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RESEARCH ARTICLE

Synthesis and characterisation of exfoliated layered double hydroxide (LDH) / sugar nanocomposites

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Abstract: In this study the preparation of layered double hydroxide (LDH)/sugar nanocomposites using an exfoliated MgAl-lactate LDH (Mg: Al = 3:1) and a sugar (sucrose and maltose) as precursors is described. The products have been characterised by powder X-ray diffraction (PXRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The properties of the composite materials have been further studied using differential scanning calorimetry (DSC).

The expanded interlayer spacing of the lactate LDH suggests the intercalation of lactate ions within the gallery region. Stirring of the MgAl-lactate LDH in water for 24 hours at room temperature resulted in a clear colloidal dispersion. Upon solvent evaporation, the resulting material consisted of a disorganized restacked LDH phase.

The most significant evidence for the formation of nanocomposites from the exfoliated clay materials is suggested by the absence of reflections associated with the LDH in the PXRD patterns. DSC results suggest that the glass transition temperatures of the composite materials with 5%, 10% and 20% LDH loading are superior to the parent maltose. Therefore, the LDH nanolayers give the LDH filled sugar nanocomposites better thermal stability than the pristine sugar, thus these composites could be used as drug excipients in the pharmaceutical industry.

Keywords: Amorphous sugar, exfoliation, layered double hydroxides, nanocomposites, thermal stability.

INTRODUCTION

Pharmaceutical products contain an active drug component together with agents that have a variety of purposes such as improving appearance and the bioavailability, enhancing stability, and modifying palatability. Excipients make up the majority of the mass or volume of oral and parenteral drug products. These pharmaceutical adjuvants, however, do not modify the intended action of the therapeutically active ingredients. Typically, most of the drug excipients used in the pharmaceutical industry are crystalline solids, due to their high levels of purity and thermodynamic stablility. Some drug excipients such as polyvinylpyrolidine, cellulose and magnesium stearate, however, intrinsically exist in an amorphous form (Ahlneck & Zografi, 1990). Lyophilized or spray-dried mixtures of proteins with various cryoprotectants and lyoprotectants are deliberately prepared in an amorphous form to physically stabilize biopharmaceutical products, while many hydrophobic drugs are made amorphous by co-precipitation or co-melting with mixtures of polymeric excipients in order to enhance their aqueous dissolution rates and oral bioavailability (Miyazaki *et al*., 2006). Although amorphous drug excipients have potential advantages over crystalline analogs, this state of matter remains thermodynamically unstable. It is therefore important to stabilize such amorphous drug excipients for use in drug formulations.

Nanotechnology is recognised as one of the most promising avenues of technology development in the 21st century. In the materials area, the development of polymer nanocomposites is a rapidly expanding multidisciplinary research activity (Leroux & Besse, 2001).

In recent years, these organic-inorganic nanocomposites have attracted interest as a result of the unexpected hybrid properties of the nanocomposites that

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are derived from the interaction of the two components. (Leroux & Besse, 2001) One extensively studied nanocomposite system is that based on organic polymers and inorganic layered materials. The dimensions and the microstructure of the dispersed inorganic phase significantly influence the properties of the parent polymer. In addition, the selection of the polymer component and the manner of interaction of the polymer with the layered material are key variables that can have a profound influence on the nature and the properties of the final composite material. Such polymer/layered material nanocomposites exhibit improved mechanical and thermal properties, gas permeability resistance and fire retardancy (Wang *et al*., 2001;Kato & Usuki, 2001).

Layered double hydroxides (LDHs) are a class of layered nanomaterials that have gained considerable interest in the preparation of such composite materials. LDHs, also known as anionic clays or hydrotalcite-like materials, consist of stacks of positively charged hydroxide layers and exchangeable interlayer charge balancing anions.(Hibino Kobayashi, 2005)

The synthesis and characterization of a composite system based on nano-inorganic clays and organic macromolecules are reported here. Exfoliated LDH/sugar nanocomposites have been prepared using MgAl-lactate LDH and sugar precursors (sucrose and maltose). The purpose of this study is to improve the thermal stability of the amorphous sugar matrix.

