Colloids and Surfaces A: Physicochem. Eng. Aspects 408 (2012) 71–78

Contents lists available at SciVerse ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Alignment of layered double hydroxide platelets

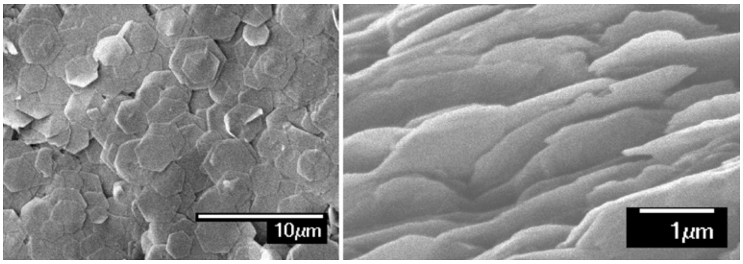
Yan Zhang, Julian R.G. Evans*

Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK

HIGHLIGHTS

- ▶ LDH tactoids were synthesized in stable and flocculating suspensions.
- ▶ Highly ordered planar random structures were made by filtration.
- ▶ In flocculating systems, edge-face interactions are overcome during filtration.
- ▶ Exfoliated LDH suspensions also assembled as rippled layered structures.
- ▶ These assemblies prepare for large-scale assembly of nacre-like nanocomposites.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 15 March 2012
Received in revised form 15 May 2012
Accepted 19 May 2012
Available online 2 June 2012

Keywords:
Layered double hydroxide
Ordered nanocomposite
Biomimetic
Self-assembly

ABSTRACT

A new generation of ordered, mineral-reinforced polymer nanocomposites is emerging for which assembly of platelets into planar-random array provides the reinforcement structure. Motivated by this goal, Co–Al layered double hydroxide (LDH) tactoids (diameter ~3 μm, thickness ~30 nm) were synthesized and their colloidal stability in water as a function of pH was characterized by sedimentation and zeta-potential measurements. The tactoids in both stable and unstable suspensions assembled into sheet materials with a layered planar random arrangement during filtration presenting a putative reinforcement structure. Exfoliated nanosheets, characterized by the disappearance of diffraction peaks in XRD patterns and by AFM, were also assembled and produced a region of 10 μm next to the filtration membrane which was highly ordered but in which the order reduced at further distances because of higher entropic undulation of very thin platelets at much reduced filtration rates. Reassembly of these exfoliated platelets confirmed that more ordered parallel structures are obtained with tactoids. Such structures resemble that of nacre and could serve as reinforcements for subsequent infiltration by matrix resins in the same way that carbon fibre woven mat is prepared for fibre reinforced polymers.

1. Introduction

There is a pervading view in the materials community that composite materials which emulate the layered bricks-and-mortar structure of nacre (mother of pearl) would deliver a combination of high elastic modulus and high work of fracture giving rise to high fracture toughness (K_{IC}) [1–3]. In selecting calcium salts for reinforcement of mollusc shells on the basis of availability and solubility, nature, faced with the very low toughness of aragonite (~1 MPa m$^{1/2}$), refined the microstructure to produce nacre with K_{IC} = 4–6 MPa m$^{1/2}$ using 5 vol.% organic material. Its toughness emerges in part from crack deviation along a tortuous path where energy is absorbed by the organic constituent, by platelet interlocking and by jamming due to platelet thickness variation [4–6]. This provides one of the best examples of the principle that underpins materials science that micro- and nano-structures have a commanding influence on properties [7–9]. In the laboratory, experiments using alumina and polymethylmethacrylate [9] have produced a composite with twenty times the toughness of either constituent simply by microstructural rearrangement of

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* Corresponding author. Tel.: +44 020 7679 4689.
E-mail address: j.r.g.evans@ucl.ac.uk (J.R.G. Evans).

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http://dx.doi.org/10.1016/j.colsurfa.2012.05.033

two inherently brittle materials, a lively demonstration of the remarkable influence of microstructure on properties which is transforming strategic thinking in composite materials [10].

Renewed interest in the biomimetic 'copying' of the nacre structure emerges from the need to find composite materials with high strength and stiffness to weight ratio as replacements for carbon fibre composites, particularly in a new generation of low fuel consumption automotive applications where the high cost of carbon fibre is considered a threat to market penetration.

Recent work on the ordering of exfoliated platelets of montmorillonite in a polyvinyl alcohol matrix [11] and the resulting mechanical properties: tensile stress of 400 MPa and modulus of 106 GPa have given hope that the long term goal of mimicking the nacre microstructure with high volume fractions of an inexpensive and plentiful mineral reinforcement is now in sight. The assembly process used was layer-by-layer deposition in which 1800 dipping and drying operations are needed to produce a film that is 1.5 μm thick. Furthermore strength was measured on samples of 1.5 μm × 1 mm × 4–6 mm so that corrections are needed for the volume dependence of strength but the important point that has been established by that work is that high-strength composites from clays and polymers can be made. The question now is: how can these composites be made in sufficient volume to provide a viable manufacturing process? Previous work at Schlumberger research [12] suggested simple methods like filtration could be effective but did not study the resulting microstructure and our previous work [13] showed that thin layered structures of natural montmorillonite could be obtained by several approaches including filtration.

