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# Delamination of layered double hydroxides in polar monomers: new LDH-acrylate nanocomposites†

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**The layered double hydroxide $Mg_2Al(OH)_6(C_{12}H_{25}SO_4)$ was delaminated to give high levels of inclusion in acrylate monomers; subsequent polymerisation of the monomers containing the LDH dispersion gave polyacrylates with the inorganic component still in the delaminated form.**

Organic polymers doped with inorganic components at the nanoscale level have recently attracted considerable interest. To date the majority of the inorganic components investigated have been layered materials, including smectite clays,[1] molybdenum sulfide[2] and titanates.[3] These layered compounds may form polymer/inorganic composites in a number of ways. Firstly, by precipitation of a layered phase in the presence of a polymer[4] or by inclusion of polymer between the layers with retention of the layered structure. This can occur either by intercalation of monomers followed by polymerisation or by direct intercalation of a molten polymer. The second method involves delamination of the layered structure into individual sheets either in a monomer, with subsequent polymerisation, or directly into a molten polymer.

The majority of the previous studies have focussed on methods of dispersing/exfoliating the montmorillonite-type of layered silicate compounds.[1] Montmorillonite has the advantage of easily exchangeable interlayer cations which allow the tailoring of its surface properties and interlayer space. Selection of a suitable interlayer cation, such as a long chain alkylammonium ion, reduces the hydrophillicity of the surface and as a result montmorillonite systems can often be delaminated merely by stirring in a suitable solvent.[5]

Layered double hydroxides (LDHs) are significantly different to montmorillonite with a net positive charge on the layers, balanced by the presence of anions in the interlayer space. While modification of LDHs can be carried out to alter the surface properties facile delamination of LDHs has proved to be very difficult to achieve. The first work to report the delamination of a LDH used refluxing butanol to delaminate $Zn_2Al(OH)_6(C_{12}H_{25}SO_4)$, dispersing 1.5 g of LDH per litre of butanol.[6] Another reported method for delaminating LDH involved intercalation of glycine into a Mg/Al LDH and refluxing in formamide. Up to 3.5 g of LDH per litre could be delaminated in this way.[7]

These levels of delamination fall well short of those obtained with montmorillonite, where levels of inorganic inclusion can exceed 50%. For instance the commercially produced doped nylon-6 incorporates up to 5% montmorillonite by weight.[5]

We wanted to study delamination of LDHs in organic solvents, particularly monomers and determine if the loading levels of the inorganic could be increased. Here we report the incorporation of a delaminated LDH into organic media at levels of up to 10%. We also report the formation of an inorganic/polymer nanocomposite containing up to 10% delaminated LDH.

$Mg_2Al(OH)_6(Cl)$ [$Mg_2Al(Cl)$] was prepared by co-precipitation from water of $MgCl_2$ and $AlCl_3$ in the presence of NaOH followed by reflux for 2 days. Exchange of chloride for dodecyl sulfate ($C_{12}H_{25}SO_4^-$) was carried out in deionised water at 70 °C, yielding $Mg_2Al(OH)_6(C_{12}H_{25}SO_4)$ [$Mg_2Al(DDS)$]. The replacement of the chloride was confirmed by elemental analysis which showed no chlorine was present. A Mg : Al ratio of 2 : 0.97 ± 0.03 was found for various samples prepared. The Al : S ratio was often found to be slightly lower than 1 : 1. This was attributed to the presence of a small amount of intercalated $CO_3^{2-}$ in the starting LDH which cannot be substituted. Powder X-ray diffraction showed an increase in *d*-spacing from 0.78 nm [$Mg_2Al(Cl)$] to 2.6 nm [$Mg_2Al(DDS)$] (Fig. 1).‡ Transmission electron micrographs showed a stacking of 100–200 layers per particle and confirmed a layer spacing of approximately 2.5 nm.‡

