# Flexible inorganic films and coatings

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This paper describes a new family of materials derived from layer minerals such as phillosilicates and includes vermiculite, montmorillonite, etc. They are structurally analogous to the organic crystalline polyethylene in which the crystalline lamellae are replaced by inorganic lamellae of comparable dimensions. Flexible films can be produced with tensile strengths of 30 to  $160 \text{ MN m}^{-2}$ , elongation of up to 6% and moduli of  $14 \text{ GN m}^{-2}$ ; they are stronger than organic films. Suspension of discrete lamellae in water can be used as coating for a variety of surfaces. The most interesting is the vermiculite-coated glass fibre which has unique properties. Finally, the suspension can be used to make a wholly inorganic foam which has similar properties to organic foams with good compressive strength.

### 1. Introduction

The evolution of the science of organic macromolecules followed directly from the knowledge developed for simple organic molecules. The valency rules for combining carbon atoms with other carbon atoms and with oxygen and nitrogen are the same for a macromolecule as for a simple compound. For example, it is easy for a graduate chemist to visualize the relationship between ethane, dodecane and polyethylene as primarily a matter of molecular weight thus:

$$CH_3CH_3$$
  $CH_3[CH_2]_{10} \cdot CH_3$   $CH_3[CH_2]_n - CH_3$ .

This simple idea combined with a system of converting any organic reaction which links molecules together into a polymerization process has produced several homologous series of macromolecules.

No such simple rules exist for the synthesis of inorganic macromolecules. It is possible to synthesize linear inorganic macromolecules but no general rules are known. Frequently the route to these is by ring opening a cyclic monomer as in the case of sulphur, selenium and tellurium. The products obtained are usually thermally unstable because of reversion to the ring form and offer little or no prospect for high-temperature use. The bulk of the studies have been on molecules which incorporate a significant fraction of organic atoms or groups. These organo-metalloid or organosilicon polymers can be synthesized but only the silicons have advantages over oganic materials for high-temperature use.

In seeking new ideas for synthesizing completely inorganic materials we decided not to follow structural concepts originating from classical organic chemistry at the molecular level but to create analogues of the supra molecular structure observed in crystalline organic macromolecules in the solid state. Small-angle neutron scattering studies support a structure for poly-olefins specimens in which the crystalline lamellae produced by the folding of many macromolecules are connected by fragments of unfolded polymer chain [1]. It has also been revealed that these structural features are preserved in highly oriented specimens [2, 3]. The thickness of these lamellae can vary but values of 5 to 24 nm are common to many systems. Moreover, the laterial dimensions can be several microns so that the lamellae have large aspect ratios. Fig. 1 illustrates the basic features of the structure.

This paper describes work in which attempts have been made to product analogues of polyethylene and polypropylene by replacing the organic crystallites with inorganic lamellae and linking these together using inorganic and organic tie molecules.



Figure 1 Diagrammatic representation of the structure of a crystalline polyolefin deduced from small-angle scattering of neutrons and X-rays. (a) Folding of polyolefin macromolecule; (b) structure equivalent to two structural elements [1-3].

A readily available source of inorganic lamellae is to be found among a very large group of natural minerals known as the phyllosilicates including vermiculite, montmorillonite, hydrobiotite and chlorite-vermiculites. These have been studied extensively by scientists concerned with the structure of soils and the manufacture of ceramic materials [4]. In their many uses advantage is taken of the very high surface area which enables them to interact with organic liquids as well as water. Ceramics technology takes advantage of the fact that the hydrated surfaces of the particles lose water on heating in a furnace forming covalent bonds which link the structure threedimensionally. Such materials are stiff and brittle. The first attempt to product flexible structures from layer minerals was by Walker [5] who succeeded in making films from chemical delaminated vermiculite. Such films were of interest at the time but compared unfavourably with films made from organic materials such as polyethylene and polyethylene terephthalate (PET).

