Organic-inorganic hybrids—the best of both worlds?

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Man has been exploiting the properties of both inorganic and organic substances for millennia, whether it be in the pottery of ancient civilisations or the pharmaceutical properties of plant extracts. The ancient Greeks regarded these as very different, the pottery being of mineral origin and the plant being vegetable. This distinction has survived largely unscathed until relatively recently, with the two types of materials generally displaying radically different properties and finding quite different applications. While the attractions of combining, for example, an inorganic glass with an organic polymer on a molecular level are manifold, it is equally self-evident that the conditions required for processing a glass are entirely incompatible with the much lower processing temperatures needed for polymers. This all changed with the realisation in the 1980s that organic components could be combined with inorganic glasses using the *sol-gel process*. Around the same time, various research groups were exploring routes to combining polymers with clay minerals to produce different types of *organic-inorganic hybrids*. This area has flourished in the past 20 years or so and this article will highlight some of the advances made by us and others in recent years.

The rationale behind all this activity is the unique combination of properties accessible via a hybrid approach. For example, a polymer can be modified by the inorganic component to provide improved thermal and mechanical properties. Alternatively, polymer-modification of a glass or ceramic can introduce improved flexibility and processability. In principle, an infinite number of combinations is possible, although this is limited in practice by processing considerations. Other benefits include the possibility of incorporating an active organic component within a porous glass to produce an active glass such as a sensor. Isolation of active organic species within an inorganic matrix can also have implications for the behaviour of, and interactions between, the organic molecules. An interesting example of this is sol-gel silica entrapped bacteria (Fig. 1), where communication (quorum sensing) between individual bacteria is hindered by the matrix [1].

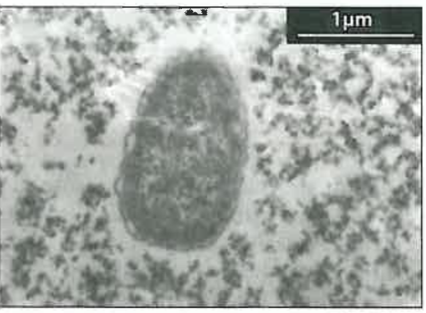

Fig. 1: Electron micrograph of an isolated bacterium trapped within a sol-gel silica matrix. [Reprinted by permission from Nature Materials (N Nassif *et al., Nature Materials*, 2002, **1**, 42-44) copyright (2002) Macmillan Publishers Ltd.]

Nanomaterials

Many of these hybrids are examples of *nanomaterials* [2], where one or more component phases exists on a nanometre scale (< *ca.* 100 nm). There has been much hype about nanomaterials, creating an impression that they are a panacea for all technical ills; the reality may sometimes be quite different, leading to a degree of creeping cynicism. In the context of organic-inorganic hybrids, a key question is whether it really matters whether they are true nanocomposites or not. For some applications (e.g. sensors), this can result in a transparent hybrid, which may be highly desirable. In terms of the effect of nanoscale morphology on mechanical properties of polymer hybrids, the existence of a large number of interfaces and consequently high interfacial area in comparison to conventional filled polymers leads to the potential for energy absorption and subsequent system toughness, although this has yet to be fully realised. Although it has been claimed that nanofillers can lead to highly rigid and strong composites, work to date has indicated that in many cases, the resultant nanocomposites behave as expected for more conventional microcomposites, such as fibre-reinforced polymers. For example, in the case of nanocomposites consisting of clay platelets dispersed in a polymer matrix (so-called exfoliated systems), certain mechanical properties such as modulus have been found to follow the classical Halpin-Tsai model for composite behaviour (equations 1 and 2). The key parameter is the aspect ratio of the clay platelets, which behave in a similar way to short glass fibres of comparable aspect ratio (represented in the equations by the shape factor, ξ).

$$\frac{E_c}{E_m} = \frac{(1+\xi\eta V_r)}{(1-\xi\eta V_r)} \qquad \textit{Equation 1}$$

and

$$\eta = \frac{(E_f - E_m)}{(E_f + \xi E_m)} \qquad \textit{Equation 2}$$

E_c = composite modulus (stiffness)
E_m = matrix modulus
E_f = fibre modulus
V_r = volume fraction of reinforcing phase
ξ = shape factor

