Supplementary Material (ESI) for Journal of Materials Chemistry

Supporting information

ALUMINUM-CONTAINING LAYERED DOUBLE HYDROXIDES: THE THERMAL, MECHANICAL, AND FIRE PROPERTIES OF (NANO)COMPOSITES OF POLY(METHYL METHACRYLATE)

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Figure S1 illustrates the XRD patterns of the 5 LDHs used in this work. The strongest diffraction peaks are in the range of 2.86- 3.23° (2 θ) and the basal spacings of these materials are in the range 3.10-2.70 nm. The spacing was found 2.76 nm for CuAl2, 2.73 nm for CoAl2, 2.70 nm for NiAl2 and 2.74 nm for ZnAl2, but 3.10 nm for ZnAl3. The basal spacings thus were found not to depend on the type of divalent metal, but do depend on divalent/trivalent ratio for the zinc aluminum systems.

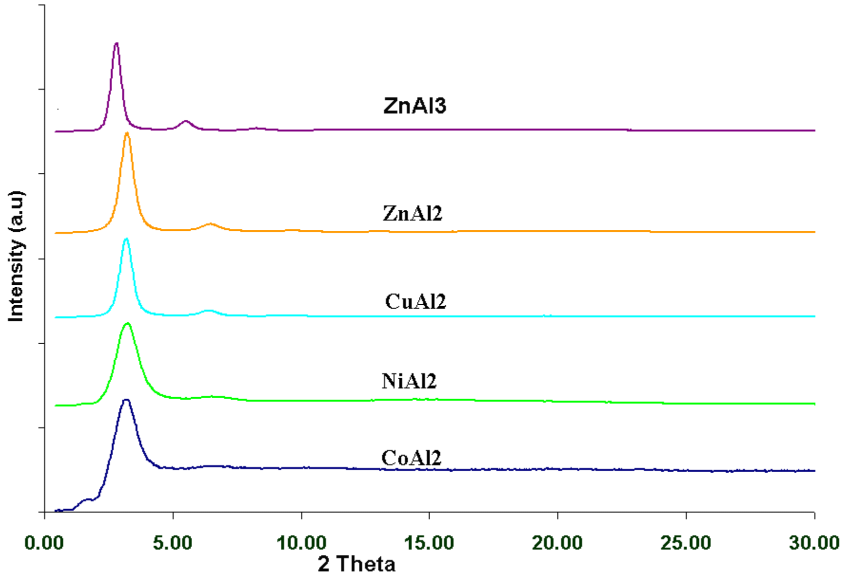

Figure S1. XRD traces of undecenoate containing LDHs of CoAl2, NiAl2, CuAl2, ZnAl2 and ZnAl3.

Since the thickness of the M(II)Al hydroxide sheet is around 4.77Å,[1] one can subtract this from the basal spacing to get the interlayer spacings, which are 2.25 nm (CoAl2), 2.28 nm (CuAl2), 2.22 nm (NiAl2), 2.26nm (ZnAl2) and 2.62 nm (ZnAl3). The length of 10-undecenoate anion (farthest distance between one carboxylate oxygen and one hydrogen from the terminal CH_2 group) was calculated to be 1.44 nm (RHF/6-311G*); it is likely that the tails of the undecenoate anions are partially interdigitated in the interlamellar space of the ZnAl2, CuAl2, CoAl2 and NiAl2. A similar model of the interdigitated anions in the gallery space of an LDH has been reported.[2] However, one cannot rule out the possibility of a bilayer arrangement with high angle of tilt.

The size of the gallery space is not controlled by the nature of the cations in the brucite-like layers, but it is mainly controlled by the size of the anion. In this case, however, the relative stoichiometry matters. Ulibarri et co-workers[3] who synthesized a CoAl-CO_3 LDH and noted that the unit layer thickness of their LDH was of the same order relative to other hydrotalcite materials with carbonate anions and water molecules in the interlayer space.[4] ZnAl3 had the largest basal spacing relative to the other LDHs. In this case, a partially interdigitated or a tilted bilayer anionic arrangement in the gallery of this LDH can be suggested. Close analysis of the XRD patterns of CoAl2 and NiAl2 **(figure S1)** shows for both materials broad diffraction peaks; the breath of the diffraction peaks may indicate some degree of disorder in the packing of the layers of these materials and a smaller degree of stacking as shown later in this text. The other LDHs, CuAl2, ZnAl2 and ZnAl3 (**figure S1**) have sharp XRD peaks. The presence of higher order diffraction peaks (006) and (009) for the latter indicates that the layers of these materials are pronounced. From the XRD traces of these LDHs, the coherence length in the stacking direction was estimated using the Debye-Scherrer equation, $\tau = \kappa \lambda / (\beta_\tau \cos \theta)$ where θ is the diffraction angle, κ is a constant (0.9 for powders)[5], $\beta_{1/2}$ is the full width at half maximum height of a diffraction peak of the layered material after correction for $CuK\alpha_2$ and the instrumental broadening and λ is the X-ray wavelength, 1.54078 for $CuK\alpha_1$. The instrument response was obtained using the National Institute of Standards and Technology (NIST) standard reference material Si powder (SRM 640C). The smallest domain sizes were found for CoAl2 (approximately 7 nm corresponding to about two to three stacked layers and NiAl2 (found to be approximately 11 nm corresponding to about 4 stacked layers), while CuAl2, ZnAl2 and ZnAl3 had about 25 nm, 28 nm and 31 nm respectively, corresponding to about 9-10 stacked layers.

