Layered Nanocomposites of Platelet Particles and Polymers

Y. Zhang* and J.R.G Evans**

* Department of Chemistry, University College London, UK, yan.w.zhang@ucl.ac.uk
** Department of Chemistry, University College London, UK, j.r.g.evans@ucl.ac.uk

ABSTRACT

Clay-polymer nanocomposites with a low addition of clay (<5 wt.%) in a polymer matrix results in significant improvement in material properties. Natural materials, such as nacre, show that a combination of a high platelet content in a polymer matrix with a layered packing of the platelets is strong and tough, even if the reinforcing component is itself brittle. This achievement of nature has inspired the synthesis of materials to mimic the nacre structure using smectite clay which has high aspect ratio and elastic modulus. This structure was reproduced by layer-by-layer assembly methods and improved the strength of such materials. A more rapid mass-production pathway has been found to produce sufficient order. We assembled a range of platelet-like particles such as clays, layered double hydroxides and graphene by similar methods and explored layered nanocomposites with polymers. We judge that these approaches will lead to a new generation of high stiffness to weight ratio materials based on biomimetic structures.

Keywords: platelet particles, nanocomposite.

1 INTRODUCTION

Carbon fibre reinforced polymer composite materials occupy a mature market and are applied in the aerospace and automobile industries. Because they have high stiffness and strength to weight ratios than metals, these vehicles become more fuel efficient. Such composites have been adopted in Boeing 787 and Airbus 380 aircraft structures. However, carbon fibre itself is expensive to produce. More recently it was found that a low addition of clay (< 5 wt%) into a polymer matrix can lead to significant property improvement while retaining a wide range of processing options. This has led to widespreaded study in both academic and industrial context in the past two decades. Compared with carbon fibres, clays are much easier to produce and the production process is more energy efficient. Such nanocomposites may also occupy a position as a new class of material and their applications in automobile industry are already in progress [1]. These clay-polymer nanocomposites can only accommodate a small addition of clay, otherwise the mechanical properties begin to deteriorate when the clay content exceeds 5 wt%. Further exploration of the combination of a high ratio of clay (> 50 wt%) and polymer with an ordered instead of a random arangement of clay platelets with polymer interlayers has resulted in nanomaterials which can be as strong as steel [2].

This structure actually mimicks a structure found in naturally occuring material such as nacre (mother of pearl) an example of which is shown in Fig. 1. The strength of nacre is believed to result from its structure: an ordered arrangement of mineral with polymer interlayers although aragonite, the mineral making up nacre, is itself brittle [3]. In principle, other platelet particles, such as clays, layered double hydroxides or possibly graphene, provided that they could pack in an ordered, layered fashion as nacre, could offer as strong, if not even better, material properties [4-6]. Hence it becomes apparent that the successful assembly of platelets is a prerequisite for preparation of such nanomaterials.

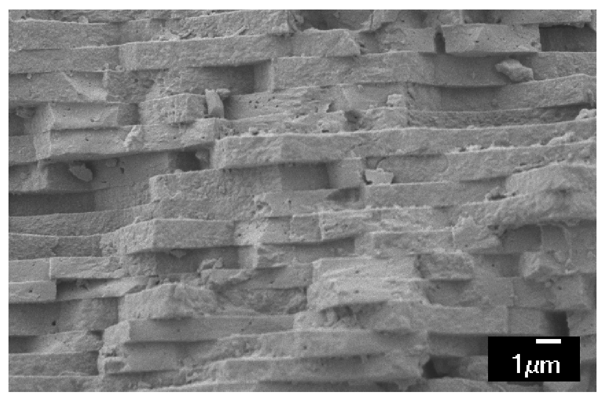


Figure 1: SEM image of the cross-section of a common mussel shell.

There are various potential methods to align platelets such as layer-by-layer deposition, filtration, drying, electrophoresis, shear-induced alignment, slip casting, sedimentation or centrifugation. The filtration method is a scalable and fast method achievable by mimicking the Fourdrinier machine used to make paper. Drying is also technically feasible and easy to scale up. In this work we applied these two methods for platelets assembly from their suspensions. Preliminary development of nanocomposites based on the assembled minerals is also reported.