METHODS AND MATERIALS

All reagents used in this study were purchased from the British Drug Company UK and were of analytical grade and used without further purification. All solutions were prepared using distilled water.

***Synthesis and exfoliation of MgAl–lactate LDH*:** MgAl–lactate LDH was prepared by the co-precipitation method described by Hibino & Kobayashi (Hibino, 2005). Typically 50 mL of an aqueous solution containing $Mg(NO_3)_2.6H_2O$ and $Al(NO_3)_3.9H_2O$, (Mg:Al=3:1) was prepared and added dropwise to a 50 mL solution containing the lactate anion (Al:lactate=1:10) under vigorous stirring conditions. During mixing of the metal solutions, the pH of the reaction mixture was maintained at 10 using 2 M NaOH solution. The solution temperature was maintained at 65 ^{o}C, and the reaction was carried out under flowing N_2 gas. The resulting slurry was then filtered, washed 3 times with distilled water and dried at room temperature. As a reference material, a MgAl-carbonate LDH was also synthesized by a similar procedure using sodium carbonate as the anion containing solution.

The ability of the lactate LDH to undergo exfoliation and refoliation was studied. Of the parent lactate LDH 0.30 g was dispersed in 150 mL of water and stirred until the mixture transformed into a stable colloidal solution. The nature and the particle size of the exfoliated LDH were studied by dynamic light scattering.

A few drops of the exfoliated LDH were placed on a glass plate and allowed to refoliate in the absence of an anion. Additionally, refoliation of the mixture in the presence of carbonate ions was performed by dropwise addition of 50 mL of 2 M Na_2CO_3 to 100 mL of exfoliated lactate LDH solution. The mixture was stirred at room temperature for 24 h. The suspension was filtered and washed 3 times with distilled water.

***Preparation of exfoliated LDH/sugar nanocomposites*:** By adding 0.45 g of the sugar precursor to a dispersion of 0.05 g LDH in 50 mL of water 0.50 g of 5% (w/w LDH/sugar) nanocomposite was prepared. The mixture was then stirred for 24 h and a dried product was obtained by freeze drying. Similarly 10% and 20% nanocomposites were also prepared.

***Characterisation*:** powder X-ray diffraction (PXRD) patterns of all synthesized samples were recorded on a Siemens D-5000 X-ray powder diffractometer, using Cu Kα radiation (λ= 0. 154 nm) over a 2θ range of 3-65^{o} with a step size of 0.06^{o} and a step time of 6 s. The patterns were indexed assuming a hexagonal closed packed unit cell. Identification of crystalline phases of lactate LDH and carbonate LDH were made by comparison with literature data.

Fourier transform infrared spectroscopy (FTIR) spectra of pristine LDHs and exfoliated and refoliated LDHs in the 400-4000 cm^{-1} region were recorded on a JASCO / FT-IR-400 spectrophotometer.

Elemental analysis for C, H and N was performed using a CE-440 (Exeter Analytical, Inc., UK) elemental analyser.

The ^{1}H NMR and ^{13}C NMR spectra of the lactate LDH were recorded on Varian 300 MHz spectrometer (Germany), using D_2O as the solvent.

The morphology of the LDHs were analysed using a Hitachi SU 6600 scanning electron microscope (Germany).

Differential scanning calorimetry (DSC) measurments were obtained using a Perkin Elmer - Pyrisl DSC instrument, under flowing N_2 at a scanning rate of 10 ^{0}C / min.

RESULTS

Characterisation of parent and exfoliated LDHs

Figure1 represents the PXRD patterns for the parent lactate and carbonate LDHs and those for refoliated materials. The PXRD pattern of the material resulting from the co-precipitation reaction in the presene of lactate anions represents a typical LDH (Hibino & Kobayashi, 2005), consisting of relatively sharp and intense basal reflections at low 2θ values and broad and asymmetric reflections at high angles. The intercalation of lactate ions was evidenced by the measured interlayer spacing compared to the carbonate LDH in Figure 1(b). The patterns have been indexed based on a three layer repeating hexagonal unit cell, and the observed interlayer distances and the unit cell parameter *c* are summarised in Table 1. *c*-parameter has been calculated refering to the first two basal reflection (*003*) and (*006*) except for the carbonate LDH resulted after exfoliation and restacking.