At the time this work was carried out there was little evidence that materials formed by the assembly of lamellae could give structures which were flexible, strong and able to undergo moderate deformation. The fact that polycrystalline organic materials contained such elements suggested that wholly inorganic analogues could be made. In this paper we describe the principles which enable high aspect ratio lamellae to be organized to form strong two- and three-dimensional structures. In particular the application of these ideas to the inorganic foams with good thermal mechanical properties. There is a need to develop such materials where applications above 200° C are



Figure 2 Crystal of vermiculite as seen by the SEM showing cleavage planes.

sought and where there is a possibility of fire. This need has intensified since the recognition of the health hazards associated with asbestos and the unsatisfactory behaviour of organic foams in fire.

#### 2. Experimental details

#### 2.1. Preparation of vermiculite suspension

Vermiculite is a magnesium aluminium silicate having a layered structure as shown in Fig. 2. Aluminium substitution in the silica layer gives rise to a charge imbalance which is satisfied by magnesium counterions in the interlamellar spaces. These divalent counterions bind the 1.45 nm layers together to form the macro crystal as shown in Fig. 3.

In order to separate the individual unit layers

of the crystal the divalent counterions are exchanged for monovalent counterions. This is achieved by heating the ore in a solution of the exchanging cation.

In a typical ion exchange process the ore is refluxed in a saturated sodium chloride solution for about 30 min and, after thorough washing to remove the magnesium ions leached from the ore and the excess sodium chloride, is refluxed in 2M *n*-butylammonium chloride for a further 30 min. The monovalent butylammonium ion then replaces the sodium ions from the first exchange and also removes residual magnesium ions. This second ion exchange could be performed without the first sodium exchange but would take several hours to go to completion because of the larger size of the butylammonium ion compared to the sodium ion. The ore is again washed thoroughly to remove excess ions. During the second washing the ore begins to expand as water is imbibed into the interlammelar spaces and bulk volume increases of up to 30 times the original volume of the ore can take place.

The chemically swollen ore is then mechanically delaminated in a high shear mixer, e.g. a Waring Blender, or a suitable colloid mill. Larger particles of the ore are removed from the well delaminated component by a sedimentation process or by sieving through a 50 micron sieve.

# 2.2. Characterization of particles *2.2.1. Sieving*

The particle-size distribution of the original vermiculite was measured by dry sieving through wire sieves, while that of the delaminated suspen-



*Figure 3* Structure of the vermiculite mineral [4].

sion was measured using a Fritsch Microprecision sieve system which enabled a size distribution down to  $5 \,\mu$ m to be determined. In the latter technique, electroformed sieves of sizes from 5 to  $50\,\mu$ m were mounted on the sieve shaker and filled with de-ionized water. 100 ml 1% suspension of the delaminated vermiculite was then placed in the top compartment and sieving was commenced. The liquid level was kept topped up during the sieving and the end point determined when water flowing through the  $5\,\mu$ m sieve was clear. After draining the stack, the sieves were dismantled, the particles washed off dried and weighed.

### 2.2.2. Sedimentation

The Stokes' diameters of the delaminated vermiculite suspension were measured on a Fritsch Pipette centrifuge. In this technique particles are sedimented under high g forces (750 to 1500 rpm) in a centrifuge and samples are extracted in a given time sequence which can last up to 2 h. The time of sampling corresponds to a particular Stokes' diameter while the concentration at that size is measured by evaporating down the extracted suspension.

### 2.2.3. Electron microscopy

A Phillips 300 transmission electron microscopy was used to examine the diameter and the shape of the vermiculite lamellae. High-resolution studies also gave an indication of platelet thickness.

Some of the products made from the vermiculite suspensions were studied using a JEOL JSM 35 scanning electron microscopy.

# 2.2.4. Platelet thickness determination by dye absorption

Dye absorption is a well known technique for the measurement of surface areas of clays [6, 7]and although the method has sometimes been questioned when comparing different clays, very good results can be obtained when comparisons are made on the same clay mineral. Worrall [8] has shown that if cationic dyes are used to determine the areas of clay minerals, it is only necessary for the cation exchange capacity of the layer mineral to be larger than the dye absorption capacity as the former provides part of the driving force for the latter.

In order to determine the surface area of the clay, the orientation of the dye molecule and hence its effective covering power, must be known.