$Mg_2Al(DDS)$ was added to a polar acrylate monomer at loadings of between 1 and 10 wt%. The temperature was raised to 70 °C and the mixture was subjected to high shear using a Heidolph RGL500 high viscosity stirrer fitted with a Heidolph radial flow impeller blade, stirring at speeds between 2500 and 3000 rpm. High shear has been shown to promote delamination in montmorillonite systems.[8] The separation of the layers is believed to occur as a result of the plates of the layered materials being forced to slide over each other. After 20 min the stirring was stopped and the reaction vessel removed from the heat. 24 h later the majority of the solid remained in suspension. There was some variation in behaviour according to the monomer used. Reactions carried out in 2-hydroxyethyl methacrylate (HEMA) resulted in the formation of suspensions which were stable for several weeks at loading levels up to 10 wt%. The exfoliation of $Mg_2Al(DDS)$ in other acrylate monomers (ethyl methacrylate, methyl methacrylate, ethyl acrylate, methyl acrylate) was also investigated. Initially they all formed homogeneous suspensions, but after several hours separation to two bands occurred, one pure monomer, the other a gelatinous suspension of LDH in the monomer. The two phases that formed were found to be stable for several weeks.

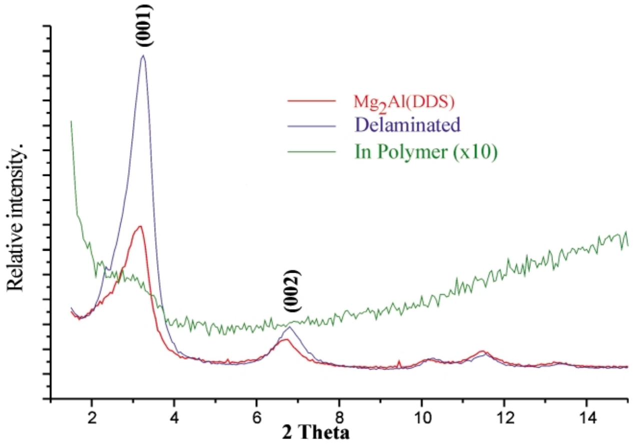

**Fig. 1** Diffraction patterns of (a) $Mg_2Al(DDS)$ as prepared, (b) $Mg_2Al(DDS)$ after delamination in HEMA and subsequent relayering and (c) $Mg_2Al(DDS)$ (5%) in polymerised HEMA (× 10). All patterns were obtained under identical conditions.

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† Electronic supplementary information (ESI) available: TEM image of $Mg_2Al(Cl)$ showing the layered structure. See http://www.rsc.org/suppdata/cc/b2/b204213d/

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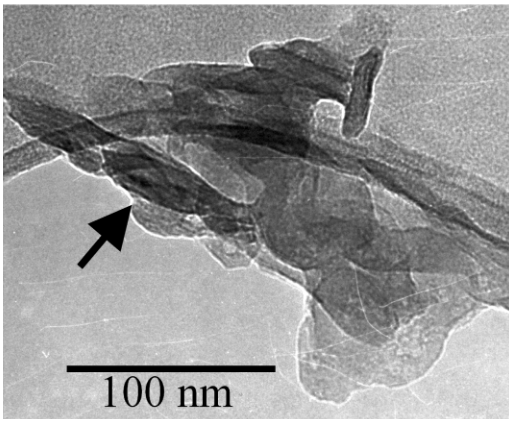

**Fig. 2** Transmission electron micrograph of individual sheets of $Mg_2Al(DDS)$ prepared by evaporation of 2-hydroxyethyl methacrylate (HEMA) from a stable suspension.

A drop of a dilute sample of $Mg_2Al(DDS)$ in HEMA was evaporated to dryness under vacuum on a glass slide resulting in the formation of a thin white film. X-Ray diffraction on this film (Fig. 1) showed one very strong Bragg reflection corresponding to a basal spacing of 2.6 nm and several much weaker reflections. The intensity of the (001) reflection is ascribed to the preferential ordering of the layers parallel to the glass plate on evaporation of the monomer. This is characteristic of a delaminated material.

TEM micrographs were taken of LDH particles coated onto grids from very dilute (0.05%) suspensions of $Mg_2Al(DDS)$ in 2-hydroxyethyl methacrylate. These images showed small collections of individual plates, oriented largely parallel to the grid surface. In the image shown (Fig. 2) the arrow indicates two of the plates that are at an angle to the grid. The view of their edge confirms that these are single plates.