The FT-IR spectra of the 5 layered materials synthesized in this study are shown in **Figure S2**. These spectra are very similar and support the fact that the undecenoate anion has been intercalated in the galleries of all 5 LDHs. Assignments of the different bands correlate with the MgAl-undecenoate LDH reported by Wang and co-workers.[6] The two bands in the range of 910-1000 cm^{-1} correspond to the out-of-plane C-H bending vibrations. The strong absorption peaks in the range of 1600-1430 cm^{-1} are assigned to the asymmetric and symmetric stretching vibrations, respectively of $RCOO^-$.[6] The C=C stretching vibration is around 1640 cm^{-1} and a very small shoulder corresponding to the C-H stretching vibration for the sp^2 carbon of the 10-undecenoate anion is located around 3080 cm^{-1}.[7] The strong and broad absorption peak near 3400 cm^{-1} is attributed to the –OH group in both the LDH sheets and the interlayer water molecules.[8] It is possible that a small amount of carbonate anions, below the detection limit of the FT-IR instrument, is also present. The synthesis was carried out under nitrogen, but the very strong affinity of the LDH for carbonate make, the synthesis of these materials very difficult if one wants to make carbonate-free materials, because the binding of monovalent anions is less than that of higher charged species in aqueous solution.[9] Iyi et al.[10] reported the trend in the affinity of the LDH toward various anions to be in the following order:[11]

$$CO_3^{2-} > SO_4^{2-} > OH^- > F^- > Cl^- > Br^- > NO_3^- > I^-$$

At any stage in the synthesis of the LDH (from boiling and degassing the water used in the synthesis to drying the final solid LDH in the vacuum oven), contamination is difficult to avoid.[12] The absence of a nitrate band (a strong band ~1380cm^{-1}) or the carbonate band (a strong band ~1365cm^{-1}) and the presence of the bands characteristics of the undecenoate anion as described above may suggest that the latter anion is largely incorporated between the layers of the LDH.