It has been shown that when the point of optimum flocculation is reached using methylene blue, faceon absorption of the dye molecule takes place. Although molecular model measurements give a surface area of about  $1 \text{ nm}^2$ , in practice the covering power of the methylene blue molecule is  $0.85 \text{ nm}^2$  per molecule. This value has been confirmed using Laponite (a synthetic Hectorite) which is essentially totally dispersed into unit layers and has a theoretical surface area of  $760 \text{ m}^2 \text{ g}^{-1}$ . Therefore, by relating the measured surface area of the vermiculite in suspension to that of Laponite a measure of the unit thickness can be obtained.

### 2.2.5. Platelet diameter determinations

In order to obtain a distribution of diameters as well as thicknesses the vermiculite suspension was fractionated by a centrifugal sedimentation technique. Knowing the equivalent spherical radius from the conditions used in the centrifugal fractionation, and measuring the thickness of each fraction by dye absorption, the particle diameter (a) was calculated using the following approximate relationship [9]:

$$a = (0.66 \cdot r^2)/b,$$

where r is the equivalent spherical radius, and b the thickness of the disc.

## 3. Results and discussion

# 3.1. Properties of colloidal particles derived from layer minerals

Layer minerals, as their name implies, are composed of crystals which have a large surface area compared with their thickness. Fig. 2 shows a scanning electron micrograph (SEM) of a crystal of vermiculite in which the edge on view shows typical cleavage planes and the basic lamellae structure. Crystallographic analysis [4] shows these structural elements result from the molecular organization shown in Fig. 3. The unit crystal consists of an inner core of magnesium oxide/ hydroxide which is connected to an outer silicate layer. This crystalline sandwich is 0.9 nm thick with a surface area that is very large in relation to the thickness. An additional feature to the surface of the crystal is that in the polymeric Si-O layer, some tetravalent Si atoms are occasionally replaced by trivalent Al-atoms and more rarely by trivalent Fe-atoms. The effect of which is to make the surface negatively charged. This is balanced by the





interlayer between lamellae having magnesium ions, with associated water molecules, so that overall the system is electrically neutral. The interlayer is 0.5 nm thick and the structure repeats itself thereafter every 1.4 nm. The lamellae are stacked together like a pack of playing cards.

Although we have described vermiculite, which is the mineral discussed in this paper, minerals such as montmorillonites, mica, chlorites belong to this class of layer minerals.

Several methods have been proposed to dissociate the macroscopic crystals into its fundamental lamellae [5]. The crudest procedure is to vaporize the water between lamellae thereby forcing the structure to expand. This is known as exfoliated vermiculite and is an article of commerce. A typical SEM of a section of such a crystal is shown in Fig. 4. It is evident that separation is imperfect and the majority of lamellae formed are several orders of magnitude thicker than the fundamental lamellae. The preferred method employs the ion exchange properties of the magnesium gegen ions in the interlamellae regions. We have used a two-stage procedure consisting of exchanging magnesium ions for sodium in concentrated brine solution followed by replacement of the latter with an organic cation of the type  $C_nH_{2n+2}NH_3^+Cl$ . The effect is to reduce the ionic forces bonding the lamellae together and then to force the lamellae apart by osmotically driven entry of water. The effect is to produce a 30fold expansion of the crystal to give a waterbased gel. This effect is shown in the photographs in Fig. 5 which show the dimensions of the initial crystal and the expanded gel produced. Within the gel, total separation of the lamellae has not occurred but the process can be completed by shearing an aqueous dispersion of the gel in a colloid mill. The process is described in detail in Section 2. The product differs fundamentally from that produced thermally. Transmission electron micrographs (TEM) of the lamellae viewed normal to the surface (Fig. 6) show that they are several microns in diameter and are exceedingly thin, thin enough to appear transparent even where the lamellae overlap. This is confirmed by viewing edge-on at 500 000 magnification as shown in Fig. 7, where six unit layers can be seen in the lamellae.

It has been found that many of the properties of films prepared from these aqueous suspensions are determined by the distribution of particle thicknesses and particle diameters. These two parameters can be measured using a combination of techniques including micron sieving, dye adsorption and centrifugal sedimentation as described in Section 2. Fig. 8 shows the type of information obtained, expressed as a weight fraction of the total material used. The relationship between Fig. 8a and b, for example, is that for any given diameter range; the distribution of particle thicknesses is given in Fig. 8b.