Figure 2 presents the FTIR spectra of MgAl-lactate and carbonate LDHs and the formation of LDH layers, and the presence of lactate and carbonate anions in the interlayer spacing are evidenced by the observed FTIR patterns.

Elemental analysis of MgAl-lactate LDH, C – 8.5%, H – 3.8% further confirms the presence of carbon arising mainly from lactate anions in the parent material. The carbon and hydrogen percentages for the carbonate LDH were 3.4% and 4.4% respectively.

The scanning electron microscopic (SEM) images of the MgAl-lactate LDH before delamination show stacks of sheets (Figure 3). According to the figure, the lactate LDH exhibits the usual plate like morphology observed for typical LDHs. The flat layering pattern is an evidence for the formation of an LDH and the morphology of the LDH is in agreement with the previously reported images for other LDHs (Hibino & Kobayashi, 2005). The plate - like structure of the parent material has been preserved after exfoliation and restacking in the presence of carbonate ions, suggesting that the individual layers are not destroyed during the exfoliation process.

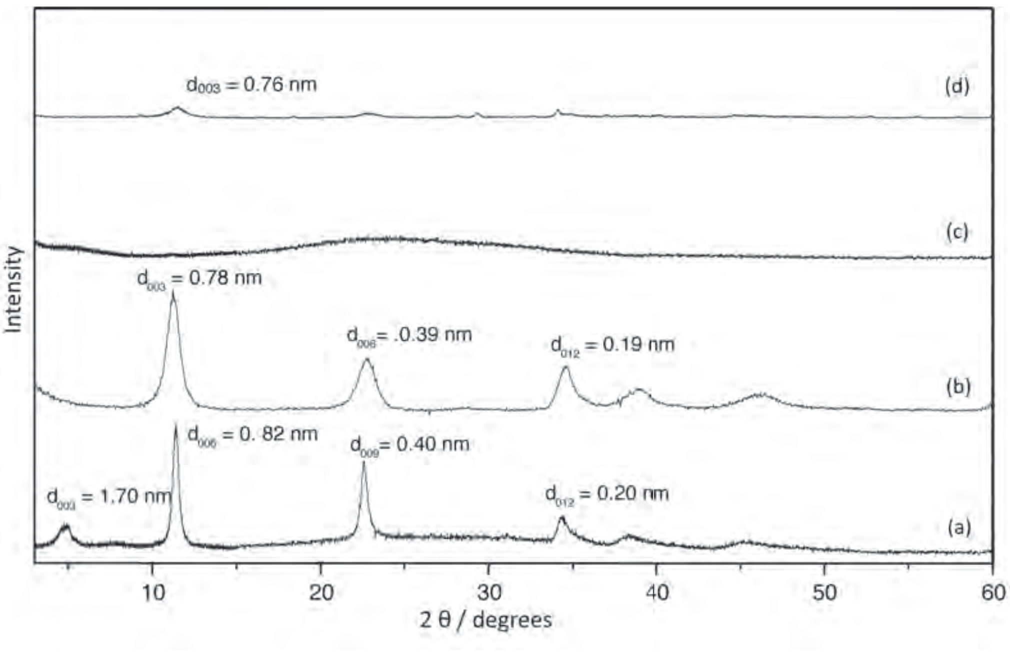


Figure 1: The PXRD patterns of (a) MgAl-lactate, (b) MgAl-carbonate LDHs and the materials obtained after refoliation, (c) in the absence of an anion and, (d) in the presence of carbonate ions

