by in situ bulk polymerization as reported by Wang et al.

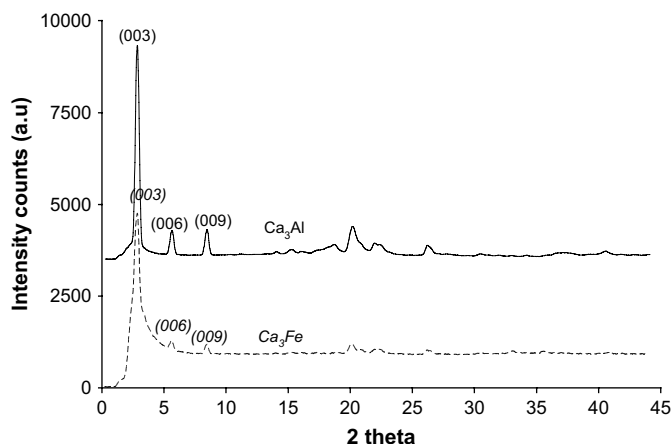


Fig. 1. XRD patterns of Ca_3Al and Ca_3Fe LDHs-undecenoate.

[25] with minor modifications. Briefly, the appropriate LDH loading was combined with MMA, total weight 140 g in a 400 ml beaker covered with aluminum foil to reduce volatilization, and the mixture was stirred vigorously for 1 day. Then, the initiator, BPO, 0.1% was added, and the mixture heated to 70°C to pre-polymerize it. The viscous mixture was cooled until a critical viscosity was reached, and another portion of initiator, 0.1% (0.14 g) was added to the viscous mixture, which was then heated to 120°C for 8 h. At the end, the polymer was placed overnight in a vacuum oven at 100°C to remove unreacted monomer and yield the LDH/PMMA nanocomposites. For the two types of LDHs prepared in this study, the

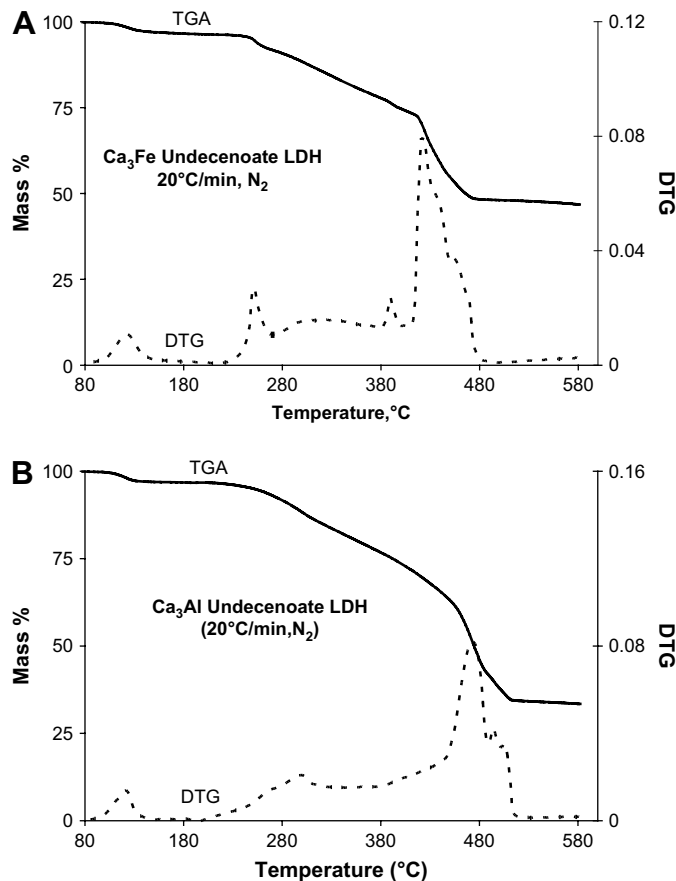


Fig. 2. TGA and DTG profiles of undecenoate-LDHs. (A) Ca_3Fe LDH; (B) Ca_3Al LDH.

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