It is also evident from Fig. 8 that samples of the mineral of different geographical origin give



Figure 5 30-fold expansion of ion-exchanged vermiculite: (a) a few seconds after immersion in pure water, (b) after several hours in the same medium.



Figure 6 Chemically delaminated vermiculite lamellae as seen in the TEM. Opaque lines are curled edges of the latter.



Figure 7 Edge of curled vermiculite lamellae crystal showing that the latter is 6 unit layers (8.7 nm).



Figure 8 Weight fractions of vermiculite lamellae by diameter and thickness.



Figure 9 Diagrammatic representation of a swollen vermiculite gel showing distribution of lamellae thicknesses.

n = number of unit layers

suspensions with the same delamination procedures, and different distributions with respect to thickness and diameter.

The origin of the distribution of lamellae thicknesses relates to the uniformity of the chemical delamination process. The weight fraction-lamellae thickness distribution plots in Fig. 8 describe the composition of the swollen gel which is illustrated in Fig. 9. The lack of uniformity in the original mineral means that delamination is incomplete and partially delaminated lamellae act as tie fragments for the whole gel structure. It is the latter which are fractured in the shear field created by the colloid mill. It is only by repetitious chemical delamination techniques that suspension of lamellae which are predominantly one unit layers in thickness can be obtained.

# 3.2. Formation and properties of films formed from suspension of lamellae

The aqueous suspension of lamellae is highly anisotropic and the phenomenon of streaming birefringence is observed on stirring or pumping through glass tubes. Moderate shear fields are sufficient to completely align the high aspect ratio lamellae. The forces exerted by surface tension on simply evaporating the water from the suspension produces total alignment of the particles and flat, highly coherent, films are obtained. These films vary in properties with the homogeneity of the suspension of the lamellae. There is also considerable variation in the optical properties of the films and clear, almost transparent, material can be obtained with very homogeneous suspensions. Some of these better films have properties which



Figure 10 Comparison of stress-strain curves for vermiculite film with copper foil and poly(ethyleneteraphthalate) film.



Figure 11 Fracture surface of vermiculite film showing parallel layers of clusters of lamellae.

are superior to films obtained from organic polymers such as polyethylene and polyethylene terephthalate (PET). A typical stress—strain curve is shown in Fig. 10 and the relevant parameters compared in Table I.

The surprising aspect of the stress-strain curve is its close similarity to the organic films notwithstanding the fundamentally different molecular structure. There is, however, no recovery if the stress is released in the Hookian region whereas the PET film will recover some of the extension on releasing the stress. In this respect vermiculite films resemble lead foil. Fig. 11 shows the SEM of a fracture surface of the film. It shows the manner in which the layer structure has been generated from individual lamellae. The latter appear to arrange themselves in sheets of about 100 nm thick, which are separated by voids of comparable thicknesses. Consequently, the density of these films is approximately 1.7 g cm<sup>-3</sup> compared to 2.4 g cm<sup>-3</sup>, the density of a single lamellae. Higher densities can be achieved by compression.

Additional evidence that voids comparable in dimensions to the wave length of light are present is obtained by treating the films with various liquids. These penetrate the structure, filling the unoccupied space and thereby reducing significantly the interfacial scattering. Phosphoric acid used in this way produces a composite structure which is translucent. Alternatively improvement in the homogeneity of the slurry by removal of lamellae with diameters greater than  $0.05 \,\mu\text{m}$  produces a film which is also translucent.

### 3.3. Nature of the forces binding lamellae

In the absence of binding cations the strength of the films derived from vermiculite lamellae is remarkable. The nature of the binding forces between lamellae in layer minerals has been discussed by Bailey and co-workers [10, 11]. Electrostatic forces or ionic forces are primarily

