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# Hierarchical self-assembly of colloidal nanoplatelets driven by evaporation

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#### Abstract

Driven colloids are out of equilibrium systems, which self-organise into diverse complex structures, and have been one of the major driving themes in materials science. We report experimental studies on the evaporation driven self-assembly of colloidal nanoplatelets of montmorillonite and laponite. The sol-gel transition is studied using a rheometer and imaging by confocal laser scanning fluorescence microscope and an electron microscope to probe the microstructures. Evaporation driven thin films prepared from the bicontinuous gel state show increasing transparency and decreasing surface roughness with increasing concentration of laponite. Polarising optical microscope shows a microstructure with string-like birefringent domains. The scanning electron microscope reveals nacre-like structure of the films and decreasing inter-layer spacing with increasing concentration of laponite. The composite films showed superior flame-shielding property compared to the films made of individual components.

Keywords: colloids, self-assembly, thin films

(Some figures may appear in colour only in the online journal)

## 1. Introduction

New functional materials are often produced by promoting the self-assembly and hierarchical structure of colloidal particles. The geometrical shape, size and interaction of colloidal particles determine the structure and functionality of the new materials [1, 2]. Spherical colloidal particles are known to form a variety of self-assembled structures and in most cases they are well understood [3]. The use of anisotropic colloidal particles has received greater attention as they are potential candidates for creating advanced materials with complex architecture. Moreover, understanding the self-assembly of the anisotropic colloids is important both from the fundamental and application points of view [4–10].

The inspiration for designing new materials often comes from the architecture of natural and biological materials. Amongst various natural materials, nacre, also known as mother-of-pearl, has received a lot of attention mainly due to its exceptional mechanical properties [11, 12]. Nacre is an organic–inorganic composite material produced by molluscs as an inner shell layer of their armour systems. It also makes up the outer coating of pearls [13, 14]. There have been numerous approaches to produce composites with a structure and mechanical properties similar to those of natural nacre [15]. It has been shown that macroscopic nacre-like composite materials can be made from freeze casting [16, 17], hot-press assisted slip casting [18], biomineralization or a bottom-up approach [19], extrusion and roll compaction, [20] and gelcasting and hot-pressing [21]. Thin nacre-like free-standing composites are also prepared by layer-by-layer self-assembly [22], biomineralization [23], centrifugation [24] and evaporation [25]. In this context, clay minerals made of anisotropic particles have emerged as ideal candidates for producing nacre-like structure [26]. The clay particles are considered as patchy colloids with directional interactions and exhibit several phases including sol, gel, repulsive and attractive glasses [27-29]. They have been used for preparing highly ordered, transparent films of higher strength and stiffness with the help of appropriate additives [30].

There are some studies reported on the structural analogues of nacre using nano-clay platelets [26, 31]. A few studies also showed the formation of artificial nacre structure from dilute

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**Figure 1.** Schematic illustration of the preparation of bicontinuous gel (BCG). (a) Fractionated montmorillonite (FMMT) and laponite (L) with composition FMMT<sub>1</sub>/L<sub>0.5</sub>. (b) Homogeneous solution and (c) BCG after 24 h. Transmission electron microscope (TEM) images of L and FMMT particles are shown on the left.



**Figure 2.** Phase diagram of the FMMT/L system. There exist different phases such as sol, BCG, glass and phase separation. The compositions used in this study are circled with dotted lines.

suspensions of montmorillonite (MMT) and in most cases some additives were used for making a nacre-like structure [26, 31]. In this paper, we report on the evaporation driven self-assembly and hierarchical structures of colloidal suspensions of mixed nano-clay platelets of MMT and laponite (L) without any additives. This paper is organised as follows: (i) sections 2 and 3.1 discuss the preparation and rheological characterisation of bicontinuous gels (BCGs); (ii) section 3.2 discusses the evaporation driven self-assembly of colloids from the BCG state and (iii) sections 3.2–3.4 discuss the characterisation of self-assembled structures followed by a simple demonstration of an application.

#### 2. Experimental

The nanoplatelets, laponite-RD (L) and Na-MMT (Cloisite-Na) were graciously gifted by BYK additives and Instruments, Germany. MMT is one of the natural clays with a high aspect ratio. The size of the MMT particle is about



**Figure 3.** Viscoelastic behaviour of a BCG (FMMT<sub>1</sub>/L<sub>0.5</sub>). (a) Evolution of storage (G') and loss (G'') moduli, complex viscosity ( $\eta^*$ ) and tan $\delta$ . The insets show two confocal images taken at sol and gel states. The SEM image in the inset is taken after freeze drying. (b) Yielding of BCG at different aging times of the same samples.