2 EXPERIMENTAL

Montmorillonite clay (Grade: Nanofil 116) was kindly donated by Rockwood Additives, Germany and used as received. Co-Al layered double hydroxide (LDH) was synthesized in the lab by co-sedimentation of a cobalt salt ($CoCl_2 \cdot 6H_2O$) and an aluminium salt ($AlCl_3 \cdot 6H_2O$) in urea solution based on a previous method [7]. Graphene oxide (GO) was synthesized in the lab by exfoliation of oxidized graphite in its dilute suspension with the assistance of ultrasound treatment according to a previous method [8].

Caprolactam and polyacrylamide solution (Mw: 10,000; 50 wt.% in H_2O) were obtained from Sigma Aldrich, UK and used as received.

The suspensions of clays, LDHs and GO in distilled water were either subjected to filtration or drying processes. To produce the clay composites, the clay films obtained were immersed in caprolactam melt at 80ºC for 5 minutes or a 5 wt% polyacrylamide solution for 24 hours. The composites obtained were dried in air for 24 hours and then under vacuum overnight.

SEM images were obtained on a JEOL JSM-7401F after coating the samples with a layer of Au 1-2 nm thick using a GATAN coater (Model 681). XRD patterns were obtained on Bruker axs D4 Endevour with scans from 2-15º 2θ with 6 s/step and 0.05º/step.

3 RESULTS AND DISCUSSION

3.1 Montmorrilonite films

Fig. 2(a) shows the photograph of a clay film obtained by drying a dilute montmorillonite suspension. It took about 9 days to dry a suspension of 10 mm depth and the film obtained was ~ 45 μm thick. The printed words underneath the film can be clearly discerned showing that the film is transparent to some extent; this possibly indicates well-ordered platelets. Fig. 2(b) shows an SEM image of the cross-section of the film and it can be seen that the platelets indeed packed into a layered structure. Although the platelets were exfoliated into single nanosheets [5], XRD patterns of the resulting film (Fig. 3) shows that they reassembled during the drying process.

Caprolactam is the monomer used to synthesize nylon in industry and it is used to infiltrate the clay film from its melt state as part of the approach towards layered nylon-clay nanocomposites. The resulting film was characterised by XRD as well. Fig. 3 shows the XRD patterns of the montmorillonite film and the infiltrated film. It can be seen that the d_{001} diffraction peak of the caprolactam infiltrated clay film shifted towards a lower angle compared with the original clay film and the interlayer distance has expanded from 1.1 nm to 1.5 nm. This was consistent on both sides of the film and near the centre (as measured on abraded film). This means that caprolactam has intercalated in the clay galaries. Such precursor films might be used for the development of intercalated hybrid polycaprolactam-clay nanocomposites by subsequent polymerisation of the intercalated monomers.

(a)

(b)

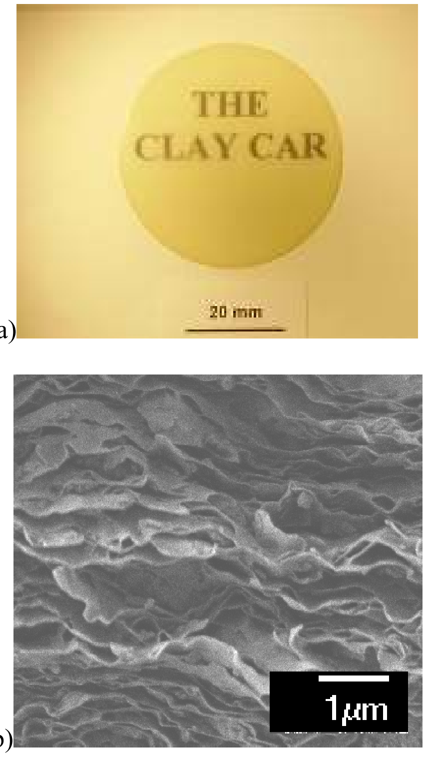


Figure 2: (a) Photograph and (b) SEM image of the cross-section for the montmorillonite film obtained by drying from its dilute suspension.