TABLE I Mechanical properties of films

Material	Tensile failure (MN m <sup>-2</sup> )	Tensile modulus (GN m <sup>-2</sup> )
Copper foil	240	27.0
Vermiculite film	160	14.1
PET film	125	4.3

responsible for keeping the clay particles together and are the dominant forces in ionic solids such as NaCl or MgO. Inhomogeneities at the molecular level at the surface of the lamellae result in the presence of local regions which are both negatively and positively charged although, overall, the lamellae carry a surplus of electrons corresponding to the gegen ion concentration originally present in the mineral. These + ve and - ve charges are, however, not mobile and are located in specific domains of the surface. This is shown diagramatically in Fig. 12a and shows that lamellae will arrange themselves with positive and negative charges opposite each other. The force of attraction, expressed as the energy required to separate the plates, is inversely proportional to the square of their distance apart. It is evident from Fig. 12b that the ionic attractive force can be effective over distances of 5 nm or more. This means that with the kind of thickness distribution shown in Fig. 8 that the irregularities in lamellae thickness will not weaken the assembly. Also shown in Fig. 12b is the contribution to be expected from dispersion or Van der Waals' type forces. These are considerably weaker, 10% of the total attraction at 1.4 nm distance, than the ionic force and would only be effective if all the lamellae had the same thickness. It should also be pointed out that the model of the surface given in Fig. 12a predicts that the structure would resist shear forces tending to separate lamellae.

It is also evident from Fig. 13 that the size of the faults at the boundaries between adjacent lamellae affect the mechanical properties. It is to be expected that increasing the diameter of lamellae will result in the size of the voids between lamellae. If the lamellae were very thin discs, as shown in Fig. 13d, then the radius of the faults between the discs would be approximately 0.11D. In fact, the electron micrographs show clearly that lamellae are irregular in shape and that the diameters quoted derive from the pore size of the filter through which they pass and represent an average dimension of a more complete shape. To



Figure 13 Application of principles of Griffiths theory to work of fracture of vermiticulite films. (a) Plot of stress against the reciprocal of the maximum diameter in the slurry. (b) The direction of the applied stress in relation to the fault in the structure. (c) Relationship between diameter of particles and radius of fault.



Figure 14 SEM of glass fibres coated with vermiculite diameter of fibres,  $15 \,\mu$ m.

identify the effect of this type of fault in the structure on the mechanical properties, particles with large diameters (D) were removed and the breaking stress on the film produced measured. The data are plotted in Fig. 13a, which shows that in accordance with Griffith's theory the brittleness of the sample is related to the radius of the larger faults. Griffith's theory states that if  $\gamma$  is the surface free energy of the material, E is Young's modulus,  $\delta$  the uniform stress required to break the specimen, and c the radius of the fault, then we have the equation:

## $\delta = (2E\gamma/\pi c)^{1/2}.$

Fig. 13b shows the arrangement of the test specimen and Fig. 13c is a diagrammatic representation of the voids between lamellae.

#### 3.4. Vermiculite coatings

The vermiculite film can also be formed around fibres or on metal surfaces. In many instances the adhesive is exceptionally good. A particular useful application is the composite system obtained by encapsulating glass fibre as single filaments, or as woven fabric. An SEM of glass fibres which have been coated with the aqueous suspension and dried is shown in Fig. 14. The unusual feature to the coating is that it totally encapsulates each fibre. This can be seen from the fracture surface shown in Fig. 15. Although the coating is 1 to  $2 \times 10^2$  nm thick it consists of at least 100 lamellae arranged in a continuous layer. The latter protects the glass from fusion on heating above its meltingpoint. This is demonstrated by comparing the photographs shown in Figs. 16 and 17. The un-



Figure 15 SEM of fracture surface of glass fibre  $15 \,\mu\text{m}$  in diameter showing layered structure of coating.

Figure 16 Melting of uncoated glass fabric in a bunsen burner flame after exposure of 14 sec.





Figure 17 Demonstration of stabilities of coated glass fabric after exposure to a flame for 42 min.



Figure 18 SEM of glass fibre exposed to a bunsen flame showing some exposed layers of vermiculite but that the underlying coating still interacted.

coated glass-fibre melts and rapidly recedes from the 900° C flame in a matter of seconds, whereas the coated fibre withstands the heat continuously and retains the integrity of the fabric structure. Electron micrograph of vermiculite coated glass fibre after heating to 800° C is shown in Fig. 18. It is evident that some lamellae have peeled off, but the majority remain and protect the underlying glass fibre. Even when the glass is completely melted by heating in a furnace at  $1200^{\circ}$  C it is evident from Fig. 19 that the vermiculite coating retains the glass globules and flow cannot occur. A similar thermal barrier can be created to prevent aluminium foil melting when exposed to hightemperature flames as shown in Fig. 20. Figure 19 Effect of heating glass fibre to  $1200^{\circ}$  C in an oven for 24 h showing that the melted fibres are still encapsulated by the coating.