To initiate the polymerisation of this dispersion, dodecyl thiol (0.4 wt%) and dodecanoyl peroxide (0.3 wt%) were added as a chain transfer agent and a radical initiator, respectively. For HEMA as the monomer the mix was poured directly into a mould. For other monomers the mix was first heated (80 °C) with stirring for a short while to thicken it so as to prevent settling of the LDH. The moulds were then placed in watertight plastic bags and suspended in a water bath at 80 °C for 18 h. The bags were removed and the plates placed in an oven at 120 °C for 2 h. The mould was then removed to give opaque homogenous solids.

Samples for powder X-ray diffraction studies were obtained by grinding portions that had been cooled with liquid nitrogen. These patterns showed only a very weak band attributable to the (001) Bragg reflection of $Mg_2Al(DDS)$. An example of such a pattern is shown in Fig. 1. It should be noted that this pattern has been expanded vertically tenfold. The strength of this reflection is very weak indicating that there is little long range order in the *c*-direction which is consistent with almost complete dispersion of the LDH layers.

In addition, transmission electron micrographs of these samples show that the LDH is present as individual sheets or in stacks of 2-5 layers (Fig. 3). This compares with stacks of over 100 layers present in the parent LDH.

Thermogravimetric analysis was carried out on samples of the pure polyacrylates and the polyacrylates containing exfoliated $Mg_2Al(DDS)$. The LDH-doped polymers showed a marked improvement in thermal stability (Fig. 4) This indicates an interaction of the two components at a molecular level, and again indicates that delamination has occurred and been maintained after the formation of the polymer.

Although we have concentrated on the incorporation of the delaminated LDH in organic polymers clearly this technique could be extended to provide delaminated LDHs for a range of applications from the preparation of oriented thin films of LDHs by spin coating the dispersed LDH on a flat substrate. The preparation of novel LDH intercalates with bulky interstitial anions should also be possible by adding these guest ions to the exfoliated $Mg_2Al(DDS)$ suspension followed by slow removal of the solvent.

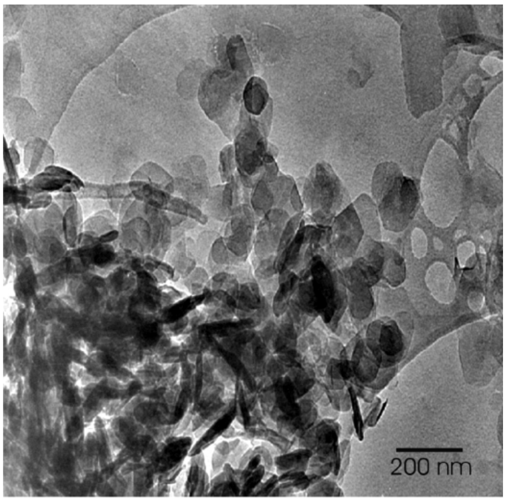

**Fig. 3** Transmission electron micrograph of a sample of poly-HEMA containing nanodispersed $Mg_2Al(DDS)$.

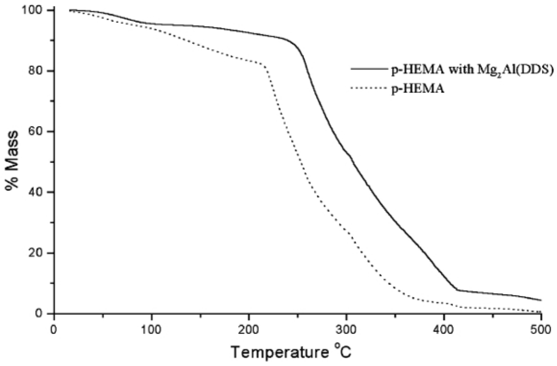

**Fig. 4** Thermal gravimetric analysis data for the degradation of p-HEMA doped with $Mg_2Al(DDS)$ and pure p-HEMA in air.

## Notes and references

‡ All powder X-ray diffraction patterns were recorded on a Philips PW 1729 powder diffractometer, running in reflection mode using Cu-Kα radiation at 40 kV and 30 mA. TGA measurements were carried using a Rheometric Scientific STA 1500 H thermal analyser. Transmission electron microscopy was carried out on a JEOL 2000FX TEM, operating at 200 kV.

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