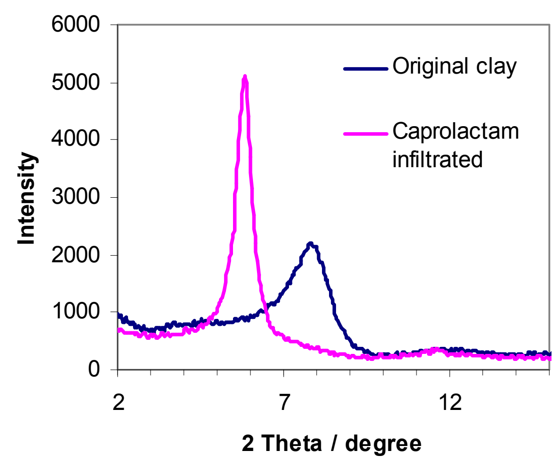


Figure 3: XRD pattern of the original montmorrilonite film obtained by drying and the film with caprolactam.

In another example, polyacrylamide was infiltrated into the clay film from solution. Fig. 4 shows the XRD patterns for an original montmorillonite film and the same film immersed in 5 wt.% polyacrylamide solution and dried. The interlayer distance expanded from 1.1 nm to 2.0 nm (d_{002} is also shown) showing that polyacrylamide intercalated into the clay interlayers. We speculate that these procedures can serve as the basis for the large-scale production of ordered nanocomposites.

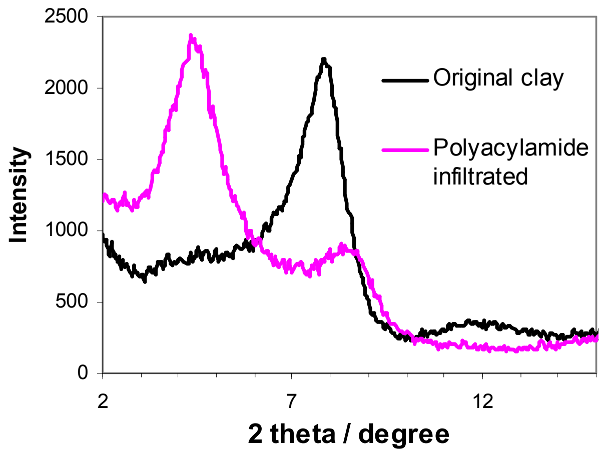


Figure 4. XRD patterns of the original montmorillonite film and the film infiltrated with polyacrylamide .

3.2 Layered double hydroxide films

The as-synthesized hexagonal LDH platelets have an average dimeter of ~ 3 µm and a thickness of ~ 30 nm found by SEM imaging and AFM. Fig. 5 shows a SEM image of the cross-section for a Co-Al layered double hydroxide film obtained by filtration. We have investigated the effects of colloidal stability on the efficiency of ordering for LDH platelets and found that the filtration method is effective for aligning the platelets for both colloidally stable and unstable platelets. When the LDH platelets were exfoliated into single sheets which are ~ 1 nm thick, the build-up of the first few layers in contact with the filter membrane blocked the flow to some extent and the nanosheets could not align themselves after the filtered film had developed to a thickness greater than ~ 10 µm. However, this limit does not apply to exfoliated clay platelets and clay films as thick as hundreds of micrometers can be produced by this method [5].

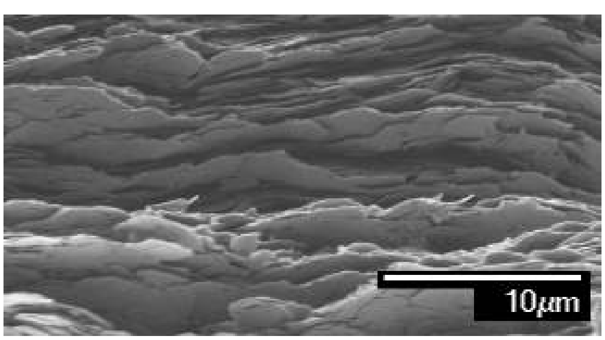
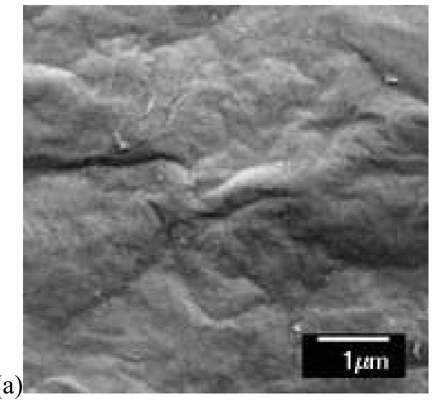