Clay nanocomposites

There are two kinds of clay nanocomposites (Figure 2), which are referred to as either intercalated or exfoliated, depending on the degree of separation of the individual clay platelets. Note that although the figure shows the platelets as rigid entities, in reality they have some flexibility which means they may not be linear in the composite. The main approaches to preparing these nanocomposites initially require the platelets to be made 'organophilic', by exchanging the interstitial metal ions with a charged organic species such as a cationic surfactant. This aids penetration of organic species into the interstices and subsequent interlayer expansion and eventual exfoliation. Preparative routes include the use of solvent blending of the polymer with the clay, *in situ* polymerisation of monomer precursors on the clay and melt blending of the polymer and clay. Whether an intercalated or exfoliated structure is formed depends on the synthetic method used and other factors, such as the nature of the clay. The presence of clay platelets in the polymer leads to a number of possible applications, including gas barrier products and fire retardant materials. One rationale behind these properties is the so-called

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tortuous path imposed by the clay platelets on molecules moving through the polymer. An interesting example of the barrier application is work by the US Army to develop impermeable food containers for long term use in the field.

The optical properties of nanocomposites have attracted much interest, particularly their transparency and 'active' optical properties. Transparent products can be obtained from layered systems under certain conditions. Hybrids of clay and nematic liquid crystals exhibit interesting electro-optical properties. These materials can be transparent (Figure 3, a) or opaque (Figure 3, c) depending on the frequency of the applied electric field[3]. The effect is reversible and can be repeated many times. The transparent and opaque states exhibit a memory effect after switching off the field (Figure 3, b and d). Such materials have potential applications in optical storage devices, displays and light-controlling glass. Poly(*p*-phenylene vinylene)s have been studied extensively for their electroluminescence and potential applications in light emitting diodes (LEDs). The synthesis of intercalated hybrids of smectic clay and a substituted poly(*p*-phenylene vinylene) has been reported—these hybrids exhibit electroluminescence and the luminescence appears to be colour tunable depending on the degree of intercalation.

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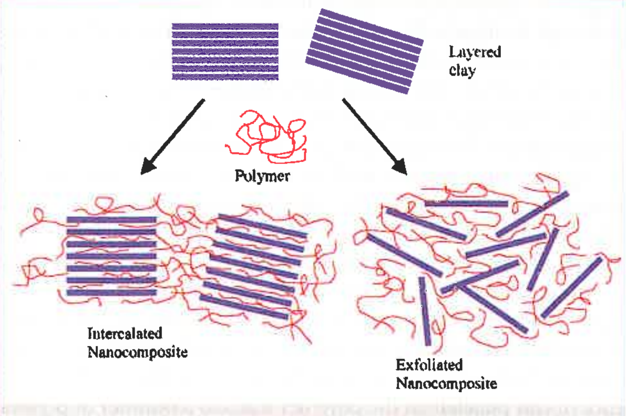
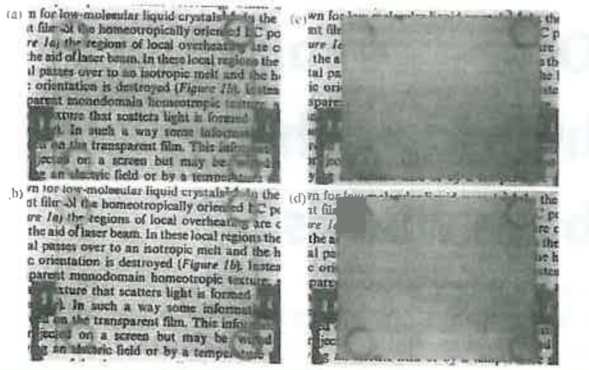
Sol-gel hybrids

The main alternative to the clay route for the formation of organic-inorganic hybrids is the sol-gel process. This is a low temperature route to inorganic oxides and glasses, which involves the hydrolysis and condensation of precursor molecules, typically alkoxides. The reaction proceeds *via* formation of a *sol*, which subsequently *gels*, hence the name. The fact that this process occurs at temperatures between ambient and about 200°C makes it possible to form a vast array of hybrids of oxides such as silica, alumina and titania with organic species ranging from polymers to small organic molecules to bacteria (Figure 1). The products can also be produced in a variety of physical forms, including coatings, monoliths, fibres and nanoparticles. The many potential applications of such sol-gel hybrids include speciality coatings, structural materials, active glasses, sensors, biomaterials, catalysts and so on. An article of this nature can barely scratch the surface of this vast topic, so the versatility of sol-gel science will be illustrated with reference to only two areas, *viz.* sensors and biomimetics.