250 nm with a thickness of about 1 nm. Laponite is a charged disc-like particle with a diameter of about 25 nm and a thickness of about 1 nm. Both clays have negative and positive charges distributed on the faces and rims, respectively [34]. Dispersions with different concentrations of clay were prepared by dispersing the desired amount of powder in milliQ water. Ionic strength was adjusted to  $5 \times 10^{-4}$  M NaCl. When required, the pH of the dispersions was adjusted using NaOH, HCl and NH<sub>4</sub>OH. Since the native clay (MMT) has a wide size distribution ranging from a few nanometres to several micrometres, fractionation was done to obtain the average size of 250 nm following the procedure described in our previous studies [33-35]. Binary dispersions of fractionated MMT (FMMT) and L were prepared by mixing individual components, keeping FMMT constant and varying the concentration of L, ranging from 0.1 to 3.0 wt.%.

Rheological experiments were performed using a MCR-501 rheometer (Anton-Paar) with a cone-plate geometry having a plate diameter of 50 mm and a cone angle of  $0.5^{\circ}$ . Real space images were captured on a confocal laser scanning fluorescence microscope (Leica SP8 with a  $100 \times$ , numerical aperture (NA) = 1.4) using an oil immersion objective.



**Figure 4.** (a), (b) Schematic diagram showing gel to film transition using slow evaporation of various compositions of fractionated MMT (FMMT) and laponite. (c) Images of several dry thin films kept on a printed paper. (VI)  $FMMT_1/L_1$ , (V)  $FMMT_1/L_{0.75}$ , (IV)  $FMMT_1/L_{0.75}$ , (IV)  $FMMT_1/L_{0.75}$ , (IV)  $FMMT_1/L_{0.75}$ , (IV)  $FMMT_1/L_{0.75}$ , (III)  $FMMT_1/L_{0.75}$ , (II) 2 wt.% of FMMT; all at room temperature and 50% relative humidity.

Particle morphology was obtained by a JEOL 2100F transmission electron microscope (TEM). Microstructures of the freeze-dried gel samples were obtained on a FEI Nova Nano Lab at 2kV. To prepare the freeze-dried samples, gels were aged until the evolution is almost stopped, and then freezedried at -90 °C under a vacuum ( $10^{-6}$  Pa). Films were prepared by evaporating the solvent in 40 and 100 mm diameter polystyrene petri-dishes at ambient temperature of 25 °C and relative humidity of 50%. The dishes were partially covered for slowing down the evaporation and prevent entrainment of airborne debris. Cross sections were studied after fracturing the films and the scanning electron microscopy (SEM) experiments were performed on a JEOL field emission microscope after sputter-coating with 4 nm platinum. A polarising optical microscope (POM) (Olympus BX-51) was used to study the crystalline properties of the films.

#### 3. Results and discussion

#### 3.1. Rheological studies

Figure 1(a) shows the TEM images of the FMMT and L particles. The individual components of the composite were dispersed in water with the required proportion. For example, figure 1(b) shows a composite with 1wt.% of FMMT and 0.5wt% of L (FMMT<sub>1</sub>/L<sub>0.5</sub>). Initially, it looks like a homogeneous solution but with aging (100 min) it becomes a gel (figure 1(c)). We have recently reported the detailed phase diagram of the FMMT/L system [32]. Figure 2 shows the complete phase diagram of the FMMT/L system. In this study we have worked in the BCG regime with a varying concentration of L. The selected compositions are marked on the phase diagram with dotted circles.

First, we measured the rheological properties of a composition (FMMT<sub>1</sub>/L<sub>0.5</sub>) to understand the gelation. Figure 3(a) shows the variation of G', G'', tan $\delta$  and complex viscosity ( $\eta^*$ ) as a function of time. It is observed that G', G'' and  $\eta^*$ increase and tan $\delta$  decreases with time. The growth of G' and G'' is slow during the initial aging (<100 min.). After about 100 min (= $t_g$ ), the gelation takes place (cross-over of G' and G''). Consequently, tan $\delta$  decreases from 1 to a small value (2 × 10<sup>-2</sup>) and tends to reach a plateau after a long waiting time. Beyond  $t_g$ , the complex shear viscosity  $\eta^*$  also increases significantly as expected.

Real space imaging experiments were carried out to explore the self-assembly of the platelets leading to BCG from a homogeneous solution phase, using a confocal microscope by labelling the clay platelets with rhodamine 6G. The process of gelation was visualised and recorded over different scanning areas. Initially, the dispersions were in the sol state and showed uniform green colour. But as the aging progressed (beyond 100 min), some darker patches started appearing and the number of such patches increases beyond the gelation time (inset of figure 3(a)). The microstructure of BCGs was further investigated on the freeze-dried samples using SEM. Freezedrying was done to prevent drying forces from altering the gel



**Figure 5.** (a)–(e) SEM images showing cross sections of the dried composite films. (f)–(j) Surface morphology of the films.

structure. The SEM image clearly shows a highly porous 3D interconnected network made of two interacting anisotropic platelets (see inset of figure 3(a)).