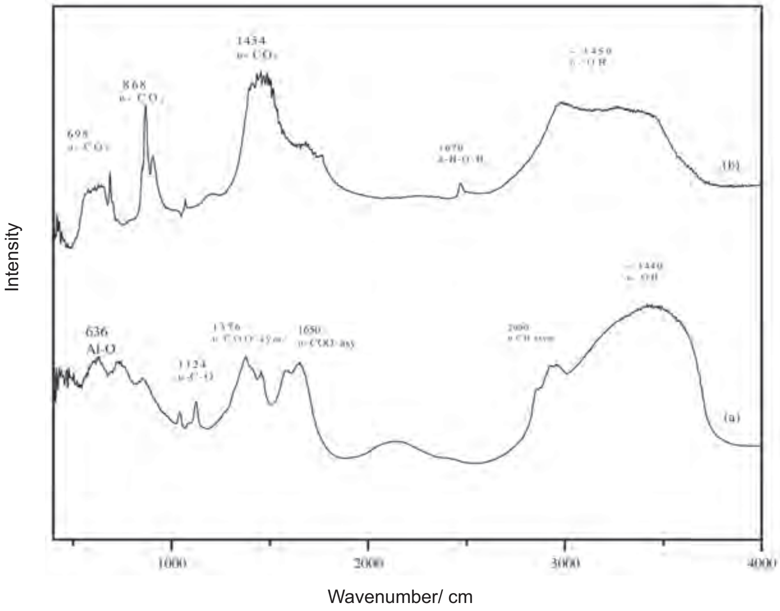
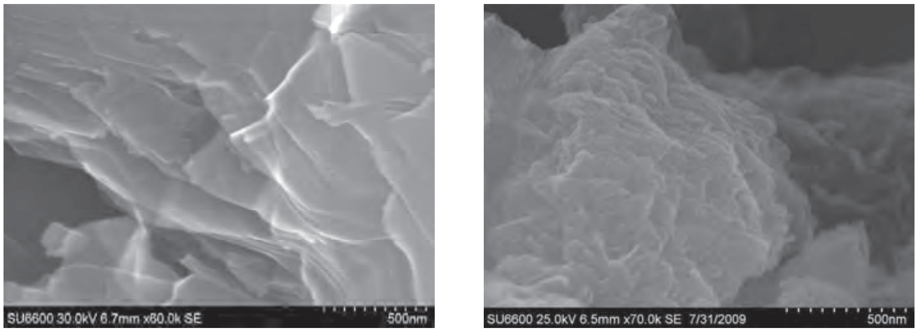


Figure 2: FTIR spectra of (a) MgAl-lactate and, (b) MgAl-carbonate LDHs



(a) (b)

Figure 3: SEM images of (a) MgAl-lactate LDH before delamination and, (b) MgAl-carbonate LDH

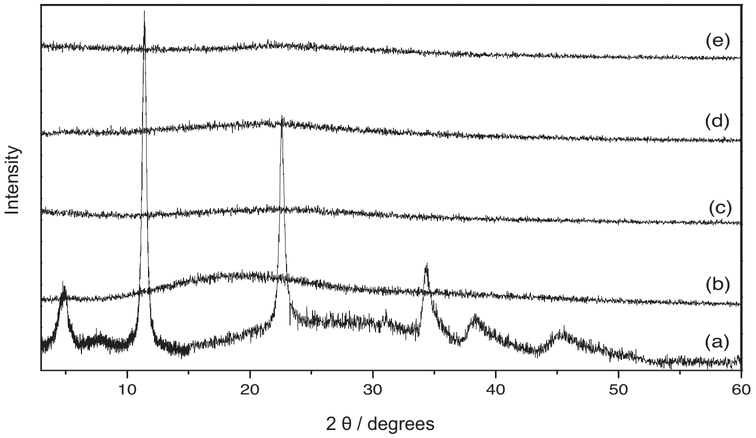


Figure 4: The PXRD patterns of (a) MgAl-lactate LDH, (b) amorphous maltose, and (c) 5%, (d) 10% and, (e) 20% LDH/maltose nanocomposites