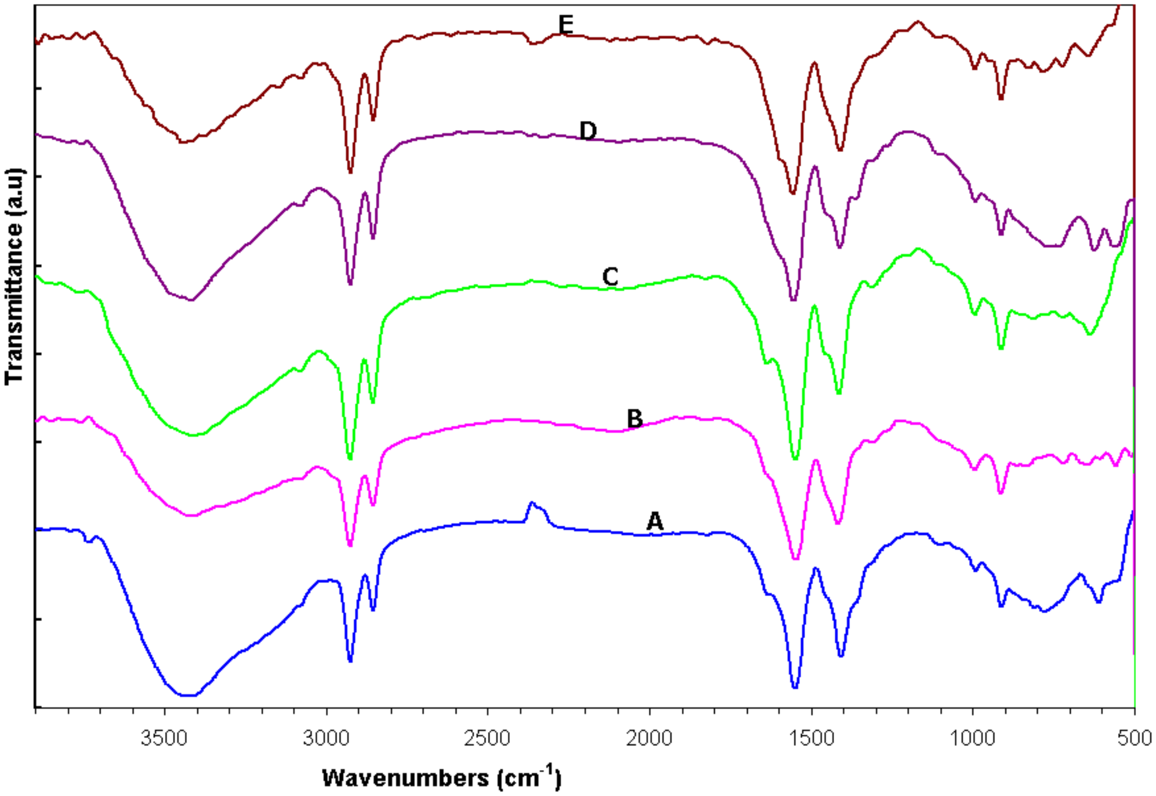

Figure S2: FT-IR of different undecenoate LDHs : (A) CoAl2; (B) CuAl2; (C) NiAl2; (D) ZnAl2 and (E) ZnAl3.

The melt blending of the polymer in Brabender mixer could cause some degradation. In order to confirm that this has not occurred, the TGA curves for virgin PMMA and a sample that have been mixed in the Brabender are compared below and one can see that degradation does not occur upon mixing; the curves roughly overlay and are shown in Figure S3.

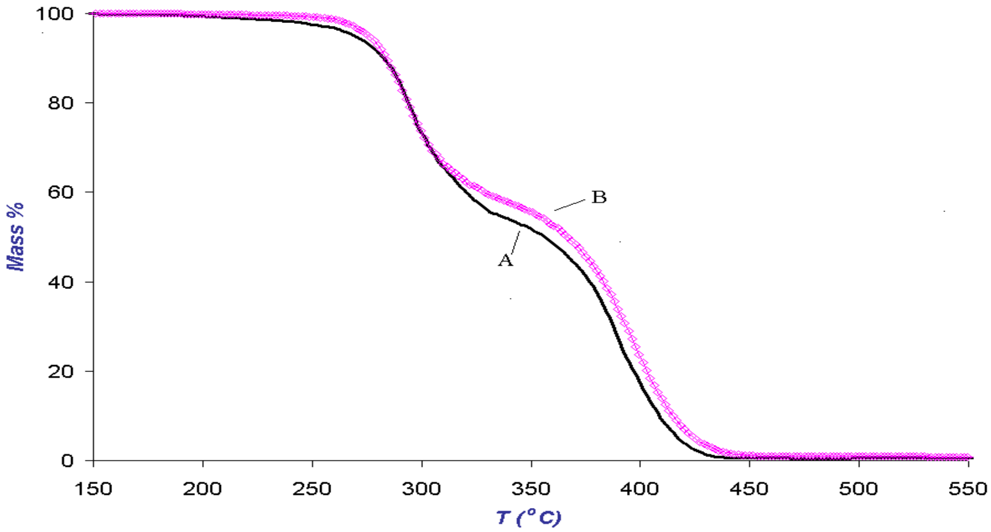

Figure S3. TGA curves of commercial PMMA (A) and the same polymer melt blended for 7 min in a Brabender mixer at 185 ºC (B). (TGA, N_2, 20 °C/min)

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[1] V.R.L. Constantino T.J. Pinnavaia, *Inorg. Chem.* 1995, **34**, 883.
[2] W. Chen B. Qu, B. *Chem. Mater*. 2003, **15**, 3208.
[3] M. A. Ulibarri, J. M. Fernández, F. M. Labajos, V. Rives, V. *Chem. Mater.* 1991, **3**, 626.
[4] C. J. Serna, J. L. Rendón, J. E. Iglesias, *Clays Clay Miner.* 1982, **30**, 180.
[5] R. Jenkins, R. L. Synder, *Introduction to X-ray Powder Diffractometry*; Wiley: New York, 1996.
[6] G.-A. Wang, C.C. Wang, C. Y.Chen, *Polymer* 2005, ***46*****,** 5065.
[7] K. M. McGrath, *Colloid. Polym. Sci*. 1996, **274**, 499.
[8] M. Taibi, S. Ammar, N. Jouini, F. Fiëvet, P. Molinié, M. Drillon, *J. Mater. Chem*. 2002, **12**,3238.
[9] K. Chibwe, W. J. Jones,*J. Chem. Soc.,Chem.Commun.*1989, **14**, ,926.
[10] N. Iyi, T. Matsumoto, Y. Kaneko, K. Kitamura, K. *Chem. Mater.* **2004**, **16**, 2926.
[11] S. Miyata. *Clays Clay Miner.* 1983, **31**, 305.
[12] F. Leroux, J. Besse,. *Chem. Mater*. 2001, **13,** 3507.