Aging has a strong effect on the yielding behaviour of the BCGs. Hence, we performed shear tests to probe the yielding of a BCG. Figure 3(b) shows the variation of shear stress ( $\tau$ ) with strain amplitude ( $\gamma$ ) at various waiting times. A two-step yielding behaviour is observed with increasing waiting time. For example, two small peaks in the stress–strain curve are observed after the gelation (2 h). After 24 h, the peak heights are enhanced and one peak at lower  $\gamma$  value is much higher than the one that occurs at higher  $\gamma$ . Similar observations were reported in many colloidal gel systems. The first yielding ( $\gamma_1$ ) is attributed to the breakage of interparticle bonding and the second one ( $\gamma_2$ ) is due to the intercluster bond breaking and fragmentation of clusters [36].

#### 3.2. Evaporation induced self-assembly

Figure 4(a) shows a schematic diagram for preparing clay films from BCGs. They are prepared by a solution casting method in polystyrene petri dishes 40 mm in diameter where the sample goes to a film state through the gel phase by slow



**Figure 6.** X-ray diffraction (XRD) profiles of powder (shown in the inset) and thin-films (20 micron) made from different compositions. The numbers indicate the interplanar spacing.

evaporation. Several dry thin films prepared from various mixing ratios are shown in figure 4(c). The drying rate was varied from 11–20 nm s<sup>-1</sup>. The use of petri dishes allowed us to separate the films easily without breaking. The dried films are kept on printed paper and the images are taken using a camera. The films made from pure FMMT are opaque (figure 4(c)(I)). The transparency of the films increases with increasing concentration of L in the composite (figure 4(c)(II)-(VI)). This indicates that the scattering of transmitted light through the films decreases with increasing concentration of L and this could be due to a reduction of the size of the microstructure and hence improved packing of the nanoplatelets. The orientational order of the nanoplatelets in the films during the drying process is expected because the dispersions contain sodium ions and during the drying, the gel concentrations increase, leading to thinner electrical double layers around the platelets. This causes a weak repulsive force which allows face-to-face arrangement of platelets through the van der Waals attraction.

Figure 5 shows the SEM micrographs of a cross-section with increasing concentration of L in 1wt% of FMMT. The pure FMMT film shows a cross-section with a wavy layered structure (figure 5(a)). The typical layer spacing in pristine FMMT is about 300 nm. Addition of a small amount of L to FMMT reduces the ripples of the layers and also the layer spacing decreases (figures 5(b)-(e)). The layer spacing is about 100 nm in figure 5(e). In addition, the surface roughness of the films also decreases as the concentration of L increases, and subsequently the films became progressively transparent (figure 4(c)). This could be due to the fact that the smaller nanoplatelets are acting like an adhesive between the bigger platelets or because of better exfoliation of FMMT particles in the mixed solution state compared to the single component FMMT dispersion (figures 5(b)–(d)) or due to the filling of voids produced in the films (within the layers or between the two successive layers) by bigger particles during the drying process. Similar observations were reported on graphene



**Figure 7.** (a), (b) Polarising optical microscope (POM) images of different parts of the film (FMMT<sub>1</sub>/L<sub>0.15</sub>), (c) fractured film showing the cross section without polariser. (d) Cross-sectional view with crossed polarisers, (e) drying of the gel in a capillary tube of diameter 1 mm, showing the birefringence at the air–sample interface. (f) Enlarged view showing the variation of retardation across the interface.

oxide/L thin films, where the addition of L reduces the ripples of graphene oxide [37].

To gain more insight into the structure of the composite films, we performed x-ray diffraction (XRD) measurements of the films as well as the L and FMMT powders. Figure 6 shows the XRD profiles of some thin films with various compositions. The layered structure is confirmed by the multiple XRD peaks. The calculated inter-planar spacing of pure FMMT and L films are given as 1.27 nm and 1.47 nm respectively. The inter-planar spacings in the composites are similar to that of the pure FMMT. This means that the addition of L does not affect the inter-planar spacing of FMMT. This suggests that the voids produced in the films are filled with the smaller L particles or better exfoliation of FMMT is responsible for reduced ripples and higher transparency.