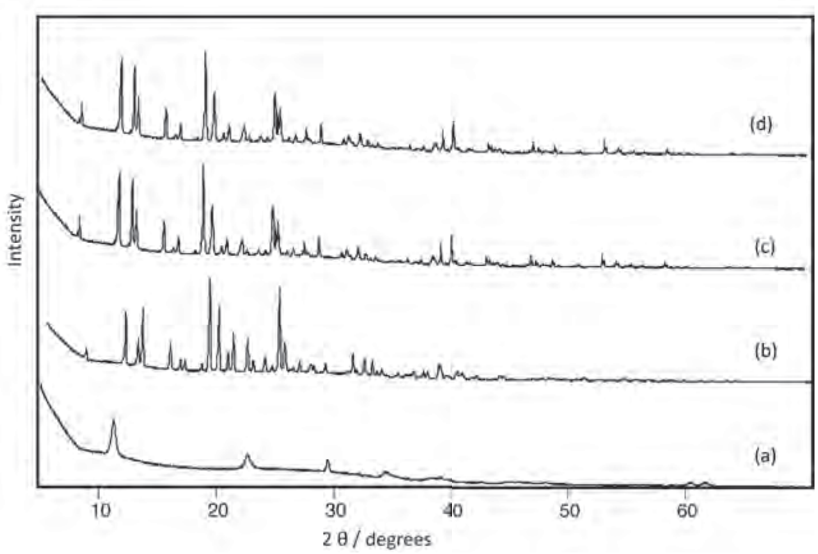


Figure 5: PXRD patterns of (a) MgAl-lactate LDH, (b) sucrose and, (c) 10% and, (d) 20% LDH / sucrose nanocomposite

Table 1: Crystallographic data for LDHs

MgAl-LDH	*c* parameter / nm	Interlayer spacing / nm	Gallery height / nm
Carbonate	2.34	0.78	0.30
Lactate	5.01	1.67	1.19
Restacked in the presence of carbonate ions	2.28	0.76	0.28

Table 2: Glass transition temperatures of the composites

LDH loading in the nanocomposite	T_g / °C
Amorphous maltose	40
5%	49
10%	50
20%	52

In ^{1}H NMR the resonances attributed to lactate anion in the exfoliated MgAl-lactate LDH were observed at 1.32 ppm and 1.30 ppm (CH_3), 4.09 ppm and 4.07 ppm (CH), and 3.33 ppm (C-OH), and in ^{13}C NMR at 20.10 ppm (C3) and 68.55 ppm (C2), thus verifying the presence of lactate anion. In addition, in exfoliated MgAl-lactate LDH, the ^{1}H NMR peak due to (C-OH) of the lactate anion is observed at a higher field compared to that of the pure lactate anion and it indicates that the lactate anion is hydrogen bonded to the hydroxyl groups of the brucite - like layers.

Characterisation of LDH/sugar nanocomposites

The PXRD patterns for lactate LDH and the maltose nanocomposites prepared with differnt levels of lactate LDH loading are summarised in Figure 4 and those for sucrose/lactate LDH nanocomposites are given in Figure 5.

The thermal stability of amorphous maltose/LDH nanocomposites were studied using DSC measurements. The glass transition temperatures (T_g) measured at the beginning of the transition, of 5%, 10% and 20% LDH/ maltose nanocomposites are summarised in Table 2. No improvement in the thermal properties of sucrose/LDH nanocomposites were observed.

DISCUSSION

The observed pattern for lactate LDHs is in close agreement with that reported by Hibino and Kobayashi (Hibino & Kobayashi 2005). Assuming a thickness of the brucite-like layer of 0.48 nm, a gallery height of 1.3 nm is indicated for the lactate LDH. Assuming an appropriate size of the lactate anion of 0.7 nm suggests that the gallery height of the MgAl-lactate LDH is approximately twice that of the lactate anion and suggests a bilayer arrangement of lactate anions within the interlayer region.