Figure 5: SEM image of layered structure of Co-Al layered double hydroxide particles.

3.3 Graphene oxide films

A dilute suspension of graphene oxide in water was filtered to produce a very ductile film that was strong enough to handle. Fig. 6 shows the bottom surface and the cross-section of a graphene oxide film obtained by filtration. As the exfoliated graphene oxide sheets are very thin, their edges can hardly be discerned by SEM imaging. Nevertheless the cross-section shows a layered packing of these graphene sheets.

(a)


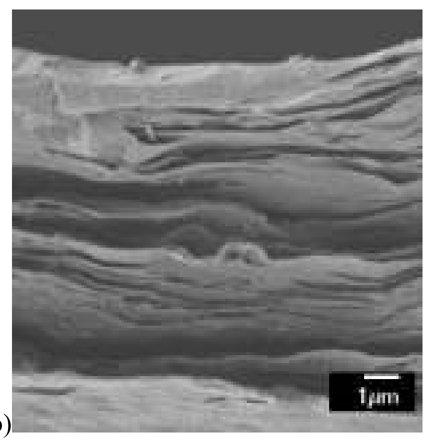
(b)


Figure 6: SEM images of (a) the surface farthest from the filter membrane and (b) cross-section of a graphene oxide film obtained by filtration of its dilute suspension.

4 CONCLUSION

Platelet particles such as clays, layered double hydroxides, and graphene oxide can be assembled into a layered structure from their suspensions. The drying method and the filtration process are both effective. Molecules such as caprolactam and polyacrylamide can be infiltrated into the resulting clay “paper” after the clay tactoids have assembled into a layered structure and produce an intercalated composite of clay tactoids. These explorations offer possibilities for large scale production of layered polymer nanocomposites.

ACKNOWLEDGMENTS

The authors are grateful for Engineering and Physical Sciences Research Council (UK) funding under Grant No: EP/H048855/1: "The Clay Aeroplane". Thanks to Mr Mark Turmaine (EM Lab, Bioscience, UCL) for help on SEM.

REFERENCES

[1] A. Okada, A. Usuki, Macromol. Mater. Eng. 292, 220, 2007.

[2] Podsiadlo, P.; Kaushik, A. K.; Arruda, E. M.; Waas, A. M.; Shim, B. S.; Xu, J.; Nandivada, H.; Pumplin, B. G.; Lahann, J.; Ramamoorthy, A.; Kotov, N. A. Science 318, 80, 2007.

[3] K.S. Katti, D.R. Katti, Mater. Sci. Eng., C, 26, 1317, 2006.

[4] Y. Zhang, J.R.G. Evans, Appl. Surf. Sci., 2011, doi: 10.1016/j.apsusc.2011.03.151.

[5] A Walther, I. Bjurhager, J.-M. Malho, J. Pere, J. Ruokolainen, L. A. Berglund, O. Ikkala, Nano Lett. 10, 2742, 2010.

[6] T. Liu, B. Chen, J.R.G. Evans, Bioinspiration Biomimetics 3, 016005, 2008.

[7] Z. Liu, R. Ma, M. Osada, N. Iyi, Y. Ebina, K. Takada, T. Sasaki, J. Am. Chem. Soc. 128, 4872, 2006.

[8] N.I. Kovtyukhova, P.J. Ollivier, B.R. Martin, T.E. Mallouk, S.A. Chizhik, E.V. Buzaneva, A.D. Gorchinskiy, Chem. Mater. 11, 771, 1999.