Further we looked at the different parts of the films under a POM. Around the periphery of the disc-like film we observed string-like birefringent domains along the radial direction (figure 7(a)). These crystalline domains are extended about 200  $\mu$ m from the rim towards the centre. On the other hand, in the central region of the film, the crystalline domains are randomly oriented (figure 7(b)). This suggests that the nanoplatelets are self-assembled during the slow evaporation due to the interfacial force of the liquid along the radial direction. In the dried state of the film, these create crystalline domains. In the central region of the film, the evaporation takes place vertically hence the crystalline domains are orientated randomly. The POM images of the cross-sections obtained by fracturing



**Figure 8.** SEM micrographs of the thin films prepared from the mixture of FMMT nanoplatelets and silica nanoparticles of average diameter 200 nm (FMMT<sub>1</sub>/Si<sub>0.1</sub>) at pH = 8.5. (a), (c) Cross-sectional view of the fractured film at different magnifications. (b) Surface of the film. (d) Magnified image showing the embedded Si nanoparticles within the layers. (e) Schematic diagram showing the embedded Si nanoparticles within the layers.



**Figure 9.** Flame-blocking test of a film of thickness 20  $\mu$ m (FMMT<sub>1</sub>/L<sub>0.5</sub>). (a)–(c) A film is kept between a cotton ball and the flame and the latter is blocked for 40 min, beyond which it penetrates and burns the cotton. (d)–(f) Optical micrographs of the surface of the films after different exposure times. (g), (h) Physical appearance of the film before and after the fire test. (i), (j) SEM micrographs of the film before and after the fire test.

the films without and with crossed polarisers are shown in figures 7(c) and (d), respectively. It clearly shows birefringent colour with a nacre-like structure.

We have also conducted the drying experiments in a capillary and observed under the POM (figures 7(e) and (f)). The birefringence is observed only very close to the sample–air interface. It indicates that the ordering of the nanoplatelets starts at the interface. Similar observations were also reported in other clay systems [38, 39].

#### 3.3. Effect of spherical silica nanoparticles

We also studied the effect of silica nanoparticles of an average diameter of 200 nm on the formation of the lamellar structure in FMMT. We added 0.1 wt.% of silica nanoparticles in 1 wt.% of FMMT during the gel preparation. This weak gel was dried slowly under ambient conditions to prepare thin films. It is interesting to note that no phase separation was observed in the gels or in the dried film. They are mixed homogeneously, and the presence of silica nanoparticles did not affect the formation of the layer-structure in the film as shown in figures 8(a)–(d). Silica particles mostly go into the voids between the films without affecting the layers. A schematic

diagram of this structure is shown in figure 8(e). This experiment might encourage further studies on the preparation of artificial nacre structures by incorporating nanoparticles of desired size, shape and functionality.

#### 3.4. Flame -blocking property of the thin films

There are some studies on the flame-blocking properties of MMT films with and without additives [31, 40, 41]. Inspired by this, we studied the flame-shielding ability of the composite films by placing a small cotton ball, 1 cm above the film (see figures 9(a)–(c)). The thickness of the film was 20  $\mu$ m. We found that the pristine FMMT film failed to block the flame for more than 10min whereas the composite films blocked the flame for more than 35 min and the flame-blocking time slightly increased with the concentration of L. The physical appearance of the films before and after burning is shown in figures 9(g) and (h). After the exposure to the fire for several minutes, the surface morphology of the films was also studied. Figures 9(d)–(f) show some optical microscope images exhibiting the microstructure of the films after different exposure times. Initially, larger domains are formed. As the exposure time is increased, the larger domains break into smaller

sizes. SEM images before and after the burning of the films are shown in figures 9(i) and (j). A substantial change in the microstructure of the burnt films is observed compared to the unburnt films.

#### 4. Conclusion

We have prepared binary mixtures of nano-clays of FMMT and L without any additives. The mixtures spontaneously evolve from a sol to a gel state with aging. The slow drying of the weak gel induces self-assembly of the nanoplatelets to form very thin layers. Several thin layers are further selfassembled to produce ordered thin films whose structure is similar to nacre, the mother-of-pearl. The L particles mostly go into the voids created by the FMMT particles, thereby reducing the ripples of the layers and the surface roughness. A small concentration of Si nanoparticles does not phase separate from FMMT. They are arrested within the layers creating a hierarchical structure. The FMMT/L films can block the flame for much longer than pristine FMMT films, and hence composite films are found to be a superior flame blocker. It may be mentioned that the drying rate was critical in the evaporation process, and even a slight increase in the drying rate can affect the self-assembly and hence the quality of films. This process has an advantage of producing thin films on any substrate since the starting material is a gel. We believe that the nacre-like structure consisting of binary nanoplatelets and nanoparticles has potential for making advanced materials with a hierarchical structure and improved physical properties for various applications.

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