Stirring 0.3 g of the MgAl-lactate LDH in 150 mL of water for 24 hours at room temperature resulted in a clear colloidal dispersion with an average particle size of 70–140 nm as determined by light scattering experiments. The delaminated LDH dispersion was then allowed to refoliate in the absence of added anions and a dried fraction characterized by PXRD [Figure 1(c)]. The PXRD pattern did not contain reflections due to the lacate LDH, suggesting the presence of a disorganised refoliated material. The material, which resulted from refoliation in the presence of carbonate ions [Figure 1(d)], contains the basal reflections, which is slightly at a higher 2θ angle than that of a typical carbonate LDH, suggesting a slight change in the vertical orientation of the carbonate anions within the gallery region.

The FTIR spectra are in good agreement with previous reports on LDHs (Lee *et al*., 2005; Jauberite *et al*., 2006). The absorption bands below 1000 cm^{-1} are associated with M-O (Mg-O, Al-O) stretching modes in the brucite–like layer. The bands at ~1680 cm^{-1} is attributed to the deformation of interlayer water molecules. The very broad band observed around 3500 cm^{-1} is due to the overlapping stretching modes of hydroxyl groups in the brucite layer and interlayer water molecules.

For the MgAl-lactate LDH characteristic absorption bands due to intercalated lactate anion ($CH_3CHOHCOO^-$) are expected and are seen at 1650 cm^{-1} and 1376 cm^{-1} (asymmetric and symmetric stretching modes of carboxylate group, respectively). The broad band observed at approximately 3000 cm^{-1} is associated with the stretching C-H mode. The weak absorption band around 1120 cm^{-1} is assigned to the rocking mode of methyl group overlapped to the stretching modes of C-O and C-C bonds. In addition, the FTIR spectra in Figure 2(b) showed the expected characteristic peaks of carbonate anion at 1454 cm^{-1}, 1070 cm^{-1}, 868 cm^{-1} and 671 cm^{-1}.

Principally, the formation of nanocomposites with exfoliated clay materials is suggested by the absence of basal reflections associated with the LDH in the PXRD pattern. The absence of the (*003*) basal reflection in 5% LDH loaded nanocomposite is, however, not a direct evidence of the formation of an exfoliated LDH/sugar nanocomposite because a 5% clay loading is likely to be very close to the minimum detection limit. However, the absence of any basal reflections in the 10% and 20% LDH/sugar nanocomposite are suggestive of exfoliated LDH in the sugar matrix. Additionally, the absence of any reflections due to crystalline sugar suggests successful synthesis of amorphous exfoliated LDH/sugar nanocompounds.

According to the DSC measurements, the glass transition temperatures (T_g) of the compounds compared to pure amorphous maltose show an increase of approximately 10 °C in all 5%, 10% and 20% LDH/maltose nanocomposites. From the DSC results, it is suggested that the T_g of amorphous maltose can be improved by nano level addition of LDHs. The improvement in the T_g may be arisen due to the higher degree of hydrogen bond formation between amorphous maltose and hydroxyl groups of the hydrotalcite like layers of the MgAl-lactate LDH.

Further LDH nanolayers give the composites a better thermal stability than the pristine sugar, due to the differences in the chemical structure of the two components and due to the restricted thermal motion of the sugar molecules in the inorganic material. The exfoliated clay particles, therefore, stabilise the amorphous sugar by increasing the glass transition temperature, thus these composites may be used as drug excipients in the pharmaceutical industry.

The PXRD patterns of 10% and 20% LDH/sucrose nanocomposites (Figure 5) exhibit reflections only due to the crystalline sucrose. The disappearance of all reflections due to MgAl-lactate LDH supported the successful preparation of exfoliated LDH/sucrose nanocomposites, i.e. the complete dispersion of LDH within the sucrose matrix. Although attempts were taken to prepare amorphous sucrose/exfoliated LDH nanocomposite, the final prouct was unstable leading to crystallisation of the sugar matrix with time under tested reaction conditions. Further studies on preparaton of sucrose /LDH nanocomposites is in progress.

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