Figure 20 Barrier properties of vermiculite-coated glass fabric. Upper surface aluminium foil.



Figure 21 Additional methods of binding vermiculite lamellae together: (a) magnesium ions derived from soluble magnesium compound; (b) growth of hydrated magnesium oxide crystals from magnesium inner core of mineral.



Figure 22 Growth of magnesium hydroxide at defects in the surface of vermiculite crystal where magnesium hydroxide core is exposed.

### 3.5. Stabilization of films and coatings

The lamellae, after removal of the water, contains about 3% *n*-butylammonium ions. This corresponds to one molecule per 0.5 to  $1 \text{ nm}^2$ . If the film is re-immersed in water then it will disperse in this medium. This can be prevented by exchanging the *n*-butylammonium ions with any multivalent ion Mg<sup>2+</sup>, Ca<sup>2+</sup>, Zn<sup>2+</sup> or ammonium ion. Magnesium ions as chlorides, hydroxides or phosphates restore the mineral to its original form. This treatment can take place during the final stages of drying, or a post-treatment is possible. The ammonia treatment can take place in aqueous solution or as a gas. The final structure is represented diagrammatically in Fig. 21a.

An additional coupling system can be obtained using  $10 \,\mu m$  MgO particles. In water, microscopic studies show that these particles dissolve slowly and deposit a hydrate in the form of needle-like growths (nemalite):

 $\begin{array}{rcl} MgO + H_2O & \longrightarrow & Mg(OH)_2 + MgO_2(OH).\\ solid & solution & insoluble \\ & & hydrate \end{array}$ 

In the presence of vermiculite lamellae the electron microscope reveals that the brucite core of the particles acts as nuclei for the formation of nemalite. The photographs in Figs. 22 and 23 were obtained by immersing a large crystal of vermiculite in a suspension of MgO particles at room temperature. Nucleation occurs at crystal faults where the brucite edge is exposed and clusters of needles radiate from these regions. Similar observations were made with isolated lamellae as shown in Fig. 23; in this case the needles are radiating from the edge of a  $5 \,\mu m$ diameter particle. These growth processes lead to the formation of crystal bridges between lamellae as shown diagrammatically in Fig. 21b. The latter increases the strength of the structure but reduces flexibility. Magnesium oxide has particular advantages for making foams of vermiculite suspensions.

### 3.6. Inorganic foams from layer minerals

Foams are readily produced by introducing small air bubbles into the suspension which has the maximum solids content whilst still retaining flow



Figure 23 Crystal bridges of magnesium hydroxide growing radially from the edge of a single lamellae.



characteristics. It is necessary to add the water stabilization agent just prior to formation of the foam. It has been found that addition of magnesium oxide particles gives foam with the highest compressive strengths due to the formation of crystal bridges between lamellae as described previously. A cross-section of a typical foam is shown in Fig. 24, and Fig. 25 gives the relationship between foam density and compressive strength. At the lower density the material is comparable with organic foams such as phenyl formaldehyde, polystyrene whereas at the higher density they have similar or superior strength to foamed glass or calcium silicates. The other property which is dependent on the density of the foam is the thermal conductivity. The relationship between these two parameters is a linear one as shown in Fig. 26.

#### 4. Future work

It is evident that layer minerals are capable of producing a range of materials with some of the properties of crystalline organic polymers. Future research will no doubt extend the range and uses of these simple structures.

These products are now being developed within



Figure 25 A plot of compression strength against density of vermiculite foam and the vermiculute/MgO foam. PS: polystyrene foam, PU: polyurethane foam, PF: phenylformaldehyde foam.



Figure 26 Thermal conductivity against density of vermiculite/MgO foam.

the inorganic materials business area of Mond Division of ICI. Production is presently at a Pilot Plant level and various industries are studying their use. The inventions described are the subject of various patents [12].

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