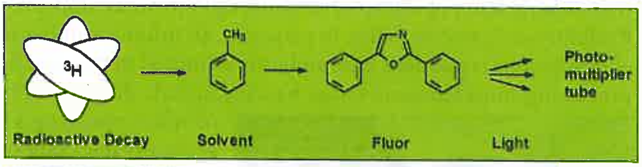


▲ Fig. 2: Formation of polymer-clay nanocomposites.



▲ Fig. 3: Electro-optical properties of clay-nematic liquid crystal hybrids: (a) low frequency, on; (b) low frequency, off; (c) high frequency, on; (d) high frequency, off. [Reprinted from Materials Science & Engineering C, Vol 6, Kawasumi *et al.*, 'Nematic liquid crystal/ clay mineral composites', pp 135-143, Copyright (1998), with permission from Elsevier].

Some of the benefits of using sol-gel hybrids as sensors are illustrated by patented work on radioactivity sensors undertaken at the University of Surrey. Detection and quantification of radioactivity in liquids is important in situations such as accidental spills into watercourses. Well-publicised cases of contamination of streams by tritiated water (tritium is a β emitter) illustrate the problem. The conventional approach to measuring this radioactivity involves addition of a so-called liquid scintillation cocktail (Figure 4) to the liquid. Energy transfer occurs from the radioactivity emitted by the radionuclide *via* the solvent to a small molecule which acts as a fluor, *i.e.* emits light which can then be 'counted'. Because the measurement is done by mixing this scintillation cocktail with the liquid whose radioactivity is to be measured, the process of making the measurement increases both the volume and complexity of the radioactive liquid tested and hence the radioactive waste to be disposed of.

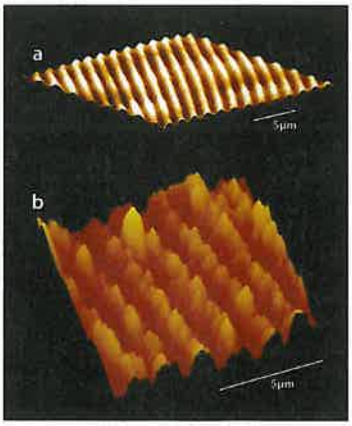


▲ Fig. 4: Schematic representation of radioactivity detection by liquid scintillation counting.

We sought to develop efficient, durable radioactivity sensors which could be used in flow systems without increasing waste production. Using sol-gel methods, the fluor can be either encapsulated or covalently bonded within a porous silica glass [4]. The products are transparent, an important consideration for sensing applications. Surprisingly, the efficiency of the radioactivity detection is hardly impaired by incorporation of the fluor in the glass. While the encapsulated system suffered from leaching of the fluor, this drawback was overcome by the simple expedient of bonding the fluor to the glass. The ready formation of the hybrid at low temperatures means that these sensors can be applied to the coating of glass tubes, capillaries, *etc.*, leading to use in flow systems and other product forms. This approach thus provides a relatively simple route to the manufacture of efficient and durable sensors and can be adapted in principle to a wide range of other types of sensor. For example, a similar hybrid approach has been used in the development of gas sensors.