Clays are natural layered aluminosilicates with cations sandwiched between the layers. Layered double hydroxides (LDHs), also known as hydrotalcite clays, are also laminar minerals with anions sandwiched between hydroxide layers. LDHs are present in nature [14] and can be synthesized in the laboratory; synthetic LDHs have better-defined geometry and crystal structure than their natural counterparts. LDHs have the general formula $[M_{1-x}{}^{2+}M_x{}^{3+}(OH)_2]^{x+}[A_{x/n}{}^{n-}\cdot mH_2O]^{x-}$, where M^{2+} and M^{3+} are di- and tri-valent metallic cations and A^{n-} represent the anions in the interlayer space [15,16]. Al^{3+} ions are the main trivalent cations. Mg–Al [17] and Zn–Al [18] LDHs are the most commonly studied. Transition metal-bearing LDHs such as Co–Al [19,20], Fe–Al [21] and Ni–Al [22] may have special applications due to their magnetic, catalytic and optical properties. Zn–Al layered hydroxides function as photocatalysts for oxidation of phenol [23] and similar Mg–Al LDH have been arranged into thin films (~1.5 μm) in conjunction with polysodium 4-styrenesulphonate using layer-by-layer (LBL) assembly [24]. Zn-, Mg- and Co-LDH were assembled into thin films by LBL and spin coating methods [25].

We synthesized Co–Al LDHs and adjusted the colloidal stability of their dispersions. We also prepared delaminated (exfoliated) LDH nanosheets by gradual ion exchange followed by redispersion in formamide. These were arranged by filtration on a 0.2 μm pore-size membrane to explore the effectiveness of this method for the assembly of planar random structures of platelets with different colloidal stability and platelet thickness.

2. Experimental details

2.1. Synthesis of LDH platelets

Co–Al LDH particles were synthesized based on a procedure [15] for producing platelets in the micrometer diameter region and with $CO_3{}^{2-}$ as the interlayer anions. Reactants consisting of 1.42 g $CoCl_2\cdot 6H_2O$, 0.72 g $AlCl_3\cdot 6H_2O$ and 1.26 g urea (obtained from Sigma Aldrich, Poole, Dorset, UK) were dissolved in 600 mL distilled water in a three-necked round bottom flask. The solution was purged with nitrogen gas for 5 min before being heated and refluxed for 48 h at 120 °C under nitrogen protection in an oil bath. The resulting particles were filtered and washed thoroughly with distilled water four times and redispersed to the initial concentration, which was measured to be 0.15 wt.% by gravimetric drying. All further experiments were derived from this stock dispersion designated LDH–$CO_3{}^{2-}$.

Ion exchange and exfoliation of the particles were carried out using modifications of previous methods [15] in which the platelets were never dried or ground. Typically 100 mL stock dispersion was filtered and redispersed into 100 mL mixture of NaCl (1 M) and HCl (3.3 mM) solution by vigorous shaking. This suspension was then mixed on a roller table for 24 h to exchange $CoCl_2\cdot 6H_2O$ for Cl^- and this product was designated as LDH–Cl^-. It was filtered and washed with distilled water four times, then redispersed into 100 mL $NaNO_3$ solution (0.1 M). This suspension was mixed for another 24 h and separated by the same method as LDH–Cl^- to produce LDH–$NO_3{}^-$. LDH–NO_3^- was then re-dispersed into 100 mL formamide and shaken vigorously and mixed on a roller table for 24 h to give a putative exfoliated LDH designated as E-LDH. Part of the E-LDH so produced was separated from formamide by centrifugation and re-dispersed in distilled water to produce re-assembled LDH.

2.2. Preparation of LDH films

In order to produce oriented LDH films, the appropriate dispersions were filtered in a disposable Nalgene filter funnel fitted with a sterile cellulose nitrate membrane of 0.2 μm pore size obtained from Thermo-Fisher Scientific (Leicestershire, UK). The filter cakes together with the filter membrane were carefully removed and dried for 24 h in air at room temperature and then in a vacuum oven at ambient temperature for 24 h. The E-LDH dispersion in formamide was filtered with a Millipore Fluoropore membrane made of hydrophilic PTFE and having the same pore size (obtained from Millipore, Hertfordshire, UK).

2.3. Characterisation methods

Part of the stock LDH–$CO_3{}^{2-}$ dispersion was diluted 10 times to 0.015 wt.% before adjusting pH with added hydrochloric acid or sodium hydroxide solutions. Zeta-potential and particle size were measured on a Zetasizer nano-ZS (Malvern Instruments, Malvern, UK) at 25 °C in clear disposable zeta cells. Sedimentation of the stock LDH–$CO_3{}^{2-}$ dispersions (0.15 wt.%) at different pH was recorded in optical quartz cells with a path length of 10 mm as a function of time. XRD measurements were run on either a Bruker AXS D4 Endeavor or a Bruker D500 Theta/2Theta diffractometer at ambient temperature. Scans were from 2 to 55° 2θ with 6 s counting time per step and 0.05° gap per step. SEM images were obtained on JEOL JSM-7401F. Samples were coated beforehand with a GATAN coater (Model 681) with a layer of Au 1–2 nm thick. AFM images were taken on a Veeco Dimension 3100 in tapping-mode and the images were analyzed with the Nanoscope v.6 software. Samples were deposited on freshly cleaved mica surfaces and dried in a nitrogen flow.

3. Results and discussion

3.1. Particle size analysis

After 11 ks (3 h) in the reaction vessel, the clear pink solution started to become turbid and a pink precipitate developed over the 48-h refluxing period. This precipitate, both in its as-prepared