Biomimetics

One area which is generating considerable excitement at present is biomimetics, where an increasing understanding of the clever 'tricks' used by Nature to produce its awesome range of biomaterials (*e.g.* bone) is inspiring scientists to copy and adapt these approaches in an effort to produce synthetic materials with a comparable range of properties. A subset of biomimetics is biomineralisation, where various biomolecules catalyse and direct the synthesis of inorganic networks to produce hybrids structures of often stunning complexity and beauty. Examples include the calcium carbonate or silica based shells of marine organisms such as coccoliths, abalone and diatoms. In the case of diatoms, research in both the USA and Germany has shown that specific proteins (silaffins) play a prominent role in controlling the growth of silica structures involving assembly of silicic acid molecules found naturally at low concentrations in sea water [5]. The knowledge of these protein structures has prompted the development of synthetic proteins and other polymers which catalyse silica formation under mild conditions. Steve Clarson and co-workers [6] at the University of Cincinnati and the US Air Force Research Laboratory have reported an elegant demonstration of the extension of this idea to the formation of novel holograms. Using a holographic photopolymerisation technique, they were able to make a polymer hologram containing a synthetic peptide similar to the silaffins. This hologram was able to catalyse subsequent formation of silica nanospheres from silicate precursor to form a hologram with the silica spheres in a regular 2-dimensional array. The atomic force micrographs show the surface features of the parent polymer hologram and the silica-polymer hybrid (Figure 5) The hybrid hologram showed a much higher diffraction efficiency than the polymer hologram. Not only does this work illustrate the use of this kind of biomimicry in nanopatterning, it also demonstrates the potential for rapid transfer of a fundamental understanding of natural processes into high tech, practical applications.



◄ **Fig. 5:** Atomic force micrographs of a polymer hologram (a) and the corresponding silica-polymer hybrid (b). [Reprinted by permission from Nature (L L Brott *et al.*, *Nature*, 2001, **413**, 291-293) copyright (2001) Macmillan Publishers Ltd.]

Conclusion

The relatively recent advances in the preparation and evaluation of organic-inorganic hybrids has opened up huge opportunities for the development of unique materials, exhibiting a range of properties rarely seen in other types of material. Starting from existing materials and precursors, scientists have the opportunity to produce a vast array of new materials with tailored properties for a wide range of applications, both in conventional markets and in new 'high tech' areas. Within the UK, a government funded network on 'Organic-Inorganic Hybrids for Structural and Semi-Structural Applications' [*HybridNet*] has been established since June 2001 with the aim of promoting and aiding the exploitation of hybrids within UK academia and industry. The network has about 30 member organisations and is coordinated by one of the authors (JNH). This and other initiatives are likely to accelerate the growth of this technology, such that we may truly be entering 'the age of the hybrid'.

About the authors

Professor John Hay, CChem, FRSC, CPhys, FInstP, joined the University of Surrey in 1994 following nearly 14 years in industry, firstly at the BP Research Centre and then in the Research Laboratory of Kobe Steel Europe. He became Professor of Materials Chemistry in 1999 and DERA (now QinetiQ) Professor of Materials Chemistry in 2000. His work has been concerned primarily with the synthesis, characterisation and applications of polymers, composites and organic-inorganic hybrids, as well as the use of supercritical fluids in polymer processing.

Professor Steve Shaw, PhD, FIM, CPhys, FInstP, is currently Technology Chief for Polymers and Adhesives within the Future

Glossary of Terms

Polymer: A large molecule (macromolecule) consisting of many smaller repeating sub-units linked together. Commonly used to refer to organic materials of this nature.

Monomer: The molecules which link together to form the sub-units of a polymer.

Ceramic: Traditionally used to describe a material produced from fired clay and used in the manufacture of pottery. Also used to describe a non-organic, non-metallic substance, often an oxide.

Clay: Sheet-like aluminosilicate minerals, where the negatively charged layers are held together by interstitial cations. Often found in sedimentary deposits.

Glass: An amorphous inorganic oxide or mixed oxide, commonly referring to silicate glasses, but more generally applicable to solids exhibiting a softening point (glass transition).

Sol: A colloidal suspension of small (*ca.* 1-1000 nm), often charged, particles in a liquid such as water.

Gel: A three-dimensional network of a polymer or inorganic oxide, which is normally highly porous and contains a substantial proportion of a liquid. In the sol-gel process, the inorganic oxide sol particles link together to form the gel.

Aspect ratio: The ratio of length to width for an elongated species such as a fibre.

Cationic surfactant: A soap-like molecule which commonly consists of a long non-polar 'tail' attached to a positively charged 'head' group.

Nematic: A type of phase found in liquid crystals. The rigid molecules are orientated parallel in one dimension, but with no specific order in the other dimensions.

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Systems Technology Division at QinetiQ, Farnborough. His current research activities include pre-bonded surface treatments for various material types, development of 'smart' adhesives, ultra-high temperature polymers and organic-inorganic hybrids. He is a QinetiQ Fellow and a Visiting Professor at the University of Surrey.

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